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Light olefins from HDPE cracking in a two-step thermal and catalytic process

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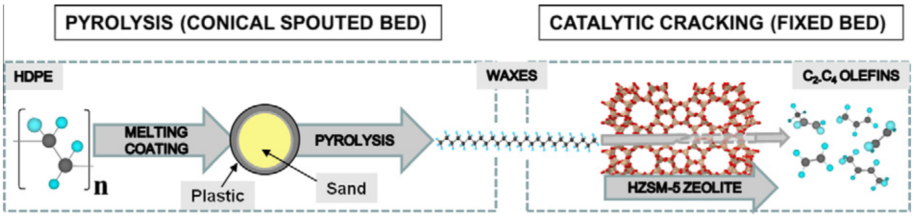
HIGHLIGHTS

- ▶ The two-step reaction system allows working with a continuous feed of HDPE.
- ▶ The product stream obtained in the pyrolysis step is mainly composed of waxes.
- ▶ The low residence time in the catalytic reactor avoids by-product formation.
- ▶ High yield of C_2–C_4 olefins (62.9 wt.%) at 550 °C and 8 g_{cat} min g_{HDPE}^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

The continuous catalytic pyrolysis of high density polyethylene (HDPE) has been carried out in a two-step reaction system involving a pyrolysis conical spouted bed reactor followed by a catalytic fixed bed reactor. The good performance of the conical spouted bed reactor has allowed using a low temperature in thermal cracking (500 °C) without defluidization problems, obtaining a volatile stream with a 90 wt.% overall yield of C_{12}–C_{20} and waxes in the first step. The effect of the second-step operating conditions on product yields and composition has been studied using a catalyst based on a HZSM-5 (SiO_2/Al_2O_3 = 30) zeolite. The influence of temperature in the 350–550 °C range and space–time in the 0–8 g_{cat} min g_{HDPE}^{-1} range has been studied. An increase in temperature or space–time gives way to an increase in the yield of light olefins, reaching a value of 62.9 wt.% at 550 °C and 8 g_{cat} min g_{HDPE}^{-1}, with the individual yields of ethylene, propylene and butenes being 10.6, 35.6 and 16.7 wt.%, respectively. Although the yield of single-ring aromatics increases when both variables studied are increased, the maximum yield obtained was lower than 13 wt.%. The yield of waxes (the main product in the first step) is negligible even at low temperatures or spaces-times, which evidences the efficiency of the catalytic step.

1. Introduction

Current plastic consumption has been quantified at 100 kg per capita/year and is expected to increase to 140 kg per capita/year by 2015 [1]. In Europe, the Waste Framework Directive (Council Directive 2008/98/EC) provides a legal basis for the waste management hierarchy with the aim of increasing waste management recovery targets and, therefore, promoting recycling.

Nowadays, energetic valorisation (incineration) is the most widely used method of thermal treatment, although it has considerable environmental limitations and is considered a temporary solution until tertiary recycling technologies become feasible. The thermal and catalytic cracking of waste plastic is considered one of the most feasible large-scale recycling methods, since waste plastic is a valuable source of liquid and gas fuels, as well as chemicals [1–5]. Cracking technologies have become highly developed, especially for valorising polyolefin (2/3 of waste plastic), and they are eco-friendly. Therefore, cracking technologies continue to provide an excellent opportunity for research.

The main difficulty facing waste plastic cracking processes is related to the sticky nature and low thermal conductivity of plastic materials. Therefore, an adequate choice of reactor is essential for minimizing the physical step limitations prior to devolatilization

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[6]. The plastic must melt and then coat the sand in order to provide the maximum contact surface for facilitating the transfer of volatiles to the gas phase. Della Zassa et al. [7] highlight the importance of separating the melting step from the pyrolysis step to improve heat and mass transfer between phases and minimize plastic degradation to carbonaceous material. Given that fluidized bed reactors attain high heat and mass transfer rates, they can operate under isothermal conditions and have been extensively used in plastic pyrolysis, even with continuous plastic feeding [8–11].

Previous studies have reported the good performance of the conical spouted bed reactor (CSBR) for the continuous pyrolysis of HDPE [12]. The plastic is fed into the reactor as solid particles and, prior to the cracking reactions, the plastic melts and coats the sand and/or catalyst particles contained in the bed. The vigorous cyclic movement of the particles in the CSBR facilitates their uniform coating with fused plastic, improving heat and mass transfer and avoiding the defluidization problems occurring in the pyrolysis of plastics in fluidized bed reactors [13]. Furthermore, the CSBR is very versatile operating in a wide range of gas residence time, from spouting conditions (gas residence time around 1 s) to dilute spouting (jet spouted bed) conditions (gas residence time around 20 ms) [14], and therefore, minimizing the secondary reactions, such as overcracking to produce methane and condensing light olefins to give polyaromatics (PAH).

Consequently, the CSBR is especially suitable for the selective production of waxes (C_{21+}) without defluidization problems [12]. These waxes are suitable for dissolving in vacuum gas oil and co-feeding into catalytic cracking units (FCC) [15], given that they contribute to increasing C_2–C_4 olefin yield and their cracking causes a synergistic effect on the cracking of vacuum gas oil [16,17].

Furthermore, the cyclic movement of particles that is characteristic of spouted beds gives way to low segregation, which is a great advantage of the CSBR reactor for using the catalyst in situ [18,19]. The use of an acid catalyst lowers the activation energy and, therefore, allows decreasing the pyrolysis temperature and increasing the selectivity of high interest products [20,21]. The use of HZSM-5 catalysts in polyolefin pyrolysis in fluidized bed reactors has been studied by several authors with the aim of obtaining a product stream composed mainly of light olefins or a gasoline fraction with low aromatic content [22–26]. In situ pyrolysis of HDPE on HZSM-5 catalysts in a CSBR reactor has also been studied [27,28]. Due to their strong acidity, HZSM-5 zeolites are highly active for cracking, isomerisation and aromatization reactions taking place by carbocation intermediates [5], whereas their shape-selectivity in the microporous structure hinders hydrogen transfer reactions and polyaromatic generation and contributes to increasing C_2–C_4 olefin selectivity with low coke generation [29]. Moreover, the three-dimensional structure of the HZSM-5 zeolite facilitates coke precursor diffusion towards the outside of the zeolite structure, which is enhanced by the high nitrogen flow rate used in the pyrolysis process in a CSBR [30].

The high yield and selectivity of waxes in a CSBR has allowed their downstream transformation by thermal cracking in a multitubular reactor at high temperatures. A high yield of C_2–C_4 olefins has been obtained, reaching a value of 76 wt.% at 900 °C, with the individual yields of ethylene, propylene and butenes being 39.8, 19.2 and 17.2 wt.%, respectively, with a low yield of aromatics (5.5 wt.%) [31].

In this study, the volatiles formed in the thermal cracking of HDPE in a CSBR (mainly waxes) have been converted in a catalytic step in a fixed bed reactor, using a HZSM-5 zeolite catalyst for the selective production of light olefins. The influence of second-step operating conditions (temperature and space–time) on product yield and composition has been studied in order to optimize the catalytic step for maximizing light olefin production.

The two-step system (thermal and catalytic) allows using different temperatures and contact times in each step. This strategy has been studied using a batch pyrolysis reactor and an in-line fixed bed catalytic reactor with an acid catalyst for obtaining monomers or fuels [32–34]. Moreover, the two-step operation has been applied to plastic gasification for obtaining H_2, using an in-line fixed bed reactor with a reforming catalyst [35].

2. Material and methods

2.1. Experimental equipment and conditions

The HDPE was supplied by the Dow Chemical Company (Tarragona, Spain) in the form of cylindrical pellets (4 mm). The properties specified by the supplier are as follows: average molecular weight, 46.2 kg mol^{-1}; polydispersity, 2.89 and density, 940 kg m^{-3}. The higher heating value, 43 kJ kg^{-1}, has been measured by differential scanning calorimetry (Setaram TG–DSC 111) and isoperibolic bomb calorimetry (Parr 1356).

Fig. 1 shows a scheme of the bench-scale plant used in this study. The solid feed system consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed. The plastic is fed into the reactor by raising the piston while the whole system is vibrated by an electric motor. A very small N_2 flow rate introduced into the vessel stops the volatile stream entering the feeding vessel. The plastic feed rate can be varied from 0.2 to 5 g min^{-1} (1 g min^{-1} in this study). The pipe that connects the feeding system with the reactor is cooled with tap water to avoid the plastic melting and clogging the system.

The dimensions of the conical spouted bed reactor used guarantee bed stability in a wide range of operating conditions and were established according to previous hydrodynamic studies [36,37]. A similar reactor has been used for the pyrolysis of different materials, such as other plastic materials (polystyrene, polymethylmethacrylate and polyethylene terephthalate) [38–40], scrap tyres [41], and lignocellulosic biomass [42]. The bed was made up of 50 g of sand (0.3–0.4 mm) and nitrogen was used to fluidize the bed. The nitrogen flowrate was 20% above that required for the minimum spouting velocity (5 L min^{-1} under ambient conditions), which ensures the vigorous movement of the sand enhances heat and mass transfer in the bed and maintains the bed isothermal. Temperature (500 °C) was controlled by a thermocouple placed in the bed. The average residence time of the volatile product ranges from approximately 30 milliseconds in the spout zone to 500 milliseconds in the annulus.

The pyrolysis volatiles formed (mainly waxes) are fed in-line to the catalytic fixed bed reactor placed in a forced convection oven kept at 270 °C to avoid the condensation of the heavy products. The fixed bed is a cylindrical stainless steel reactor, with an internal diameter of 13.1 mm and a total length of 305 mm. The residence time in this reactor is of around 30 milliseconds. Upstream from the catalytic fixed bed reactor, a high efficiency cyclone is placed inside the oven to retain the fine sand particles entrained from the bed. The catalytic bed consists of 8 g (sand + catalyst), with the amount of catalyst (1–2 mm) being 0, 4, 6 and 8 g, corresponding to the values of space–time of 0, 4, 6 and 8 g_{cat} min $g_{HDPE}{}^{-1}$, respectively. A K-type thermocouple is used to control and monitor the temperature in the reactor and the runs have been carried out at 350, 400, 450, 500 and 550 °C. The continuous runs have been held for 5 h to obtain enough liquid for its subsequent analysis and to qualitatively assess the significance of catalyst deactivation by coke deposition.

The products formed in the catalytic step circulate through a volatile condensation system. It consists of a double-shell tube condenser cooled with tap water, a Peltier cooler and a