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Catalytic Cracking of HDPE Pyrolysis Volatiles over a Spent FCC Catalyst

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The effect of temperature in the catalytic cracking of HDPE over a spent FCC catalyst on the product distribution has been studied using a two-step reaction system. Thermal pyrolysis of HDPE has been carried out in a conical spouted bed reactor and the volatiles formed (mainly waxes) have been fed in-line into a catalytic fixed bed reactor. An increase in the second stage temperature from 450 °C to 550 °C gives way to an enhancement of cracking reactions, achieving full conversion of waxes at 550 °C. At this temperature, gasoline and light olefins are the main product fractions obtained, with a yield of 52 wt% and 28 wt%, respectively.

1. Introduction

The increase in the production and consumption of plastic materials leads to a serious environmental issue since the amount of post-consumer plastic waste recovered increases annually, reaching a value of 25.2 Mt in Europe in 2012 (Plastics Europe, 2013). Thermal or catalytic pyrolysis is considered one of the most feasible plastic recycling methods at large scale, as well as environmentally friendly and economically viable waste managing procedure (Oyedun et al., 2013).The main problem of this recycling method lies in the low thermal conductivity and sticky nature of plastic materials, which makes essential an adequate choice of the pyrolysis reactor. Fluidized bed reactors have been widely used for plastic pyrolysis (Donaj et al., 2012) because of their high heat and mass transfer rates. However, fused plastic aggregates are formed at low temperature causing bed defluidization (Mastellone et al., 2004).

The conical spouted bed reactor has been used in plastic pyrolysis without defluidization problems even under maximum plastic stickiness conditions (Artetxe et al., 2010). The characteristic cyclic movement of this reactor gives way to high heat and mass transfer rates and uniform particle coating with fused plastic in the bed. Furthermore, the vigorous movement of bed particles avoids the formation of fused plastic aggregates, which makes possible working in continuous mode during a long period without defluidization problems. Besides, the conical spouted bed reactor has limited segregation which makes it suitable for working with catalyst and sand in the bed (Amutio et al., 2012).

Thermal pyrolysis of plastics gives way to a wide product distribution. Therefore, acid catalysts (Hβ, HY, HZSM-5 zeolites…) have been used to increase the selectivity to high value added products, such as light olefins, gasoline or diesel fraction (Serrano et al., 2012). The use of a spent FCC catalyst is especially interesting given that not only a waste material from an FCC unit is used but it is also a no-cost catalyst. Several studies on plastic catalytic pyrolysis over FCC catalysts show that the spent FCC catalyst still has cracking activity and high selectivity to gasoline and light olefin fractions (Salmiaton et al., 2011).

Plastic catalytic cracking using in situ catalysts occurs via the steps of plastic melting and sand coating (physical steps), and thermal cracking and catalytic cracking over the catalyst surface, and therefore there are reactions competing in the process. By separating the process into two steps (thermal pyrolysis and catalytic cracking), the physical steps of melting and coating and the thermal pyrolysis occur in the first reactor. Hence,

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the catalyst is used only in the second step for treating a more suitable stream for cracking, which improves significantly catalyst efficiency (Artetxe et al., 2013).

This study addresses the catalytic pyrolysis of HDPE over a spent FCC catalyst in a two-step system: i) thermal pyrolysis of HDPE in a conical spouted bed reactor; ii) catalytic cracking of the volatiles formed in the first step over a spent FCC catalyst in a fixed bed reactor. The aim is to study the effect of the second step temperature (450-550 °C) on the product distribution obtained.

2. Experimental

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).

Figure 1 shows the experimental bench scale plant used in this study. The solid feeding 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. The pipe that connects the plastic feeding system with the reactor is cooled by tap water in order to avoid plastic melting and system blockage. The feeding system allows plastic feed rates in the 0.2-5 g min^{-1} range. In this study, the plastic feed rate has been 1 g min^{-1}.

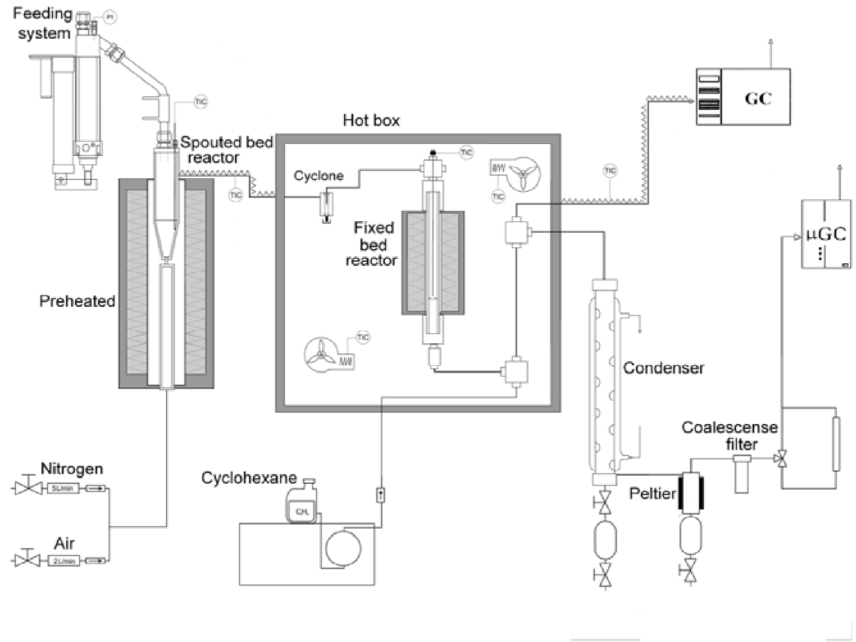

Figure 1: Experimental bench scale plant

The main element of the unit is the conical spouted bed reactor, which has been designed based on previous hydrodynamic studies. A similar reactor has been used for the pyrolysis of different materials, such as other plastic materials (Artetxe et. al, 2010), scrap tyres (Lopez et al., 2009) or biomass (Amutio et al., 2012). Pyrolysis has been carried out at 500 °C and the bed was made up of 50 g of sand (0.3-0.4 mm). Nitrogen has been used as fluidizing agent (5 L min^{-1}; 1.2 times that corresponding to the minimum spouting velocity), which has been heated to the reaction temperature by means of a preheater. The volatiles formed in the conical spouted bed reactor (mainly waxes) are fed in-line into the catalytic fixed bed reactor in which the spent FCC catalyst has been placed. The space time used in this study has been 6 g_{cat} min g_{HDPE}^{-1}. The product stream formed in the second reactor circulate through a condensation system, which consists of a double shell tube condenser, a Peltier condenser and a coalescence filter, ensuring the total condensation of volatile hydrocarbons.

The product stream leaving the pyrolysis and catalytic reactors has been analyzed by an on-line Varian 3,900 chromatograph connected through a line thermostated at 280 ºC to avoid the condensation of heavy products. Cyclohexane (not formed in the process) has been used as an internal standard to validate the mass balance. This compound has been fed into the product stream at the outlet of the catalytic reactor. Furthermore, the non-condensable gases have been analyzed by means of a micro GC Varian 4,900, which allows detailed quantification of the product stream.

2.2 Catalyst

The spent FCC catalyst (Albemarle) has been supplied by a Spanish refinery (Petronor, Somorrostro, Spain). Prior to agglomeration, the spent FCC catalyst has been regenerated with air at 550 °C for 1 h. Then, it has been agglomerated by wet extrusion with bentonite (50 wt%) in orde to confer mechanical and thermal resistance upon the catalyst. Besides, bentonite provides the catalyst with meso and macropores, which attenuate catalyst deactivation by coke deposition, since the coke formed is deposited outside the micropores, thus minimizing external blockage of the channels. Table 1 summarizes the main physical and acid properties of the catalyst used. The physical properties have been measured by N_2 adsorption-desorption (Micromeritics ASAP 2010). The acid properties of the catalyst have been measured by NH_3 adsorption-desorption. The values of total acidity and average acid strength have been obtained by monitoring the differential adsorption of NH_3 simultaneously by calorimetry and thermogravimetry in a Setaram TG-DSC 111.

Table 1: Main properties of the catalyst used.

Properties	Spent FCC catalyst
S_{BET} (m^2 g^{-1})	84
$S_{micropore}$ (m^2 g^{-1})	55
$V_{mesopore}$ (cm^3 g^{-1})	0.06
Pore volume distribution (%)	
<20/20<dp(Å)<500/>500	3.3/10/86.8
D_p (Å)	63
A_T (μmol_{NH3} g^{-1})	59
S_a (KJ mol_{NH3})	105

3. Results

The products obtained have been grouped into six fractions: light olefins (C_2-C_4), light alkanes (C_1-C_4), non-aromatic C_5-C_{11} hydrocarbons, single ring aromatics, C_{12}-C_{21} hydrocarbons and waxes. It should be noted that the pyrolysis of HDPE in a conical spouted bed reactor at 500 °C (first step) gives way to a product stream mainly composed of C_{12}-C_{21} hydrocarbons and waxes (90 wt%) due to the low residence time and low temperature used. These characteristics make the conical spouted bed reactor especially suitable for a selective production of waxes (Elordi et al., 2011) and a good quality product stream for a downstream cracking. Besides, continuous operation leads to a constant stream at the outlet of the first step, which is essential to analyse accurately the effect of operating conditions in the second step.

Figure 2 displays the effect of the catalytic step temperature on the product fraction yields obtained. It is observed that an increase in temperature from 450 °C to 550 °C gives way to a significant increase in the yield of light olefins (from 12 to 28 wt%) and non-aromatic C_5-C_{11} compounds (from 34 to 52 wt%). This effect is due to the enhancement of cracking reactions as temperature is increased, which gives way to a severe decrease in the yield of waxes (from 36 to 1 wt%). Moreover, a slight increase in the yield of aromatics is observed when temperature is increased from 450 to 550 °C, which is due to the fact that cyclization and aromatization secondary reactions are enhanced as temperature is increased (Mastral et al., 2006). However, due to the low residence time of the volatiles in the reactor and the moderate acid strength of the agglomerated spent FFC catalyst, the yield of aromatic compounds at 550 °C, 3 wt%, is still low.

It should be noted that the temperature of 550 °C results especially interesting since waxes (the main product fraction in the first step) are fully converted, evidencing that the spent FCC catalyst not only has activity for hydrocarbon cracking reactions but also produces selectively light olefins and non-aromatic C_5-C_{11} hydrocarbons.

Figure 3 displays the effect of the catalytic step temperature on the individual compound yields in the C_1-C_4 fraction (light olefins and light alkanes). It is observed that an increase in temperature from 450 to 550 °C leads to an increase in the individual yields of three light olefins, reaching a value of 5, 8 and 13 wt% of ethylene, propylene and butane, respectively. Moreover, temperature also has an impact on the selectivity of the three light olefins. At 450 °C propylene is the main light olefin (5 wt%), but as temperature is increased butane selectivity increases and becomes the main light olefin above 500 °C.

As observed, the individual yield of light alkanes (below 3 wt%) is low in the temperature range studied. The high light alkane yield obtained by other authors (Marcilla et al., 2009) is related to the higher residence time of the volatiles in the reactor. In the system proposed in this work, the low residence time of the volatiles in the reactor contributes to minimizing secondary reactions, such as bimolecular cracking reactions to produce methane and ethane and hydrogen transfer reactions to produce light alkanes from light olefins.

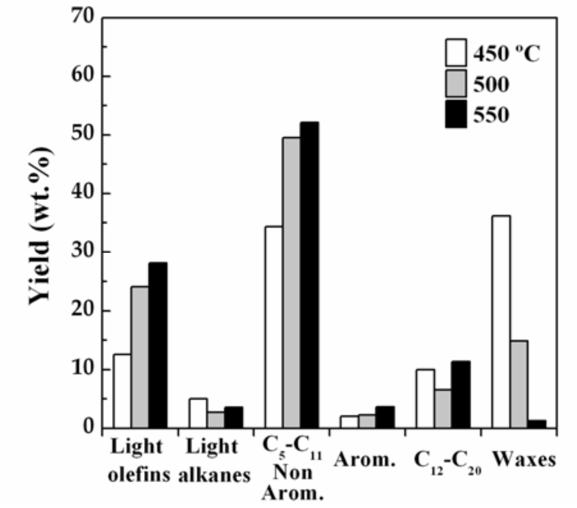

Figure 2: Effect of temperature on the product fraction yields

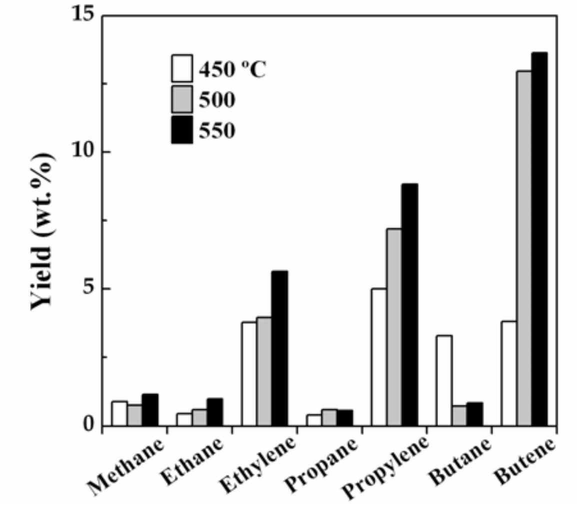

Figure 3: Effect of temperature on the individual compounds in the C_1-C_4 fraction

Figure 4 shows the yield of the different lumps in the gasoline fraction (non-aromatic C_5-C_{11} hydrocarbons and the aromatic fraction) ordered according to the number of carbon atoms (a) and chemical bond (b). An increase in temperature gives way to an increase in all lumps of the gasoline fraction according to the number of carbon atoms as well as chemical bond. The olefinic nature of C_5 and C_6 lumps is noteworthy. These lumps are the main products in the gasoline fraction obtained and their yield increases when temperature is increased due to the cracking of heavier hydrocarbons. Moreover, an increase is observed in the aromatic fraction made up mainly of compounds with C_7 and C_8 carbon atoms, whose formation by cyclization and aromatization reaction is favoured at high temperatures (Mastral et al., 2006). Other authors (Lee et al., 2002) obtained a similar gasoline composition in the catalytic cracking of HDPE over spent FCC catalysts in a stirred semi-batch reactor, with olefins being the prevailing compounds in the gasoline fraction, which are formed easily by primary cracking, but their transformation into paraffins by hydrogenation is not favoured over spent FCC catalysts.

Elordi et al. 2012 have carried out the catalytic pyrolysis of HDPE over a spent FCC catalyst using the catalyst in situ in a conical spouted bed reactor at 500 °C. They obtained similar product yields: 50 wt % of non-aromatic C_5-C_{11} compounds, 30 wt % of light olefins and 10 wt % of waxes (in this work 49, 24 and 15, respectively). However, they used 30 g of catalyst (6 g of catalyst have been used in this work), and therefore a higher efficiency of the catalysts is attained using the two-step reaction system, in which the physical steps and the pyrolysis step are separated from the catalytic step, thus avoiding reaction competition on the catalyst acid sites.

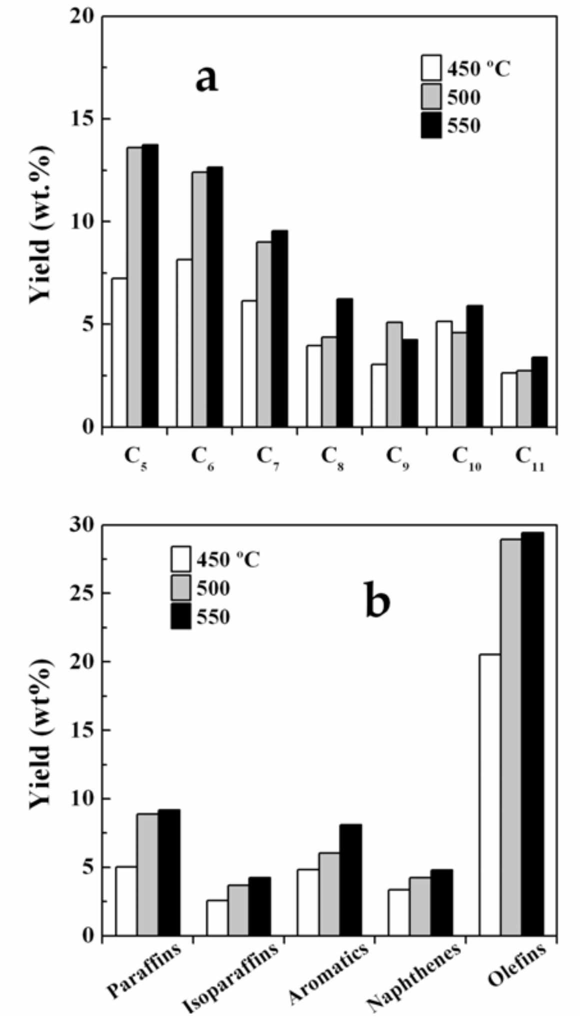

Figure 4: Effect of temperature on the different lumps of the gasoline fraction ordered according to the number of carbon atoms (a) and chemical bond (b)

4. Conclusions

The two-step system (pyrolysis-catalytic cracking) is an interesting technology for the catalytic cracking of HDPE over spent FCC catalysts. The conical spouted bed reactor is especially suitable for continuous plastic pyrolysis at low temperature without defluidization problems. Besides, the low residence time characteristic of this reactor leads to a selective production of pyrolysis primary products, obtaining a continuous product stream mainly composed of waxes for downstream cracking.

The spent FCC catalyst has high activity for hydrocarbon cracking reactions and selectivity to non-aromatic C_5-C_{11} hydrocarbons and light olefins. An increase in the catalytic cracking temperature enhances heavy hydrocarbon cracking reactions, achieving full conversion of waxes at 550 °C and reaching maximum yields of light olefins and non-aromatic C_5-C_{11} hydrocarbons, 24 and 49 wt%, respectively. Secondary reactions such as cyclization and aromatization are also favoured at high temperatures. Nevertheless, the low residence time used in this work and the moderate acid strength of the catalyst used minimize the formation of secondary products, such as light alkanes (5 wt%) and aromatics (3 wt%).

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