CONTINUOUS POLYOLEFIN CRACKING ON AN HZSM-5 ZEOLITE CATALYST IN A CONICAL SPOUTED BED REACTOR

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Abstract

The effect of operating conditions on product yields and compositions has been studied in the catalytic cracking of polyolefins (high and low density polyethylene and polypropylene) in a conical spouted bed reactor. The catalyst has been prepared by agglomerating an HZSM-5 zeolite (SiO₂/Al₂O₃=30) with bentonite and alumina. The study has been carried out in continuous mode, in the 450-570 °C range, with polyolefin flow rates between 1 and 2 g min⁻¹ and feeding up to 1 kg of polyolefin into a 30 g catalyst bed. The result is an excellent performance of the reactor-catalyst pairing for continuous catalytic pyrolysis, given that the yields obtained in the pyrolysis of high density polyethylene at 500 °C without defluidization problems and very low catalyst deactivation are as follows: 60 wt% of C₂-C₄ olefins, 15 wt% of non-aromatic C₅-C₁₁ hydrocarbons, 10 wt% of single-ring aromatics and 14 wt% of C₄ alkanes. Only small differences are observed in the pyrolysis of the different polyolefins.

Keywords: spouted bed, catalytic pyrolysis, waste plastic, HZSM-5 zeolite, polyolefin recycling

1. Introduction

The pyrolysis of waste plastics is an interesting route for the large-scale production of fuels and monomer recovery [1]. Different laboratory or pilot scale reactors have been studied. The sticky nature of the fused plastic and the limitations of heat and mass transfer between phases are the main difficulties that limit the larger scale implementation.

The conical spouted bed reactor performs well in terms of heat and mass transfer, and it allows for minimizing the problem of defluidization caused by a very sticky reaction medium. It allows for operating with the catalyst in situ without segregation problems due to the rapid and uniform coating of sand particles with fused plastic. The residence time of the volatiles is low (centiseconds), minimizing their transformation into secondary products.

The use of acid catalysts (based on zeolites HY, HZSM-5, H₅, MCM-41) in situ allows for decreasing pyrolysis temperature (essential for the viability of a highly endothermic process) and increasing selectivity to products of high interest, as are olefins. The good performance of the HZSM-5 zeolite in attenuating coke deactivation is well-known in catalytic processes and it has been confirmed in this case, in which a high flow rate of N₂ helps the sweeping of coke precursors towards the outside of the zeolite crystals. This phenomenon helps to attenuate deactivation by coke, which is lower than in the case of the catalysts prepared based on H₅ and HY zeolites [2].

2. Materials and Methods

HDPE, LDPE, and PP polyolefins have been supplied by Dow Chemical (Tarragona, Spain) in the form of chippings (4 mm).

The pyrolysis pilot plant and its dimensions have been described elsewhere [3]. The system for feeding polyolefins involves a hopper (2 L) with a three-way hollow ball valve. The device is actuated by a frequency programmed automaton every 7.5 s for a total feed of 1 g min⁻¹ into a bed of 30 g of catalyst. The pipe to feed the polyolefin into the reactor (half an inch in diameter and cooled by tap water) is located over the fountain zone of the spouted bed in order to facilitate the steps of plastic fusion and coating of the catalyst particles prior to cracking. The on-line analysis of the outlet volatile stream (very diluted in N₂) has been carried out by periodically sending samples to a GC (Agilent 6890) equipped with an FID. Identification has been carried out by means of a GC coupled with an MS (Shimadzu QP2010S).

A catalyst has been prepared based on an HZSM-5 zeolite with a ratio of SiO₂/Al₂O₃=30. In order to obtain particles of a suitable size (0.6-1.2 mm diameter range) and mechanical resistance for the conical spouted bed reactor, the zeolite particles (25 wt%) have been agglomerated by wet extrusion with bentonite (30 wt%) and inert alumina (45 wt%). The agglomeration generates meso- and macropores in the particles, attenuating deactivation. Prior to use, the catalyst has been calcined at 575 °C for 2 h in a N₂ atmosphere.
3. Results and Discussion

Figure 1 shows the effect of temperature, in the 450-570 °C range for the transformation of HDPE. Product fractions have been classified as follows: light olefins (C₂-C₄), light alkanes (C₄), light liquid fraction (C₅-C₁₁, without aromatic components), single-ring aromatics, heavy liquid fraction (C₁₂-C₂₀), and waxes (C₂₁+).

Regarding the gaseous product fraction, C₂-C₄ olefins are the main products according to the following yield order: propylene > butenes > ethylene. As temperature is increased the yield of ethylene increases, but it is steady above 525 °C, around a value of 11.0 wt%. The yield of propylene peaks around 500 °C with a yield of 28.7 wt%. The yield of butenes decreases as temperature is increased and reaches a steady value of around 17.5 wt% above 525 °C. This re-distribution of olefins is due to the oligomerization-cracking mechanisms.

Analyzing the C₅-C₁₁ fraction, as the temperature is increased the yield of C₅ components decreases, but increases in the cases of C₇, C₈, and C₉, which is explained by the olefinic nature of C₅ compounds and the aromatic character of C₇-C₉ compounds. This effect of temperature is explained by the cracking of C₇-C₉ olefins to form C₂-C₄ light olefins and the formation of aromatics by the condensation of C₂-C₄ olefins. Nevertheless, the aromatic components are not cracked under these conditions. Likewise, there is no significant effect of temperature on the yields of paraffins, isoparaffins, and naphthenes in the C₅-C₁₁ fraction.

When the flow rate of HDPE is doubled at 500 °C, the yield of C₂-C₄ olefins decreases slightly (from 56 wt% for 1.0 g min⁻¹ to 54 wt% for 2.0 g min⁻¹), with propylene being the one more affected, and the yields of single-ring aromatics and light alkanes increase slightly.

A slightly lower yield of light olefins and a higher yield of light alkanes and aromatics are observed for LDPE. These differences are attributed to the shorter chains with a higher branching degree for LDPE, which makes its cracking easier and, consequently, facilitates a more rapid formation of olefins and their condensation steps to form aromatics or C₁₂+ hydrocarbons. The higher yield of C₁₂+ in the pyrolysis of PP is associated with the polymerizing capacity of propylene.

In order to avoid the operational problems observed at temperatures below 450 °C, operation should be carried out at 500 °C. The yields for C₂-C₄ olefins, non-aromatic fraction, single-ring aromatics, and C₄ alkanes are 60 wt%, 15 wt%, 10 wt%, and 14 wt%, respectively.

The variation of the flow rate of HDPE fed into the reactor shows the versatility of the spouted bed reactor, i.e., there are small differences in the yields as the flow rate of HDPE is increased and the transformation into light products is completed thanks to the efficient coating of catalyst particles with the fused plastic. The yields are very similar for the different polyolefins (HDPE, LDPE, PP), although lower for olefins (due to a lower yield of propylene and butenes), and higher for light alkanes and aromatics when LDPE is in the feed.

4. Conclusions

The conical spouted bed reactor is suitable for the catalytic pyrolysis of polyolefins (HDPE, LDPE, PP) in continuous mode for obtaining high yields of olefins and hydrocarbons of interest as fuel. The small difference in the results shows that this technology with an HZSM-5 zeolite catalyst is suitable for the pyrolysis of different polyolefins.

References