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Catalytic conversion of waste high-density polyethylene into useful hydrocarbons

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HIGHLIGHTS

▶ New catalyst have been tried.

- ▶ The conversion efficiency of the catalyst has been compared.
- ▶ The product obtained has been characterized.
- ▶ The fuel valve of the products have been compared with gosoline.

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ABSTRACT

Waste high-density polyethylene (HDPE) was catalytically degraded using CaCO₃ as a basic catalyst. Various parameters like temperature, catalyst to polymer ratio (cat/pol) and reaction time were explored in order to find out optimum reaction conditions. Total conversion of 97.20% was achieved with 52.33% oil yield and 53.84% oil selectivity. Sufficient quantity of the oil product was collected for further physico-chemical study. The oil obtained was fractionated at different temperatures and physical parameters were studied for all the fractions including parent catalytic oil. The ASTM distillation study of the catalytically derived oil showed that its 40% fraction was in the boiling point range of light naphtha, 24% fraction was in the range of heavy naphtha and 36% fraction was in the boiling point range of middle distillate. The oils obtained were analyzed by GC/MS to find out its composition. Major constituent hydrocarbons were found to be in the range of C_7-C_{28} distributed in various fractions derived at different temperatures. Different fractions showed varied compositions with constituents common to two or more sample fractions showing overlap of the distillation ranges. Comparing the physical parameters of the sample oils with standard fuels it was observed that the collected fractions were either in the range of gasoline, kerosene or diesel oil. © 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The solid waste management of waste polyethylene is a burning issue nowadays. Degradation of polymer wastes into useful chemical feedstock (fuel oil) is attractive and suitable solution to the increasing environmental problems created by the waste plastics and decreasing energy sources [1,2]. Catalytic degradation of plastic waste is more advantageous than simple thermal degradation as the latter requires comparatively high temperature and produce low quality reaction products. Catalytic degradation takes place at a considerably lower temperature and produce hydrocarbons in the range of motor engine fuel eliminating further up gradation steps [3]. Scientists have attempted to use different types of Zeolites and clays as catalysts in the catalytic conversion process of plastics or more specifically high-density polyethylene (HDPE) [4,5].

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Mastral et al. [6] used nano crystalline HZSM-5 zeolite for the catalytic degradation of HDPE using a laboratory fluidized bed reactor at temperatures between 350 and 550 °C yielding gases and wax as major products. Manos et al. [7,8] applied different zeolite catalysts to investigate the impact of catalyst's acidity and other reaction conditions on the degradation process. Mosiewski et al. [9] performed the catalytic degradation process under high pressure using acidic aluminosilicate and Ni-Mo/Al2O3 catalysts and found that the former yields more low-boiling liquid fractions, more isoalkanes and more aromatics, while the latter yielded only saturated hydrocarbons. Neves et al. [10] studied the impact of different types of Y-zeolites on the catalytic degradation of HDPE using thermogravimetric (TGA) and differential scanning calorimetric (DSC) techniques. They found that HY(20) zeolite is the most active catalyst among the other catalysts used so for. Aguado et al. [11] investigated the effect of zeolitic materials and mesostructured solids on the catalytic conversion of polyethylene using TGA. They found that nano crystalline n-ZSM-5 from zeolite catalysts, and Al-MCM-41 from mesostructured solids catalysts





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have highest degradation activity. Salmiaton and Garforth [12] used fluid catalytic cracking (FCC) catalysts and Farid et al. [13] used ZSM-5, US-Y and Mordenite catalysts for the catalytic cracking of HDPE using a laboratory fluidized bed reactor. Mikulec and Vrbova [14] studied the role of natural zeolite Clinoptilolite, ZSM-5, HZSM-5 and their mixture in various volume ratios in the catalytic conversion of polyethylene into petrochemical feedstock. A number of studies have been reported regarding the types of catalysts used to convert polyethylene into useful products and the techniques like GC–MS to characterize the products [15–18]. An acidic catalyst, US-Y was used for the degradation of HDPE and effects of different parameters on the % conversion and product distribution were investigated in one of our previous studies [19].

Manos et al. [20] studied the catalytic degradation of HDPE over Ultra-stable Y zeolite in a semi batch reactor at different heating rates and reaction temperatures and found that solid state reactions occur only in the presence of a catalyst. Fernandes Ir et al. [21] investigated the degradation of HDPE at 450 °C in the presence of HZSM-5 zeolite under the nitrogen static atmosphere and used GC for analysis of the products. Lee and Shin [22] carried out the Liquid-phase catalytic degradation of waste HDPE, LDPE and PP over spent fluid catalytic cracking (FCC) catalyst at atmospheric pressure with a stirred semi-batch operation. They investigated the effect of catalyst amount, reaction temperature, plastic types and weight ratio of mixed plastic on the yield and accumulative amount distribution of liquid product. Elordi et al. [23] studied the pyrolysis of HDPE, continuously fed into a conical spouted bed reactor (CSBR) at 500 °C using HZSM-5, HY and Hb zeolite catalysts at atmospheric pressure and assessed the yields and composition of the light olefins and automotive fuel hydrocarbons. In another study [24] the catalytic pyrolysis of HDPE was carried out in the presence of HY zeolite catalyst in a CSBR at 500 °C and it was observed that 69 wt.% of the product stream corresponds to the gasoline fraction (C_5-C_{10}) . Mastral et al. [25] carried out the thermal degradation of HDPE using a fluidized bed reactor under different temperature conditions in the presence of inert nitrogen and nitrogen/air mixture and investigated the influence of the operating parameters on the product distribution and gas composition using GC and GC/MS for the analysis of gas, wax and oil fractions.

Mosiewski et al. [26] investigated a high pressure thermal and catalytic cracking of low-density polyethylene using a closed autoclave. The compositions of gaseous and liquid products were analyzed by means of GC/FID and GC/MS chromatographic methods. The co-pyrolytic behaviors of different plastics (high density polyethylene, low density polyethylene and polypropylene), low volatile coal and their blends with the addition of the plastic of 5 wt.% have been studied using a thermogravimetric analyzer [27]. A basic catalyst, MgCO₃ has been used for the conversion of waste HDPE into fuel oil where the effect of catalyst on the products yield was studied and the liquid products were characterized using different fuel tests [28].

The up to date literature reveals that mostly acidic catalysts have been used for the catalytic degradation of HDPE. This work aims to investigate the impact of cheaply available basic catalyst (CaCO₃) on the product distribution and different parameters of the catalytic degradation process of HDPE.

2. Experimental

2.1. Materials and methods

Municipal waste High-density polyethylene (HDPE) bottles were cut into pieces of 5–10 mm² sizes and used as a feed for the degradation process. The percentage of additives in the employed HDPE has not been investigated; however the previous studies show that they may range from ppm level up to 2% [29]. Powdered

CaCO₃ (purchased from MERCK Pakistan, 99.8% pure, particle size 100 µm) was used as a basic catalyst for the catalytic degradation reaction. The degradation reaction was carried out in a batch Pyrex reactor with height; 22 cm, i.d. 70 mm and wall thickness of 2.4 mm. The glass reactor was heated with the help of an electrical furnace equipped with temperature controller. A fixed amount of HDPE sample and catalyst was loaded in the pre-weighed reactor and placed in the electrical furnace. As the reactor used in this study was batch type, thus the reaction time was maintained by noting the time before starting reaction and the reaction was then carried out for a fixed desired time and then stopped. The reactor was heated to the required temperature with the help of temperature controller. The evaporated reaction products were collected in the form of non-condensable gaseous products, condensable oil, wax and solid residue. The glass reactor was removed from the furnace at the end of catalytic degradation process. The oil fraction was weighed at the end of each degradation reaction. This whole process was repeated for every reaction either for different temperatures, different cat/pol ratios or different reaction time. The flow sheet diagram of reaction assembly and the percentage calculation of reaction products are given elsewhere [28].

2.2. Physical parameters study

Physical properties of the catalytically derived oils were determined by using the following IP and ASTM standard methods for fuel; IP-59/82 for density, IP-160/87/ASTM-D1298-85 for API gravity, IP-711/87/ASTM-D445-87 for kinematic viscosity, IP-36/84, ASTM-D92-78 Cleveland open cup method for flash point, IP-191/ 83/ASTM-D216-77 for distillation of oil. Specific gravity was calculated mathematically, viscosity by using viscometer and pour point was determined with the help of pour point apparatus. Gross calorific values of the samples were determined by using Parr 6200 (Model: A1290DDEE) Bomb Calorimeter. The refractive index was determined with Abbe's Refractometer (NAR-IT ATAGO CO., Tokyo, Japan) at 20 °C.

2.3. GC/MS study

The oil product of the degradation reaction was analyzed by JEOL MS Route system (JMS-600H), with HP-5 column (30 m \times 0.32 mm, with 0.25 μ m film thickness), with Helium as a carrier gas. The GC oven temperature was kept at 40 °C for 10 min and programmed to 240 °C at a rate of 4 °C/min and then kept constant at this temperature for 10 min. The Injector and the detector temperatures were 250 °C and 270 °C respectively. Split flow was adjusted at 1 mL/min. The mass m/z was recorded from minimum to 554 with El-as ionization mode and the MS were recorded at 70 eV.

3. Results and discussion

3.1. Effect of temperature

The effect of temperature on product distribution from thermocatalytic degradation of waste HDPE using $CaCO_3$ catalyst is given in Fig. 1. The temperature was optimized in the range of 250 °C to 480 °C. The degradation reactions were batch type and every reaction was carried out for one hour at each temperature. Initially at lower temperatures i.e. 250, 300 and 350 °C, there was no degradation of HDPE but at 400 °C, the degradation was started with production of gas and wax. Above 400 °C the reactions were carried out at various temperatures with a successive increase of 20 °C interval. The product distribution changed significantly when temperature increased from 400 °C to 460 °C. The gas yield increased Download English Version:

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