



A process study on the pyrolysis of waste polyethylene



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HIGHLIGHTS

- Waste HDPE converted to high amounts of gases (>90%).
- Induction heating introduced as an energy efficient method to pyrolyse waste HDPE.
- The effect of hydrogen cracking on the P/O ratio is investigated.
- Catalyst deactivation and regeneration assessed for continuous mode of operation.

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ABSTRACT

The thermo-catalytic cracking of waste polyethylene bottles was thoroughly examined to determine the possibility of operating the process in continuous mode. Two types of zeolite catalysts renowned for their strong catalytic properties and precise selectivity, HUSY and HBeta, were used to study the slates and yields of the products generated under various operating conditions. The liquid and gas samples were analyzed via GC–MS to determine the hydrocarbons chain distribution in terms of paraffins, olefins and aromatics. Under thermal heating, the gas yield reached 17.8% in the absence of catalysts and it increased to 93–96% when HUSY and HBeta were used in vapor contact mode. This yield dropped to 57% when energy-efficient induction heating was applied. Under hydrogen cracking, the gas yield decreased further to 51.6% while the P/O ratio increased due to a rise in the C₁₃–C₂₃₊ paraffin contents. The catalyst deactivation stage showed that both HUSY and HBeta started to lose their activity as waste HDPE charges were continuously fed to the reactor. After the third HDPE charge, the amount of solid and liquid wax products dramatically increased and the process started to resemble to thermal pyrolysis. High gas yields of greater than 90% were achieved when the catalysts were regenerated with industrial air at 550 °C, indicating full catalyst recovery.

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1. Introduction

Research scientists and engineers have spent decades trying to improve the pyrolysis process and bring back the waste plastic into the manufacturing line by generating high quality chemicals and alternative fuel-like products [1–3]. The main focus has been on the evolved products in order to find an appropriate catalyst and reactor configuration that can achieve desired outcomes. For the case of processing high and low density polyethylene wastes, fluidized bed reactors were found [4–10] to promote high gas yields (~90%) with all types of catalysts. HZSM-5 and HMOR produced 60% in the range of C₃–C₅. Aromatics with a narrow distribution were mainly obtained with HUSY. When E-Cat FCC catalysts were used, higher amounts of aromatic compounds were found in the

produced gasoline. While MCM-41 and SAHA catalysts promoted a wider range of carbon chains in the gasoline range. At 400–450 °C NCM and FCC catalysts gave high yields of liquid in the gasoline range of C₈–C₁₃ with low sulfur contents and a little amount of gas.

Batch, semi-batch and autoclave reactors were also tested to pyrolyse polyethylene with different catalysts. MCM-41 promoted the cracking of high-density polyethylene (HDPE) into lighter liquid and gaseous products [11] at 380 °C; Paraffins and aromatic compounds were strongly present. At 550 °C, HZSM-5 favored the formation of gases in the light fraction (C₂–C₄) and the condensed products were mainly aromatics [12]. With 430 °C semi-batch experiments [13], a KFS-16B catalyst gave lighter condensate products and a slower deactivation in comparison to other catalysts. The ZSM-5 catalyst promoted gas production significantly in the C₄–C₅ range, and gave light liquid hydrocarbons. Silica–Alumina SA-1 and SA-2 promoted liquid production with a narrow range

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of carbon number. A 38–57% conversion was achieved when Mordenite catalysts were used at 420 °C to pyrolyse low-density polyethylene (LDPE) [14]. When a Rh/Al₂O₄ catalyst was used at 425 °C, a high liquid yield of 85% was reached in a pressurized autoclave [15] with an increased yield of alkanes at the expense of alkenes in the gas fraction. Methane gas was at a dominating fraction of 46%.

In fixed bed reactors [5,16], the presence of a fluid catalytic cracking catalyst (FCC), KOB-627, increased the conversion of HDPE at 450–500 °C and produced significant amounts of gasoline. When H-beta catalyst was used, the gas yield was richer in C₄ and C₅ in comparison to HZSM-5 but it exhibited higher production of coke deposits. Undesirable polycyclic aromatics were obtained with Zn-ZSM-11 and H-ZSM-11 catalysts at 500 °C under shorter experiment residence time (e.g., 20 min). As the residence time increased the yield of gaseous fractions increased and no polycyclic aromatics were detected over both catalysts at 60 min residence time [17].

Unconventional reactor systems such as conical-spouted [18,19], cycled spheres [20] and screw kilns [21,22] were also inspected in terms of yields and product quality. These were found to produce gasoline of high quality and LPG with little dry gas, and small amount of coke. In Some cases, the obtained gasoline [19] was in agreement with EU requirements containing no sulphur, negligible benzene, and a RON index of 96.5. Furthermore, microwave assisted pyrolysis furnaces have been used as an efficient route to handle plastic waste [23]. These pyrolysed waste HDPE to produce 49.7% liquids composed of linear alkanes, 1-alkenes, and low amounts of aromatics.

As opposed to investigating various reactor systems, the catalyst activity and ability for regeneration during pyrolysis, received relatively less attention in literature. In a recent study [24], two commercial zeolites were used to study the deactivation mechanisms during the pyrolysis of polyethylene. With the help of TG/FT-IR analysis the authors noticed that as the catalysts were undergoing de-activation the process gradually became similar to thermal pyrolysis. The characteristics of the products produced with the deactivated catalysts were the same as those obtained from thermal runs and the catalyst lost its activity after six runs. In another polyethylene pyrolysis catalyst deactivation study [25], two different mechanisms were identified when deactivation and regeneration were conducted. A reversible deactivation by coke deposition, which can be removed by regeneration with air at 550 °C, took place along with an irreversible deactivation. The coke deposited on the external surface (and the super-micropores/mesopores) was easily removed by regeneration. Permanent deactivation

is generally caused by changes to the zeolites structure at high temperatures (e.g partial extraction of metal species from the catalyst structure, amorphization etc.), formation of stable coke species and/or poisoning of the acid sites by metals originating from the polymer itself. This was not observed in polyethylene pyrolysis experiments running at moderate temperatures. In a subsequent study [26], the authors found that after one pyrolysis experiment the zeolite catalyst lost its activity in terms of yields and product quality. This deactivation was found to be reversible when the catalyst was subjected to regeneration at 550 °C in an air atmosphere. The catalyst recovered its activity, generating similar products with equivalent proportions to those obtained with fresh catalyst.

In this study, the catalytic pyrolysis of waste HDPE is carried out in a tubular reactor using two different types of zeolite catalysts. The experiments are conducted in vapor-contact mode and under defined sets of operational procedures: thermal heating, induction heating, hydrogen cracking, deactivation and regeneration. The yield and composition of the generated products are closely inspected to help elucidate the performance and limitations of the process under various conditions. The outcome from this work is anticipated to help determine the possibility of running the pyrolysis process in continuous mode.

2. Experimental

HDPE was obtained from collected waste shampoo bottles. These were cleaned, cut and ground into small pieces of 3–5 mm in diameter. Two acidic catalysts, HUSY (surface area = 510 m²/g, SiO₂/Al₂O₃ = 5.2 molar ratio, pore volume = 0.36 cm³/g and pore diameter = 10.2 nm) and HBeta (surface area = 527 m²/g, SiO₂/Al₂O₃ = 300 molar ratio, pore volume = 0.336 cm³/g and pore diameter = 9.2 nm) from Zeolyst International were used in all catalytic experiments. In a typical experiment, the half-inch O.D. tube reactor was packed with 10 g of waste plastic followed by a 1-g charge of catalyst. The plastic shreds and catalyst charge were separated by glass cotton inside the reactor. Nitrogen was fed into the tube reactor where the pressure was maintained at ~0.3 barg. During thermal heating, the final reactor temperature was maintained at 450–470 °C for 45 min using a horizontal Carbolite furnace. This range of temperature was identified after carrying out several experimental trials; the waste HDPE was first subjected to a TGA analysis using Netzsch TG 209 F1 Libra. The heating rate was 10 °C/min. As illustrated in Fig. 1 and 98.2% of the waste HDPE was pyrolysed by the time the temperature reached 500 °C.

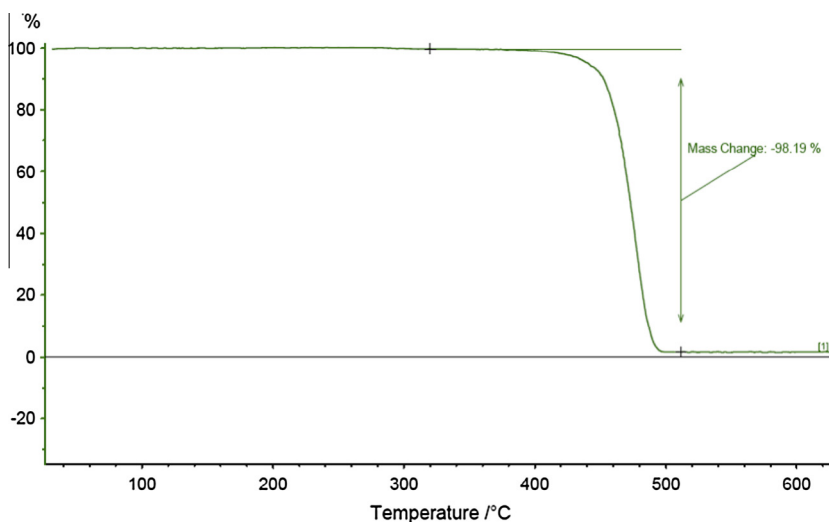


Fig. 1. TGA results of the waste HDPE shampoo bottles.

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