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Research Paper

Transforming Low Density Polyethylene Waste into Diesel Grade Fuel by Catalytic Pyrolysis

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Abstract: *Environmental problems due to plastic waste are well known nevertheless, its use without alternative cannot be stopped. On other hand, petroleum resources are vanishing due to high demand of fuel for growing population and limited resources in India. Plastic is made from hydrocarbons so it can be an alternative fuel for fossil fuels after recycling by pyrolysis method. Low density polyethylene is one of the main components of household plastic waste. We can convert this plastic waste into petroleum products by pyrolysis method. Catalyst helps in enhancing yield of liquid product and reduces reaction time. In present research work, small capacity borosilicate glass reactor was designed for pyrolysis process. Waste low density polyethylene milk carrybags were used as raw material. Screening and selection of catalysts were done depending on cost effectiveness, easy availability and stability of material and for enhancing quantity and quality of liquid fuel product at low temperature. It was observed that among the Scolecite and Dolomite, Dolomite is best catalyst in pyrolysis as it fulfils most of the criteria decided during study. Liquid fuel samples obtained without catalyst and with catalysts were characterized for GC-MS and calorific values. It showed increase in the concentration of C10-C20 hydrocarbon fractions and calorific values of liquid fuel samples obtained with Dolomite as compared to Scolecite and without catalyst.*

Keywords: Low density polyethylene, catalytic Pyrolysis, diesel grade fuel, Dolomite, GC/MS, Calorific value.

Introduction

Low density polyethylene (LDPE) is one of the main plastic types with environment residence period of about 500 years. In household plastic waste, about 65-70% contributes HDPE, LDPE and PP waste. LDPE is mainly used in the packaging and food industry. As compared to HDPE and PP, LDPE has low density, light weight and low cost so it is thrown away in the environment without recycling. Its improper disposal causes death of domestic and marine animals due to eating as a food material or getting entangled in it. Non-biodegradable nature of this plastic causes health and sanitation issues. Pyrolysis is one of the emerging technologies to convert waste plastic into diesel grade liquid fuel. Many authors studied pyrolysis process for polyethylene waste recycling with and without catalysts. Studies on thermal pyrolysis of polyethylene were done at different temperature ranges from 250^0C-550^0C[1,2]. LDPE waste gives liquid fuel at temperature range 120-430^0C without any catalyst by liquefaction process[3]. Polymer degradation study was carried out by using different catalysts such as silica alumina, zeolites[4], H-ZSM-5, Y-type zeolites, natural zeolite[5,6,7], mesoporous silica catalysts (silicalite, mesoporous silica gel and mesoporous folded silica [8], various fly ash-derived silica–alumina catalysts (FSAs), iron subgroup metal salts etc[9,10]. These catalysts give good results in pyrolysis process either in terms of quantity or quality. There is need to find out cost effective and easy available catalyst which will enhance quantity and mainly quality of liquid fuel for LDPE waste, as enhanced quality will help to get low molecular weight hydrocarbon fractions which are more applicable for fulfilling growing demand of energy sector.

In present work, screening of easily available, cost effective raw materials were done to find out best catalyst which will fulfil the above mentioned criteria. It was observed that liquid fuel obtained with Dolomite in pyrolysis, enhanced quantity and quality. In earlier research, pyrolysis of plastic waste was studied by using calcined Dolomite at 900^0C[11]. But no studies were found on effect of raw Dolomite on pyrolysis process for enhancing yield of liquid products compared to without catalyst. There is also no study observed as use of Scolecite as catalyst in pyrolysis, so present study focuses to study effect of raw Dolomite and Scolecite for enhancing quantity and quality of liquid production in pyrolysis process.

Material and Methods

Raw material

It was found that LDPE waste included different sized carrybags, bottles and containers. So to keep parameters constant for reaction, waste LDPE milk carry bags of Katraj dairy were collected from different societies. They were washed, shredded into pieces of 5×5 cm and dried in sunlight for 4-5 hours. 100 g prepared waste material was used for pyrolysis experiments.

Catalysts

Depending on easy availability, cost effectiveness and stability, different raw materials like Sand, Limestone powder, White Cement, Alumina, Dolomite, Scolecite were tried as catalysts in the experiments. Catalyst to feed ratio was kept constant i.e. 1:10 for each experiment to avoid cost of process. As maximum liquid fuel obtained with Scolecite (SC) and Dolomite (DM), studies on optimization of catalyst to feed ratio was done by using 5 %, 10%,15 % and 20 weight % Scolecite and Dolomite. Catalyst study was also carried out for SEM (scanning electron microscopy), EDS(energy dispersive spectroscopy) and XRD (X-ray diffraction) to study surface morphology, particle size and chemical composition and crystal structure.

Pyrolysis Reactor set up and process

Pyrolysis set up used for these experiments is shown in figure 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 cylinder and outlet tube connected to condenser. Heating was provided with heating mantle of 450 Watt with 1 litre capacity with the heating rate of 100C/min rise. Temperature was measured by k type of thermocouple which was fixed inside the reactor and with display unit. Energy required for the reaction was recorded with Energy meter. In Experiments, 100g 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 in between 430- 4500C and reaction time was kept around 2 hrs for every reaction.

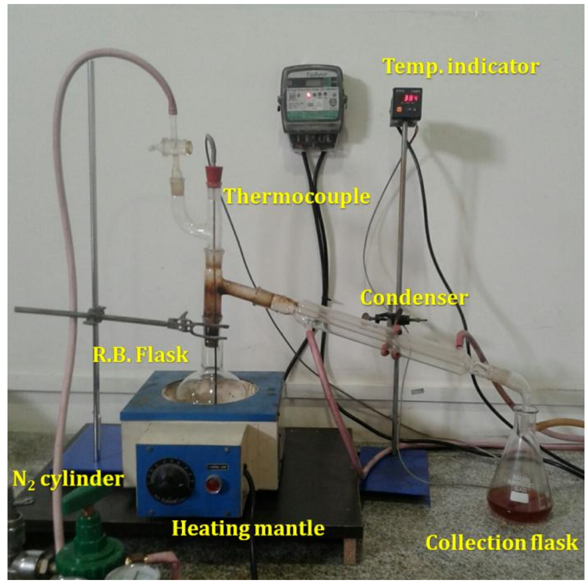

Figure 1: Pyrolysis Experimental Set up

Condensable liquid products were collected in collection flask through condenser and uncondensed gases were collected in gas bladder partially filled with cold water. By measuring density, mass of liquid product was calculated. Waxy residue obtained was weighed and weight of gases was calculated from material balance. Different reactions were carried out on waste LDPE without and with catalysts by keeping temperature constant.

Characterization of liquid product

Characterization of oil samples was done for GC-MS (GC make Agilent and model 7890, MS make Jeol, model Accu TOF GCV) with mass range 10-2000 amu and mass resolution 6000 was used to detect hydrocarbons. Calorific values were determined with the help of bomb calorimeter of make-Rico Scientific and model RSBT-6 with gas auto filling unit. Distillation of oil samples was done in temperature range of 30-350^0C by keeping heating rate with rise of 5^0C/min and collecting the condensate fractions at temperature difference of 50^0C. Distillation was done by attaching borosilicate glass fractionating column to distillation apparatus. It was done to know percentage of gasoline, kerosene and diesel fractions present in oil samples.

Results and Discussion

Effect of catalysts on yield of liquid fuel

Figure 2 represents graph of catalysts used versus yield of liquid fuel. Yield of liquid product obtained without catalyst in pyrolysis process was around 74%. It was found that Sand, Red brick powder, ceramic powder decreased yield of liquid fuel in pyrolysis as compared to without catalyst, while Limestone powder, Alumina, Scolecite and Dolomite showed increase in the yield of liquid fuel. Liquid fuel obtained with Limestone powder was about 81%, with Scolecite it was 82%. With Alumina the obtained fuel was 76% and by using Dolomite it was highest i.e. 84 %. Oil obtained with limestone was turbid in nature while Alumina was found expensive as compared to other catalysts. The cost of alumina was around Rs.500/kg. As compared to other catalysts, cost of Dolomite was Rs.10/kg and cost of scolecite is 20/kg and yield obtained was satisfactory so experiments were conducted by using Scolecite and Dolomite for optimization of catalyst to feed ratio.

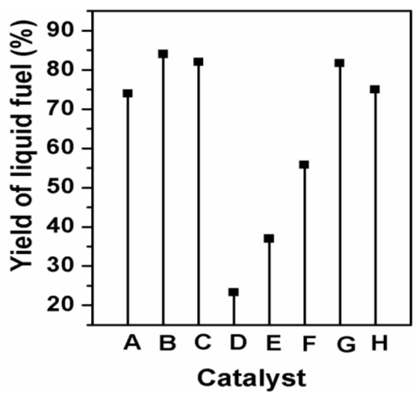

Figure 2: Liquid fuel Yield from LDPE waste by different catalysts (A) Without catalyst (74%), (B) Dolomite (84%), (C) Scolecite(82%),(D)Ceramic powder (75%), (E) Sand (23%), (F) White cement (37%), (G) Alumina (76%), (H) Limestone powder (81%)

Optimization of Catalyst to feed ratio for enhancing yield of liquid fuel

Pyrolysis reactions were carried out at 450^{0}C by using 5, 10, 15 and 20 weight % Dolomite and Scolecite. Figure 3 shows comparative yield of liquid fuel obtained Dolomite and by using different catalyst to feed ratios in pyrolysis.

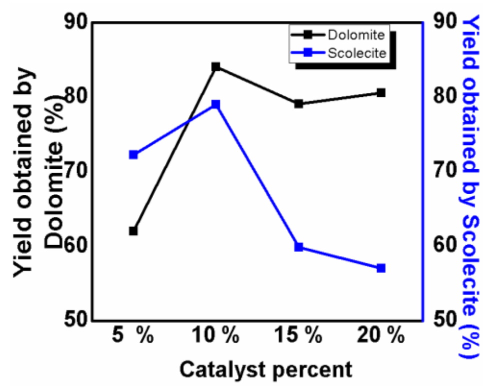

Figure 3: Yield of liquid fuel obtained with Dolomite at different catalyst to feed ratio

For 5 wt % Dolomite, only 62% liquid fuel was obtained. By using 10 % Dolomite, maximum yield obtained i.e. about 84 %. For 15 % and 20 % yield of liquid fuel obtained was 79 and 80 % respectively. By using 5 % Scolecite, the obtained yield was 72 %, it has increased upto 79 % by using 10 %. With 15 % and 20% Scolecite, yield decreased upto 59 and 57% respectively. So from results, it was observed that 10% catalyst gives maximum amount of liquid fuel in pyrolysis. The comparative results of liquid fuel yield and by products obtained in pyrolysis process is shown in Table 1. Compared to without catalyst by using Dolomite, wax content reduced from 23% to 10% and the concentration of hydrocarbon gases increased from 5% to 7% while by using scolecite, wax content obtained was around 16% and generated HC gases were 5 %. The time required for the reaction reduced from 2 hours to 1.5 hrs by using both catalysts so electricity consumption was also reduced from 0.5 KWh to 0.3and 0.4 KWh respectively.

Table 1: Comparative results for pyrolysis without catalyst and with 10 % Dolomite

Waste LDPE (Parameters)	Yield obtained without catalyst	Yield obtained with 10% DM	Yield obtained with 10 % SC
Liquid fuel	72%	84%	79%
Wax	23 %	10 %	16%
HC gases	5 %	7%	5%
Electricity(KWh)	0.5	0.3	0.4
R. Time (Hrs)	2	1.5	1.5

Characterization of fuel

Calorific value

Diesel has a calorific value in the range of 45000 KJ/Kg while obtained liquid fuel by pyrolysis without catalyst has calorific value of about 40709 KJ/Kg. By using 10 wt % Dolomite, calorific value of liquid fuel enhanced to 43856 KJ/Kg and it has enhanced to 41742 KJ/Kg by using Scolecite.

GC-MS

Figure 4a and b and c represents Gas chromatographs for LDPE oil without catalyst, with 10% Dolomite and with 10% Scolecite respectively. Graph represents time of illution of hydrocarbon fractions versus intensity of peak. It is observed that there is a wide distribution of hydrocarbon fractions (i.e. C10-C30) in the liquid fuel obtained without catalyst which is seen in graph a, while by using 10% Dolomite and Scolecite, concentration of low molecular weight hydrocarbon fractions in the range of C10 to C20 enhanced significantly but there are few high molecular weight hydrocarbons obtained by using Scolecite which can be seen in graph.

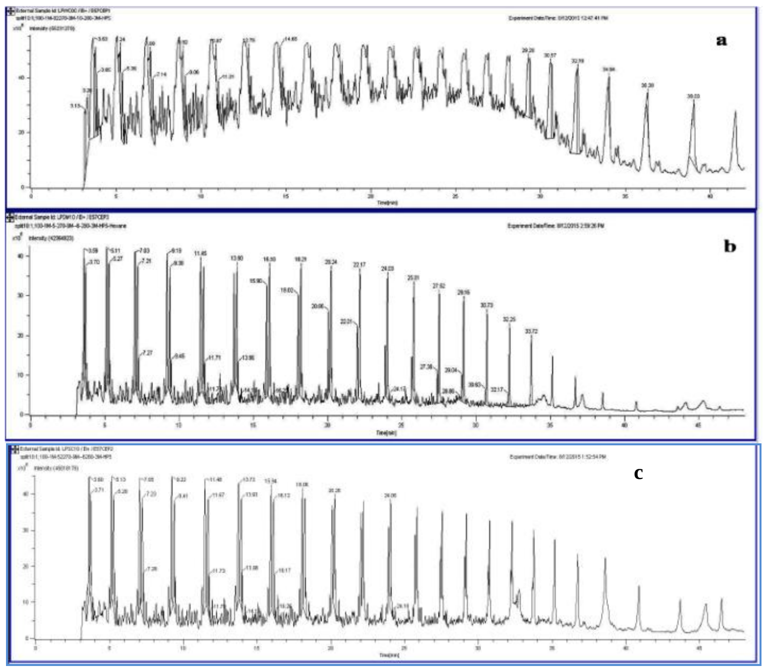

Figure 4: Gas chromatograph of liquid fuel a) without catalyst and b) with 10 wt % Dolomite

The major components obtained were detected with the help of mass spectroscopy (MS). MS showed presence of alkanes (Nonane, Dodecane, Tridecane, Tetradecane) and alkenes (Dodecene, Undedecene, Tridecene etc.). High molecular weight fractions like Heptadecane and Heneicosane were observed in liquid fuel without catalyst and they were also observed in liquid fuel with Scolecite but their concentration was negligible in liquid fuel with Dolomite.

Distillation of Liquid fuel

Liquid fuel obtained without catalyst and with 10 wt % Dolomite and with 10 wt % Scolecite was distilled by using fractionating column and fractions were collected at a temperature difference of 500^0C. Literature showed boiling range for gasoline, kerosene, diesel fractions around 260^0C, 304^0C and 360^0C respectively. The percent of gasoline, kerosene and diesel fractions obtained without catalyst were 18, 16 and 18 respectively. By using Scolecite, yield for gasoline and kerosene fractions was decreased to 12.2 % and 13.5 % respectively while yield of diesel fractions increased upto 21.6 %. By using Dolomite, gasoline fractions enhanced by 1 %, kerosene fractions enhanced to 1.5 % and diesel fractions enhanced upto 5 % that of without catalyst. Their percent were 19, 17.5 and 23 respectively. Overall percent of fractions upto 3500C enhanced from 52% to 59.5% by using Dolomite.

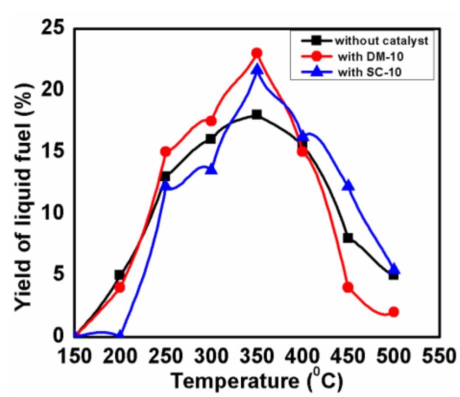

Figure 1: Percent liquid fuel fractions obtained without catalyst and with 10% Dolomite

Characterization of Catalyst
To study the reason behind enhancing yield by catalyst, their XRD, SEM and EDS results were studied.

Scanning electron microscopy
From SEM, particle size of Dolomite and Scolecite was determined. The particle size of Dolomite and Scolecite ranges from 0.5µm to 10 µm and particles shows agglomeration. Chemically Dolomite is Calcium magnesium carbonate with formula $CaMg(CO_3)_2$.

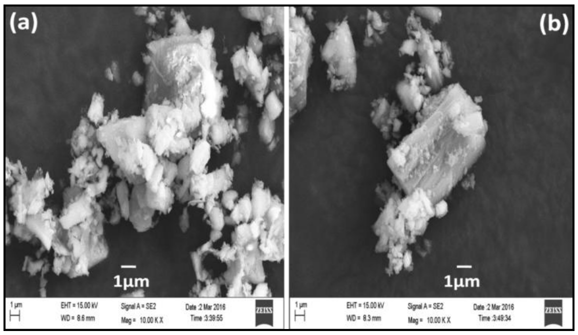

Figure 6: Scanning electron microscopic images for a. Dolomite, b. Scolecite

From energy dispersion spectroscopy, its elemental composition was found to be 20.46% Carbon, 59.73% Oxygen, 8.15% Magnesium and 11.21% Calcium. Scolecite is Calcium Aluminium Silicate Hydrate with formula $CaAl_2Si_3O_{10}(H_2O)_3$ and its elemental composition is carbon 7.71%, oxygen 64.48%, aluminium 8.36%, silicon 12.88% and calcium 4.79%.

X-ray diffraction study
X-ray diffraction pattern for Dolomite and Scolecite is shown in graphs.

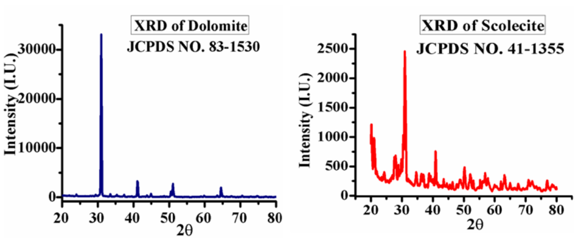

Figure 7 (a): XRD patterns of Dolomite (b): XRD pattern of Scolecite

XRD pattern of Dolomite shows major peaks at 2Ɵ values of 31.27, 42.8, 51.71 which matches with JCPDS no. 83-1530, it shows rhombohedral structure while XRD of Scolecite has major peaks at 2Ɵ values of 22.022,30.943, 41.116, 50.52, 52.33, etc which resembles with JCPDS no. 41-1355 and shows monoclinic structure.

Conclusion
In the pyrolysis process, by using 10 wt% Dolomite, yield of liquid fuel enhanced from 74% to 83% and reduced wax quantity significantly. Due to decrease in reaction time for pyrolysis process with Dolomite, electricity consumption also reduced from 0.5 KWh to 0.3 KWh which made process less expensive as compared to without catalyst. Liquid fuel obtained with 10 wt% Dolomite has increased concentration of low molecular hydrocarbons (C_{10} to C_{20}) and calorific values as compared to liquid fuel obtained without catalyst and with Scolecite. Crystal structure and chemical composition of Dolomite helped to enhance the yield for LDPE waste.High calorific values of obtained liquid fuel show its applicability as an alternate source for running diesel generators and boilers in inductrial sectors.

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