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Original Research Paper

High Calorific Value Fuel from Household Plastic Waste by Catalytic Pyrolysis

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ABSTRACT

Plastic waste pollution causes several impacts on the environment, so its proper disposal is very essential. On the other hand, petroleum resources are vanishing due to high demand of fuel for growing population and limited resources in India. So, there is a need to save existing resources and find an alternative source for fossil fuels. We can convert household plastic waste into petroleum products by pyrolysis method. In the present study, lab scale borosilicate pyrolysis reactor set up was designed for plastic waste treatment. Major components of household plastic waste are HDPE, LDPE and PP material, so were used in pyrolysis. Shredding, washing and drying of plastic waste was done manually. Pyrolysis experiments were carried out for 100g of HDPE, LDPE and PP waste with and without catalyst. Temperature and reaction time were optimized for each type of waste. Different catalysts like alumina, scolecite, dolomite, ceramic powder, white cement, sand and red brick powder were tried in the pyrolysis process. As dolomite yielded maximum liquid fuel and is cost effective, it has been used in pyrolysis experiments with different catalysts to feed ratios. Liquid fuel obtained for HDPE, LDPE and PP enhanced from 72%, 73% and 84% to 82%, 83% and 85% respectively, by using 10% dolomite. For mixed plastic waste, liquid fuel obtained was about 72.96% without catalyst and 82% with 10 % dolomite. Liquid fuel was characterized for GC-MS, FTIR and calorific values. Results showed the presence of alkanes and alkenes in major quantity and increase in concentration of low molecular weight hydrocarbon fractions (C_{10} - C_{25}) in the liquid fuel. Liquid fuel obtained from HDPE, LDPE and PP by using 10% dolomite showed higher calorific values (43000-46000 kJ/kg) as compared to that of without catalyst (40000-42000 kJ/kg). This liquid fuel can be used as a fuel in different industrial sectors.

INTRODUCTION

Improper solid waste management causes health and sanitation issues. Main non-biodegradable component of solid waste is plastic. In India, out of total plastic waste, only 60% is recycled and 40% remains untreated (Sonawane et al. 2016). Plastic waste is generally disposed off by land filling and incineration. Unscientific incineration of plastic produces carcinogenic chemicals and could also lead to formation of unacceptable emissions of greenhouse gases (Sarker et al. 2011). Plastic waste is mistaken as a food by sea birds, sea turtles, whales and other marine mammals and they die every year, which ultimately causes loss of marine biodiversity (Allsopp et al. 2006). Feedstock recycling of plastic waste involves different processes like pyrolysis, gasification, catalytic cracking, depolymerisation, hydrogenation, etc. (Kumar & Singh 2011). Research studies have been done on pyrolysis of plastic waste for converting it into different petroleum products, hydrogen gas, carbon nanotubes, etc. (Kiran et al. 2000, Alvarez et al. 2014 Williams et al. 2014). Researchers have taken many efforts to enhance the yield of liquid fuel in pyrolysis of plastic waste by using different catalysts. Catalytic degradation of polyethylene and polypropylene waste has been carried out by using HZSM-5, natural zeolite, alumina, Y-zeolite, silicoaluminophosphate, silica-alumina, modernite, kaolin and mesoporous silica catalysts (Park 1999, Schirmer et al. 2001, Sonawane et al. 2014, Lee et al. 2003, Fernandes et al. 2002, Panda et al. 2012, Sakata et al. 1999), and it has been noted that these catalysts enhance yield and quality of fuel as compared to without catalyst. Some researchers have studied the effect of different catalysts on mixture of different plastic wastes (Lopez 2012, Miskolczi, 2009, Lin, 2010) and it also showed increase in yield of fuel by using catalysts.

Though pyrolysis is a good option for recovery of petroleum products from plastic waste, the process requires high investment and process cost and yield obtained is comparatively low. Use of expensive catalysts makes process more expensive, so there is a need to find out cost effective catalysts which will help to minimize the process costs and will enhance quantity and quality of the liquid product. Dolomite is a very cost effective catalyst with calcium and magnesium source. There is only one study found on effect of dolomite in pyrolysis of plastic waste (Srinakruang 2013). It shows good effect of dolomite on pyrolysis of plastic waste after heating at 900°C. Present research focuses on the use of raw dolomite for enhancing quantity and quality of liquid fuel in pyrolysis of HDPE, LDPE and PP waste.

MATERIALS AND METHODS

Raw material: Plastic waste was collected from household sources and segregated into HDPE, LDPE and PP waste according to the symbols given. It was then shredded, washed and dried manually. 100 grams of waste material was used for each reaction.

Catalysts: Scolecite, limestone powder, white cement, sand, red brick powder, dolomite, etc. have been tried in the experiments. Experiments have also been carried out by using dolomite with 5 wt %, 10 wt % and 20 wt % for HDPE, LDPE, PP waste.

Pyrolysis reactor set up and process: Pyrolysis setup used for these experiments is shown in Fig. 1. It consisted of 500 mL capacity round bottom flask as a reactor made from borosilicate glass fitted with inlet tube for purging nitrogen gas from the cylinder and outlet tube connected to condenser. Heating was provided with heating mantle of 450 Watt with 1 litre capacity with heating rate of 20°C/min rise. Temperature was measured by k type of thermocouple which was fixed inside the reactor and with a display unit. Energy required for the reaction was recorded with energy meter.

In experiments, 100 g plastic waste was loaded in the reactor and nitrogen with flow rate of 50 mL/min was purged for 8 minutes to remove oxygen present and then switched off the supply. Temperature range was kept between 400- 450° C and reaction time was kept around 1-2.5 hrs for reaction depending on the type of plastic waste. Condensable liquid products were collected in collection flask through condenser and uncondensed gases were collected in a gas bladder partially filled with ice.

Characterization techniques used: Densities of oil samples were determined by using specific gravity bottle, and percent yield obtained was calculated by multiplying density with quantity of liquid fuel in mL.

Bruker FT-IR spectrophotometer in the normal IR region (4000-400 cm⁻¹) was used to identify functional groups present in the liquid fuel samples.

GC-MS: GC make model Agilent-7890, with FID detector was used and MS make model Jeol, Accu, TOF, GCV with mass range 10-2000 amu and mass resolution 6000 was used to detect the hydrocarbons present in oil samples.

Calorific value: Calorific values were determined with the help of bomb calorimeter of make-Rico Scientific, model RSBT-6 with gas auto filling unit.

RESULTS AND DISCUSSION



Fig. 1: Pyrolysis experimental setup.



Fig. 2: FTIR spectrum of liquid fuel obtained with HDPE, LDPE, PP.

Experimental studies on HDPE, LDPE and PP have been carried out with the temperature variation of 350°C, 450°C and 550°C. At 350°C, there was no liquid fuel obtained for HDPE and LDPE and at 550°C the evolution of gases is maximum and oil obtained has waxy fractions in it. Optimum temperature required for conversion of HDPE and LDPE into liquid fuel was observed as 430°C and 450°C respectively. For PP, optimum temperature was observed



Fig. 3: Gas chromatographs for liquid fuel obtained in pyrolysis process without and with dolomite.

Table 1: Yield of liquid fuel obtained for different wastes by using dolomite.

Material	Yield obtained without catalyst (%)	Yield perc 5 % DM	ent by using Do 10 % DM	blomite (%) 20 % DM
HDPE	72.66	81.8	80.73	40.85
LDPE	73.91	62.05	83.04	80.54
PP	83.81	85.2	85.91	83.39

about 380-400°C. Reaction time required for the completion of process was about 2.5 hours for converting 100 grams of HDPE and LDPE plastic waste into liquid fuel and 1.5 hours for that of PP. Experiments were replicated twice to obtain statistically significant results and average values were considered for final results. By using dolomite catalyst, reaction time for process reduced by 30 minutes for all the types of wastes.

Yield percent: Table 1 shows comparative results obtained for liquid fuel yield by pyrolysis for HDPE, LDPE and PP waste. Without catalyst, the liquid fuel obtained in pyrolysis process is about 72.66% (HDPE), 73.91% (LDPE), 83.81% (PP). For HDPE, maximum yield was obtained by using 5% dolomite i.e., 81.8%. For LDPE and PP waste, 10% dolomite gave maximum yield of liquid fuel. There was a decrease in per cent liquid fuel by 20% dolomite.

Table 2 shows densities and gross calorific values of liquid fuel samples by with and without dolomite. From Table 2, it can be seen that by using dolomite catalyst, calorific values of liquid fuel samples enhanced significantly.

Result shows positive effect of dolomite for enhancing quality of liquid fuel in pyrolysis process.

Fourier-transform infra red spectroscopy: The FTIR spectra show typical hydrocarbon vibrations in liquid fuel obtained by both, with and without dolomite in pyrolysis of waste HDPE, LDPE and PP. Considerable infrared absorption bands have been observed between 3000 and 2800 cm⁻¹, 1500 and 1200 cm⁻¹, and 1000 and 500 cm⁻¹ wave number ranges. Based on the FTIR absorption bands in the range of 1500-500 cm⁻¹, it is observed that the type of raw materials affected the structure of products. Graph for oil obtained from HDPE, LDPE and PP shows -C-H in plane bending, out plane bending, C-H stretching, scissoring and =C-H bending at different wavelength ranges, which indicates presence of alkanes and alkenes (Fig. 2).

GC-MS analysis: Gas chromatography (Fig. 3) and mass spectro-scopic study show presence of hydrocarbons in the range of C_6 to C_{30} for oil obtained with HDPE, LDPE and PP samples without catalyst and with dolomite. Concentration of low molecular weight fractions was observed higher in liquid fuel obtained with 10% dolomite as compared to that of without catalyst. The major components observed in HDPE liquid fuel were octane, octene-2, 1-decene, dodecane, tridecane, dodecane, tridecene, tetradecane, 1-tetradecene, 1-hexadecene, heneicosane, pentacosane, etc. From LDPE liquid samples obtained hydrocarbons were 1-undecene, cyclododecane, 1-tridecene, dodecene, tetradecene, 1-pentadecene, 1-Z-5 nonadecene, 1-octadecanol, etc., while in liquid samples obtained from PP waste, compo-

Plastic waste Property	HDPE WC	10 % DM	LDPE WC	10 % DM	PP WC	10 % DM
Density (kg/m ³)	0.760	0.758	0.763	0.756	0.749	0.750
Calorific value(kJ/kg)	40614	42332	41742	46509	42200	43139

Table 2: Density and calorific value of liquid fuels.

nents like 2,4 dimethyl-1-heptene, 3 hexadecene, cyclohexene, 3,3,5-trimethyl, cyclopentane, 1,2,3,4,5-pentamethyl, 2,4,6-trimethyl-3-heptene, 3-undecene, 4-undecene, octane and 3,3-dimethyl were obtained.

CONCLUSION

The optimum temperature range of about 400-450°C maximizes percent of oil and lessen the percent of wax. Maximum percent of liquid fuel can be obtained in pyrolysis process with polypropylene waste which also has higher calorific value that broadens its applications.

By using 5-10% dolomite, the percent of liquid fuel can be enhanced for all types of plastic wastes i.e., HDPE, LDPE and PP waste. Use of dolomite also helps to enhance concentration of low molecular weight components in liquid fuel which enhances calorific value of liquid fuel. As dolomite enhances quantity and quality of liquid fuel obtained from HDPE, LDPE and PP waste, it will help for treatment of household plastic waste which has a mixture of plastic waste, so there will be no need of segregation of household plastic waste.

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