PYROLYSIS OF HIGH DENSITY POLYETHYLENE CARRIED OUT IN CONTINUOUS MODE IN A CONICAL SPOUTED BED REACTOR IN THE 500-700 ºC RANGE

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Abstract

The pyrolysis of high density polyethylene (HDPE) carried out in continuous mode in a conical spouted bed reactor has been studied in the range between 500 and 700 °C. The products have been grouped into the lumps of gas (C_{4-}), gasoline (C_5-C_{11}), diesel (C_{12}-C_{20}) and waxes (C_{21+}). The product yields and compositions of these fractions have been compared both to those previously obtained in the pyrolysis performed in discontinuous mode and to those obtained by other authors in fluidized bed reactors. The results confirm the optimal performance of the conical spouted bed reactor (CSBR) in obtaining high yields of waxes and fuels with low aromatic content, which is explained by the appropriate conditions of the CSBR needed to enhance heat and mass transfer between phases (capacity for coating the sand with plastic) and minimize secondary reactions (short residence time of the volatiles).

Keywords: *pyrolysis, plastic wastes, spouted bed, waxes, fuels*

1. Introduction

The pyrolysis of plastics arouses great interest for their valorization, as it allows obtaining high yields of fuels and raw materials for the petrochemical industry. Moreover, the pyrolysis process has few environmental issues [1].

The pyrolysis of polyolefins takes place through a complex free-radical mechanism, which gives way to a wide product distribution that depends on pyrolysis conditions: heating rate, temperature, and residence time. The selection of reactor is a key factor for the kinetics of pyrolysis as well as for the product distribution obtained. The following steps take place from the moment that the waste plastic particles are fed into the reactor: i) Fusion of the plastic; ii) fused plastic pyrolysis. The design of the reactor, with a continuous feeding system, must attain the fast fusion of the plastic in order for pyrolysis (the second step) to be the controlling one. The yields of products of commercial interest may be optimized by selecting appropriate pyrolysis conditions.

Solid materials are used in the reactors in order to be coated with the fused plastic, facilitating heat and mass transfer between the plastic and the gas. The main advantages of the CSBR, Figure 1, are: i) Cyclic movement of the particles suitable for fast and uniform coating of the sand or catalyst particles with the fused plastic. This movement is characteristic of spouted beds. ii) More vigorous particle circulation than in bubbling fluidized bed reactors, thus minimizing defluidization problems, which is a well-known limitation for FBRs. iii) Short residence time of the volatiles (in the order of centiseconds), which minimizes the formation of secondary products.

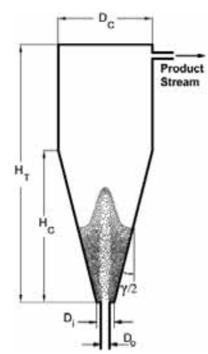

Fig. 1. Reactor diagram.

2. Materials and Methods

The HDPE has been provided by Dow Chemical in the form of 4 mm size chippings. The pyrolysis pilot plant has previously been described [2]. Pyrolysis has been carried out in the 500 to 700 °C range. A quantity of 30 g of sand with a particle diameter in the 0.6-1.2 mm range has been determined as the most suitable bed.

The on-line analysis of the outlet volatile stream has been carried out by a GC (Agilent 6890) provided with an FID. Identification of the liquid fraction components and waxes (diluted in tetrahydrofuran at 55 °C) has been carried out by means of a GC coupled with an MS (Shimadzu QP2010S). The simulated distillation of the condensed liquid and waxes has been developed according to the ASTM-D2887-04 standard. The waxes have also been analysed by means of high resolution liquid chromatography (HP 1100) provided by a GPC column. The nature of the bonds has been studied by FTIR spectrophotometry in a Nicolet 6700.

3. Results and Discussion

Figure 2 shows that the waxes are the fraction of highest yield from 500 to 650 °C. Their yield accounts for almost 70 wt% at 500 °C, and when added to the yield of the diesel fraction, the joint yield accounts for more than 90 wt%. The yield of waxes diminishes as temperature is raised, whereas the yields of gasoline and gas increase and that of diesel peaks at 30 wt% at 550 °C. For temperatures above 675 °C, the highest yield corresponds to the gas fraction.

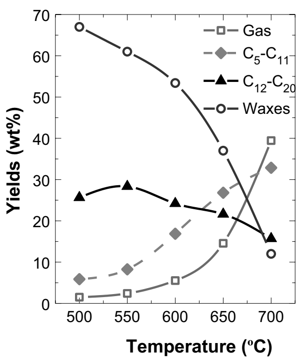

Fig. 2. Effect of temperature on the yields of product fractions (wt%).

Thermal pyrolysis above 550 °C gives way to high yields of C_2-C_4 olefins (37 wt% at 700 °C) and a low aromatic content in the gasoline fraction is obtained. The light alkanes are by-products of low interest, which are best used to supply energy to the process.

Regarding the gas fraction, the yield of ethylene is the one that increases in a more pronounced way, from 0.08 wt% at 500 °C to 17.82 wt% at 700 °C. This high increase in the yield of ethylene is in line with the results in the literature obtained in fluidized bed reactors. The yield of propylene also increases considerably as temperature is raised.

The yields of the components in the gasoline fraction increase as temperature is raised. The distribution of the yields for the components with a different number of carbon atoms is fairly uniform in the 500-650 °C range. At 700 °C, the yields of C_5-C_7 components are higher, especially that of C_6.

An analysis of the nature of the bonds reveals that the highest yield is that of olefins, and it increases considerably as temperature is raised. The yield of isoparaffins is also significant, although it increases with temperature to a lesser extent than that of olefins, and even decreases at 700 °C. The yield of aromatic components also increases with temperature, but to a lesser extent than that of olefins. The yields of both linear paraffins and naphthenes are low and hardly vary with temperature.

In the diesel fraction, the yields of the diolefin components are more significant than in the case of the gasoline fraction. The yield of the heaviest components decreases as temperature is increased and the yield distribution obtained becomes more uniform. The yield of olefins is the highest one for the whole temperature range studied, peaking at 600 °C. The yield of diolefin components increases by increasing temperature from 500 to 600 °C, whereas that of paraffins decreases linearly when temperature is raised.

Two waxes fractions have been quantified: i) Light waxes, i.e., the C_{21}-C_{40} fraction; ii) Heavy waxes (the remaining waxes). As the reaction temperature is raised, the content of light fraction compounds (C_{20-}) dissolved in the waxes increases. An increase in reaction temperature involves the production of lighter waxes.

4. Conclusions

The conical spouted bed reactor performs well for polyolefin pyrolysis carried out in continuous mode. The cyclic movement of the particles facilitates their uniform coating with fused plastic, improving the heat and mass transfer rate between the phases. Besides, the short residence time of the volatiles minimizes by-product formation (methane and polyaromatic hydrocarbons).

The HDPE pyrolysis process is versatile in the 500-700 °C range. The yield of waxes (C_{21+}) accounts for 67 wt% at 500 °C and decreases to 12 wt% in this range. An increase in temperature involves an increase in the gases (C_{4-}) and gasoline fraction (C_5-C_{11}), which account for 39 wt% and 33 wt% at 700 °C, whereas that of diesel (C_{12}-C_{20}) decreases (16 wt% at 700 °C). Consequently, the CSBR is an excellent technology for obtaining waxes at low temperatures (500 °C) without defluidization problems, making them a suitable feed for FCC units. On the other hand, the operation at high temperature (700 °C) is promising for obtaining gasoline (33 wt% with a significant content of C_5-C_7 olefins), together with a high yield of C_2-C_4 olefins (37.7 wt%).

The results obtained in the literature in fluidized bed [3] are consistent with those obtained in this study.

References

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