INFLUENCE OF TEMPERATURE IN THE CATALYTIC PYROLYSIS OF HDPE IN TWO STEPS

M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao and M. Olazar

University of the Basque Country, Department of Chemical Engineering, P.O. Box 644 - E48080 (Bilbao) Spain
e-mail: maite.artetxe@ehu.es

Abstract

Continuous pyrolysis of high density polyethylene was carried out in a two step reaction system consisting of an initial pyrolytic spouted bed reactor followed by a catalytic fixed bed reactor. The pyrolysis has been carried out at 500 ºC and HDPE continuous feed rate was 1g min^{-1}. The effect of the catalytic step temperature on product yields and composition have been studied using a catalyst based on HZSM-5 (SiO_2/Al_2O_3= 30) zeolite. 8 g of catalyst have been used in each run and the influence of the catalytic step temperature was studied in the 350-550 ºC range. The products have been grouped into five lumps: light olefins (C_2-C_4), light alkanes (C_1-C_4), non aromatic C_5-C_{11} compounds, single-ring aromatic compounds and C_{12}-C_{21} hydrocarbons. An increase in temperature gives way to an increase in the yield of light olefins, from 31.5 wt% at 350 ºC to 63 wt% at 550 ºC, and an increase in the yield of single-ring aromatics, from 3 wt% at 350 ºC to 10 wt% at 550 ºC. On the other hand, a great decrease is observed in the yield of non-aromatic C_5-C_{11} compounds, from 50 wt% at 350 ºC to 21 wt% at 550ºC.

Keywords: *plastic waste, catalytic pyrolysis, two step process, spouted bed, HZSM-5 zeolite, HDPE recycling*

1. Introduction

The thermal and catalytic cracking of plastic waste has been regarded as one of the most feasible plastic recycling method at industrial scale, since used plastic could become a valuable source of chemicals, and gas and liquid fuels [1]. The main difficulties that limit the larger scale implementation of the process are the sticky nature of the fused plastic and the low thermal conductivity of plastics, which restricts heat and mass transfer and hinders be isothermicity. Therefore, an adequate choice of the pyrolysis reactor is essential. The conical spouted bed reactor has been used in polyolefin pyrolysis under conditions of maximum particle stickiness. The cyclic movement of sand particles enhances their uniform coating with fused plastic and avoids bed agglomeration [2]. Furthermore, it is a simple device with isothermal bed and suitable for continuous operation and scaling-up.

The use of acid catalysts (HZSM-5, HY and Hβ) *in situ* allows for increasing the selectivity of high interest products, such as olefins in the pyrolysis of polyolefins, and decreasing pyrolysis temperature [3]. Two-step catalytic pyrolysis not only allows using different temperatures in the pyrolytic and catalytic reforming stages but also ensuring the contact between pyrolysis volatile products and the catalyst. Furthermore, this strategy may be implemented with cracking catalysts for obtaining the monomer or fuels and with reforming catalysts for obtaining H_2 [4].

This work approaches continuous thermal cracking of HDPE in a spouted bed reactor followed by a catalytic step in a fixed bed reactor in order to study the effect of the catalytic step temperature on product yields and compositions.

2. Materials and Methods

The high density polyethylene (HDPE) used has been supplied by Dow Chemical (Tarragona, Spain) in the form of cylindrical pellets (4 mm).

The catalysts consists of 25 wt% of HZSM-5 zeolite provided by Zeolyst International (Kansas, USA), agglomerated by wet extrusion with bentonite (30 wt%) and with inert alumina (45 wt%). The catalyst was calcined at 575 ºC for 2 h in order to achieve resistance to irreversible deactivation by dealumination. The most important properties of the catalyst have been measured; BET surface area is 184 m^2 g^{-1}, total acidity 0.2 mmol NH_3 g^{-1} and average acid strength 100 kJ (mol NH_3)$^{-1}$.

Continuous pyrolysis of HDPE was carried out in a conical spouted bed reactor at 500 ºC. The bed was made up with 50 g of sand (0.3-0.4 mm) and the plastic was fed continuously with a feedrate of 1 g min^{-1}. Nitrogen was used to fluidize the bed and the flowrate was 20 % in excess of that required for minimum spouting velocity (5 L min^{-1} at room conditions). The pyrolysis volatiles (mainly waxes) formed are fed in line to a catalytic fixed bed reactor. The bed consists of 8 g of catalyst (1-2 mm) and the experiments have been carried out at 350, 400, 450, 500 and 550 ºC. Each continuous run lasts for around 10 min, and the experiments have been repeated several times to ensure a good reproducibility of the results. The product stream has been analyzed by a Varian 3900 chromatograph and a

μGC (Varian Q4900) connected on-line to the reactor. At the same time, a mass spectrometer (Shimadzu QP2010S) and a microGC-MS spectrometer (Agilent MSD5975B) have been used to identify the compounds.

3. Results and Discussion

Product streams have been grouped into five lumps: light olefins (C_2-C_4), light alkanes (C_1-C_4), single-ring aromatics, non-aromatic C_5-C_{11} compounds and C_{12}-C_{21} hydrocarbons. The yield of waxes, which is the main product in the first step, is negligible.

Figure 1 shows the effect of temperature on product fraction yields. An significant effect of temperature has been observed, increasing the yield of light olefins from 31.5 wt% at 350 ºC to 63 wt% at 550 ºC and decreasing the yield of non-aromatic C_5-C_{11} compounds from 50 wt% at 350 ºC to 21 wt% at 550 ºC. Moreover, the yield of single-ring aromatic compounds increases when temperature is raised, from 3 wt% at 350 ºC to 10 wt% at 550 ºC. The effect of temperature on light alkanes and C_{12}-C_{20} hydrocarbons is less significant. Elordi et al. observed similar product yields in a study carried out in a conical spouted bed reactor at 500 ºC using HZSM-5 zeolite based catalyst *in situ* [3].

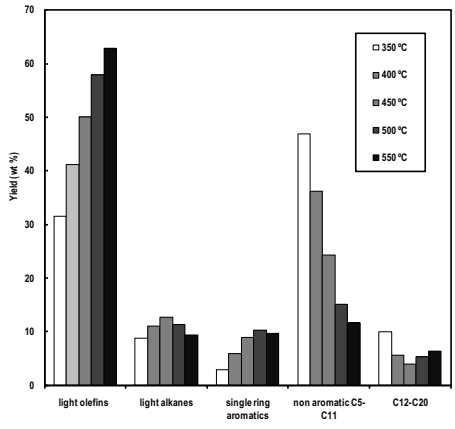

Fig.1. Effect of temperature on product fraction yields.

Regarding the gas fraction, light olefin fraction is mainly composed of propylene. The yield of propylene increases as temperature is increased, reaching a value of 35.5 wt% at 550 ºC. Furthermore, the yield of ethylene increases when temperature is increased, from 0.8 wt% at 350 ºC to 10 wt% at 550 ºC, whereas the yield of butene (18 wt%) remains almost constant. The main compound in the lump of light alkanes is butane, with a yield of 6.5 wt% at 550 ºC. The yields of methane and ethane are very low (below 0.4 wt%).

In the gasoline fraction, which is made up of single-ring aromatic fraction and non-aromatic C_5-C_{11} compounds, C_5 and C_6 olefins are the main products at low temperature. As temperature is raised, the yields of C_5 and C_6 olefins decrease and the yields of C_6, C_7 and C_8 aromatic compounds increase. This effect of temperature is explained by the cracking of C_{5+} olefins to form C_2-C_4 light olefins and the formation of aromatics by the condensation of C_2-C_4 olefins. The main compounds in the single-ring aromatic fraction are toluene and xylenes, with a yield of 4 wt% and 3 wt% at 550 ºC, respectively. Furthermore, the yields of paraffins, isoparaffins and naphthenes in the C_5-C_{11} fraction decrease steadily as temperature is increased.

The main products in the C_{12}-C_{21} fraction are paraffins and the yield of this fraction decreases as the temperature increases from 350 ºC to 400 ºC, whereas no significant effect of temperature has been observed on the yield of C_{12}-C_{21} hydrocarbons in the 400-550 ºC range.

4. Conclusions

The conical spouted bed reactor is a suitable technology for HDPE continuous pyrolysis, given that high heat transfer and bed turbulence avoid defluidization problems.

The catalyst based on HZSM-5 zeolite exhibits high activity transforming waxes into C_{20-} hydrocarbons even at 350 ºC. Besides, the catalyst used is highly selective for producing light olefins, reaching a value of 63 wt% at 550 ºC, with propylene being the main product with a yield of 35.5 wt%.

The increase in the temperature in the 350-500 ºC range gives way to an increase in the yield of light olefins and a decrease in the yield of non-aromatic C_5-C_{11} compounds. Furthermore, temperature also affects single-ring aromatic compounds by increasing their yield when this variable is increased.

References

[1] J. Aguado, D.P. Serrano and J.M. Escola. Fuels from Waste Plastic by Thermal and catalytic Proces: A Review. *Industrial Engineering Chemical Research* 47(2008) 7982-7992.

[2] R. Aguado, R. Prieto, M.J. San José, S. Alvarez, M. Olazar and J. Bilbao. Defluidization modelling of pyrolysis of plastics in a conical spouted bed reactor. *Chemical Engineering and Processing* 44(2005) 231–235.

[3] G. Elordi, M. Olazar, G. opez, M. Amutio, M. Artetxe, R. Aguado and J. Bilbao. Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spoted bed reactor. *Journal of Analytical and Applied pyrolysis* 85(2009) 345-351

[4] Ch. Wu and P.T. Williams. Pyrolysis-gasification of plastics, mixed plastics and real-world plastic waste with and without Ni-Mg-Al catalyst. *Fuel* 89(2010) 3022-3032.