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Pyrolysis of Polyolefins in a Conical Spouted Bed Reactor: A Way to Obtain Valuable Products

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Additional information is available at the end of the chapter

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Abstract

The amount of waste plastic increases every single year, which causes a critical environmental issue. Polyolefins (mainly high- and low-density polyethylene and polypropylene) are the most common types of plastics, accounting for 60 wt% of the plastic waste. Pyrolysis, the thermal degradation in an inert atmosphere, is considered to be one of the most appealing technologies for the recycling of plastic materials. The conical spouted bed reactor is suitable for the pyrolysis of plastic waste due to its ability to avoid agglomeration problems that may be caused by the melted plastic. The pyrolysis process may be carried out at different temperatures and with or without the presence of catalysts in the reaction environment in order to streamline product distribution. The resulting products are hydrocarbons: non-condensable gases (C_1 – C_4), gasoline fraction, diesel fraction, and waxes. These fractions might be used directly as feed streams for refinery units or as pools to be mixed with other streams from refineries.

Keywords: spouted bed, pyrolysis, catalytic pyrolysis, zeolites, pyrolysis products

1. Introduction

The polyolefins are polymers produced from the polymerization of olefins. The polyolefins are the most common and cheapest plastics. Polyolefins (particularly polyethylene and polypropylene (PP)) are the most important group of plastics.

The world's plastic production reached 311 million tonnes in 2014 (thermoplastics and polyurethanes and other plastics such as thermosets, adhesives, coatings, and sealants) [1].

Polyolefins (particularly polyethylene and polypropylene) are the most important group of plastics. The advantages of polyolefins include the following: they are odourless, they are non-toxic, and they have relatively good chemical resistance. The worldwide market for polypropylene will reach 62.4 million metric tonnes by 2020, driven by growth in the Asia Pacific region, the Middle East, and Africa [2]. This increase in the production of plastics is accompanied by a growth in the generation of plastic wastes, of which about 60 wt % in weight corresponds to polyolefinic plastics.

The interest in the valorization of plastic wastes arises from the need to avoid their stockpiling, where they cause serious environmental problems and deteriorate the landscape. In the EU member states, directive 2008/98/EC of the European Parliament states that no less than 30% of plastic solid waste (PSW) should be utilized for re-use or recycled use. The directive clearly states that by 2020, all solid waste streams (including plastics) should be diverted towards thermal and/or mechanical treatment and energy recovery, reducing the percentage of solid waste being landfilled to a minimum. Consequently, the recycling of plastics is the objective of various studies and brings the proposition of various technological alternatives. In this sense, the thermal degradation of plastics allows obtaining monomers, combustible gases, and/or energy, with the reduction of landfills as an added advantage [3].

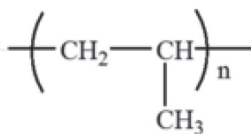
1.1. Properties

High-density polyethylene (HDPE) and low-density polypropylene (LDPE) are thermoplastic polymers formed by repetitive units of ethylene. Their chemical formula is $(-\text{CH}_2-\text{CH}_2-)_n$.

HDPE is a polymer of a linear chain without ramification, so its density is high and also the intermolecular forces.

LDPE is a polymer of a branched chain, so its density is lower.

PP is a thermoplastic polymer formed by repetitive units of propylene. Its chemical formula is



The properties of polypropylene are similar to the ones of polyethylenes. The major differences are that it has a lower density, a higher fusion temperature (160–170°C as opposed to 135°C), and it has a higher grade of crystallinity (it is almost crystalline, compared with around 90% crystallinity for HDPE and 40–50% crystallinity for LDPE). The crystallinity is related to the branched structure and the molecular weight, as the more branched the structure and the higher the molecular weight are, the lower the crystallinity is.

In **Table 1**, the following properties of the polyolefins are shown: molecular weight, polydispersity, density and higher heating value.

| Property | HDPE | LDPE | PP |
|------------------------------|--------|--------|--------|
| Mw (g/mol) | 46,200 | 92,200 | 70,000 |
| Polydispersity | 2.89 | 5.13 | 2.00 |
| ρ (kg/m ³) | 940 | 923 | 890 |
| Higher heating value (kJ/kg) | 46.2 | 46.5 | 46.05 |

Table 1. Properties of polyolefins.

The polydispersity value (ratio between the weight average molecular weight and the number average molecular weight) indicates the heterogeneity of the molecular weight of macromolecules that form the polymer. Any industrial polymer consists of fractions of different macromolecules of different molecular weights. The polydispersity value depends on the conditions in which polymerization has been carried out. Its minimum value is 1 for monodispersed species.

The Mw, polydispersity, and density are provided by the manufacturer of the materials (Dow Chemical, Spain), and the higher heating value is measured in a calorimetric pump (Parr 1356).

The LDPE has the highest average molecular weight, whereas HDPE has the lowest one among the three. The polydispersity value is the highest for LDPE due to its more branched structure. The PP has the lowest density, and the three polyolefins have similar higher heating values.

1.2. The recycling of polyolefins

The options to recycle plastic wastes are: primary recycling (re-extrusion), secondary recycling (mechanical recycling), tertiary recycling (chemical recycling), and quaternary recycling (energy recovery) processes.

Primary recycling: involves the re-introduction of clean scrap of a single polymers to the extrusion cycle in order to produce products of similar material. It is commonly applied to the processing line itself.

Mechanical recycling: waste polymers are sorted, ground, sometimes washed and dried, and then granulated. The applications of these granulates are limited to the production of the lower quality products (pipelines, rubbish bag, garden furniture, protective slope containers on roads or motorways, synthetic grass, pavements, etc.) [4].

Chemical recycling: It is the thermo-chemical treatment aimed at degrading the polymer under controlled temperatures in inert atmospheres. After carrying out this process (pyrolysis), the monomers that form the polymer or other products are obtained. The catalytic cracking of polyolefins leads to combustibles for automobiles, and by means of gasification (at high temperatures and with a gasification agent, oxygen, water steam, etc.) synthesis gas is obtained. Synthesis gas is the raw material to obtain methanol, DME, and fuels for automobiles (Fischer-Tropsch way). These processes can be incorporated into a refinery, contributing to

the development of the waste-Refinery concept, which allows for the use of the refinery units in the valorization processes of intermediate products to commercial products.

Energy recovery: This implies burning waste to produce energy in the form of heat, steam, and electricity. The disadvantage of this method is the irretrievable loss of hydrocarbon materials [5].

Other method of polyolefin waste reutilization is by using them in construction and building materials, such as polymer-bitumen mixtures [6] or sand bricks and cement concentrates [7, 8] and different polymer-based composites [9, 10]. Among these options, pyrolysis is the method of valorization of greater interest, especially for addition polymers (which are the most consumed plastics, and within them are the polyolefins). Pyrolysis presents some advantages: operational, environmental, and economical.

The operational advantages include the joint treatment of waste and energetic integration. The main environmental advantage is the valorization of dangerous or disagreeable waste. Among the economic advantages, on the one hand, the the pyrolysis process could be integrated into a refinery with amortized units and on the other hand, the process is energetically efficient.

Proposed pyrolysis processes are flexible and can treat mixtures of plastics such as those obtained from municipal solid wastes [11, 12] or mixtures of these with other residual materials such as biomass [13] and plastic materials derived from car recycling [14], electronics and computers [15], construction (such as polymethyl metacrylate [16], and healthcare [17].

1.2.1. *Pyrolysis of polyolefins*

Pyrolysis of polyolefins consists of treating them in the presence of heat under controlled temperatures in an inert atmosphere without catalysts. As a result, three fractions of products can be obtained: gas fraction (composed mainly of the monomers that form the polyolefins), liquid fraction (composed of hydrocarbons larger than C_5), and solid fraction (char) formed at temperatures higher than 700°C.

Various technologies have been proposed with different types of reactors. In the processes carried out at high temperatures (650–850°C), the rotary kilns were a primitive solution to solve the problems related to the physical use of materials of different physical properties and of mixtures of wastes (biomass, plastics, tires, etc.). The fluidized bed reactor (with sand to help the fluidization) provides a good heat and mass transfer rate, and as a consequence, a uniform temperature is attained in the reactor. The principal international reference is the “Hamburg process” [18, 19].

The processes at low temperatures (350–550°C) are carried out in fluidized beds (G-S), with the previously mentioned advantages. The products are predominantly liquids and/or waxes with yields in the interval of 60–85 wt%. The temperature is one of the most important variables, and an increase in temperature accelerates the degradation process, resulting in a higher yield of gases.

The conical spouted bed reactor is an appropriate reactor for working at low and high temperatures to carry out the pyrolysis of plastic materials. It is suitable because the cyclic movements described by the sand particles in the bed prevent the bed agglomeration that

may be produced by the plastic materials when they melt. Furthermore, it makes it feasible to treat materials of different densities and granulometries.

1.2.1.1. Conical spouted bed reactor

The advantages that the conical spouted bed reactor offers are characteristic of conventional spouted beds (cylindrical with a conical base), and they are improved by the exclusively conical geometry of the reactor: construction and design simplicity, low charge loss, vigorous contact between particles, high heat and mass transfer rate between phases, versatility in the gas flux, low residence time of gas, and ease of the operation in a continuous regime with solids.

Working at low temperatures, the problems of particle agglomeration with melted plastic are aggravated. The conical spouted bed reactor provides an appropriate contact to avoid this problem, [20] and pyrolysis occurs according to the following stages, as shown in **Figure 1** [21]: (i) melting of plastic, which coats the sand particles; (ii) cyclic movement of the sand particles coated by plastic during their devolatilization.

The conical spouted bed reactor has also been used for the catalytic cracking of polyolefins (or catalytic pyrolysis) using catalysts in situ in the bed. Contrary to what happens in the thermal process, in this case, the reaction does not progress through intermediate radicals but through carbocationic ones due to the Bronsted-Lewis acidity of the catalysts. The advantages of catalytic cracking with respect to the thermal one are the following:

- (i) Reduces the required temperature (decreases the activation energy of the C—C link breakage) with subsequent energy saving.
- (ii) Decreases the residence time of plastics (increasing the production per reactor unit volume and the energy consumed per unit).
- (iii) Improves the selectivity of the products of interest as well as controls molecular weight intervals.

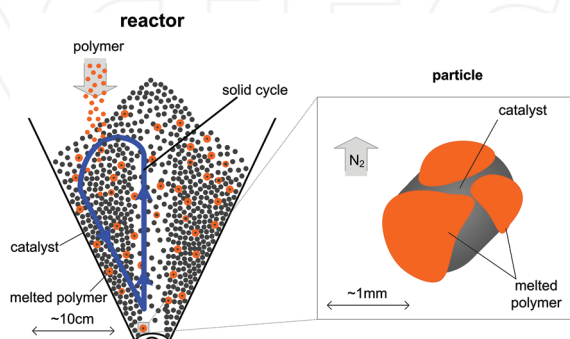


Figure 1. Scheme of the stages of the polyolefin pyrolysis in the conical spouted bed reactor.

The viability of pyrolysis and catalytic pyrolysis has the drawback of the high fixed asset necessary to install a new industrial unit. This viability is increased if the valorization process is integrated into the operations and processes of a refinery (waste Refinery), which allows for the use of amortized facilities and the treatment and posterior commercialization with as common products.

2. Experimental

2.1. Pyrolysis pilot plant

The thermal and catalytic pyrolysis of high-density polyethylene has been carried out in a conical spouted bed reactor.

The general scheme of the plant used to carry out pyrolysis is shown in **Figure 2**. The principal components of the plant are the following: (1) the solid feeding system, (2) gas mixture and feeding system, (3) preheater of gases, (4) reactor, and (5) condensers and filter system.

The most important component is the conical spouted bed reactor. It has a conical form at the bottom and a cylindrical section at the top for the development of the fountain. The angle of the conical zone is 28° . The diameter of the cylindrical part, D_c , is 2.3 cm; the diameter of the base, D_i , is 2 cm; and the diameter of the gas entrance, D_o , is 1 cm (**Figure 3**).

The feeding system consists of a hopper, a hollow ball valve where the plastic to be fed is located, an inlet tube cooled by tap water, and a support. Below the reactor is a cartridge

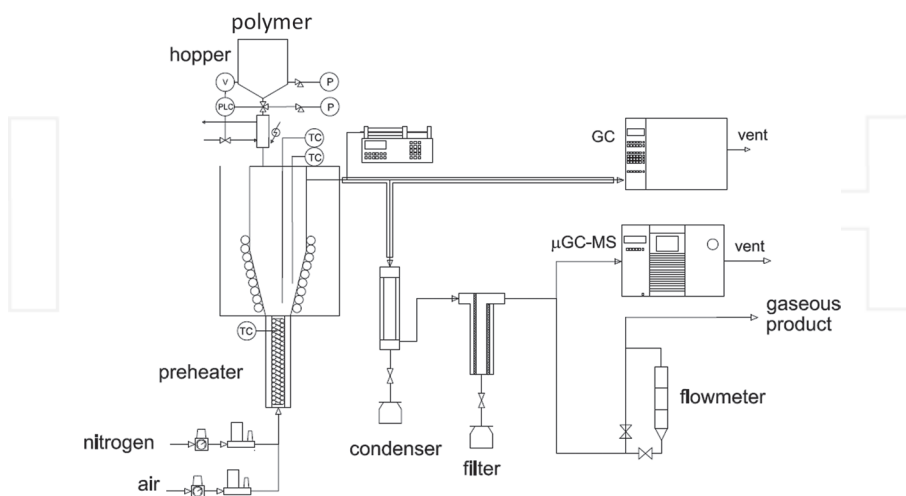


Figure 2. General scheme of the pilot plant used.

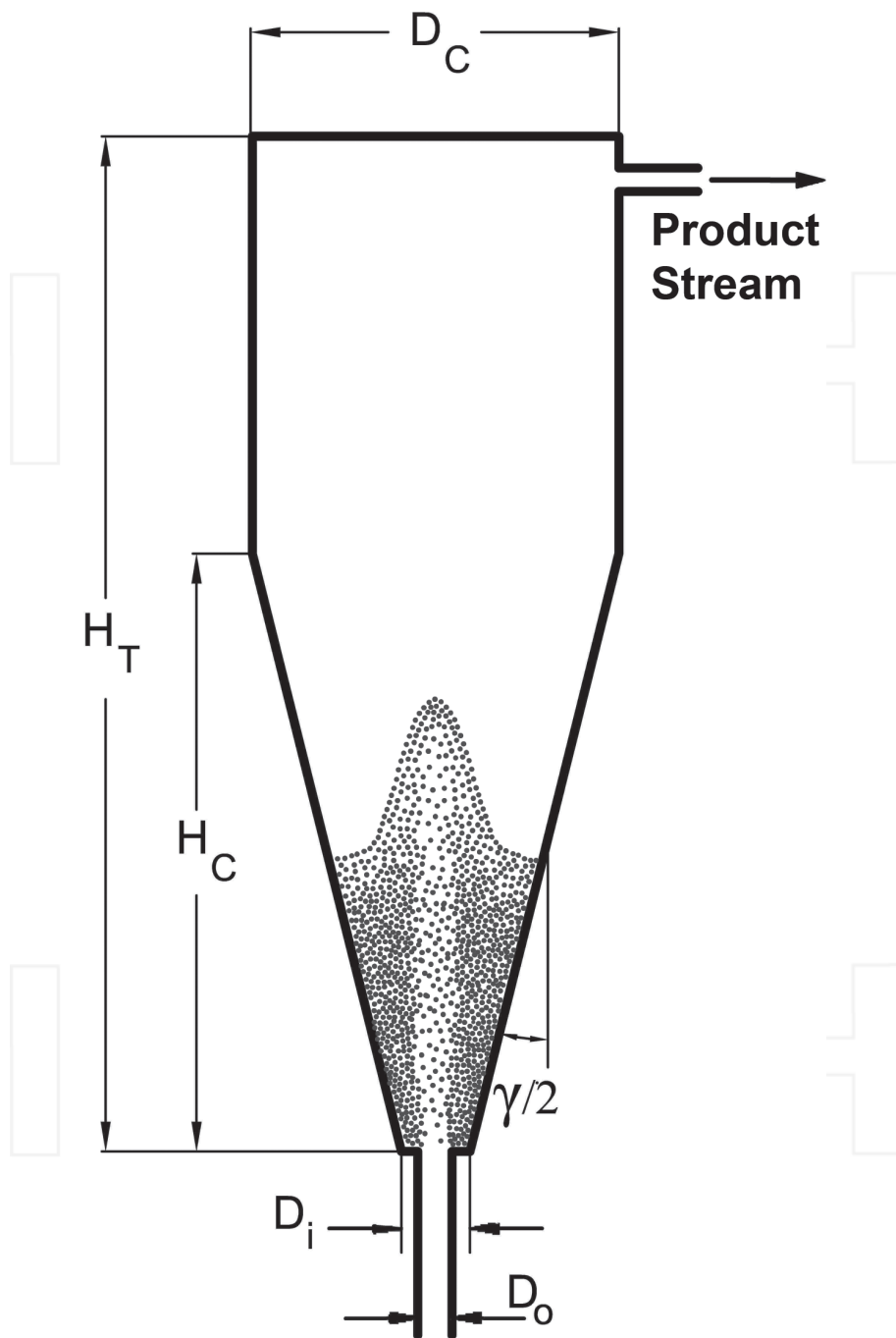


Figure 3. Design parameters of the conical spouted bed reactor.

containing a ceramic resistance, which is inside a metallic casing and thermally insulated. This resistance heats the N_2 stream to the reaction temperature.

The condensation system is formed by a typical condenser refrigerated by water, and by a coalescence filter to coalesce the fog formed in the volatiles of their collision against the surface.

2.2. Characterization techniques

2.2.1. Characterization techniques for volatiles

The volatiles formed during pyrolysis are analysed by means of an Agilent 6890 gas chromatograph provided with the flame ionization detector (FID). This chromatograph is connected online to the reactor by means of a calorifugated line at 290°C. Moreover, non-condensable gases have been analysed and identified by means of an mGC-MS spectrometer (Agilent MSD5975B) connected online at the exit of the coalescence filter. The products condensed in the condenser have been identified by means of a mass spectrometer (Shimadzu GC-MS-QP2010S).

2.2.2. Characterization techniques for waxes

2.2.2.1. Simulated distillation

This analysis was carried out in an Agilent 6890 gas chromatograph provided with an FID and a SimDis 2887 fast column (10 m × 0.53 mm × 0.88 μm), the maximum operation temperature is being 375°C. This column has been previously calibrated using sample patterns of the known boiling points in order to obtain a relationship between the time at which peaks that appear and the boiling temperature.

2.2.2.2. Fourier Transform Infrared (FTIR) spectrophotometry

The nature of the bonds was analyzed using a Nicolet 6700 spectrometer. A 200 mg KBr pellet was pressed, and a drop of wax dissolved in tetrahydrofuran added over it. The pellet impregnated with wax was located over the sample holder and analyzed under wavelengths between 500–4000 cm^{-1} .

2.2.2.3. Heating value

The calorific power of waxes has been measured in an isoperibolic calorimetric bomb PARR 1356. It is composed of an oxygen bomb where the sample is introduced for its combustion, a recipient with 2 kg of distilled water, and a jacket situated into the calorimeter.

3. Results

3.1. Pyrolysis

In the pyrolysis of high-density polyethylene carried out in a conical spouted bed reactor, the products obtained are grouped in the following fractions: gas fraction (C_1 – C_4), gasoline

fraction (C_5 – C_{11}), diesel fraction (C_{12} – C_{20}), and wax fraction ($>C_{21}$). The yields obtained are shown in **Figure 4** [22].

The thermal pyrolysis was carried out in the temperature range of 500–700°C, using 30 g of sand (particle diameter between 0.6 and 1.2 mm) in the bed and using N_2 as a fluidization agent. The HDPE pellets with a diameter of 4mm were fed continuously at a rate of 1 g/min.

The most abundant gas fractions are C_2 , C_3 , and C_4 lumps. More specifically ethylene, propylene, and 1-butene, in a minor proportion are the main components, especially at 700°C.

In the gasoline fraction (C_5 – C_{11}), the distribution of different lumps is affected by the temperature. At lower temperatures, the yields of all lumps are quite similar; at medium temperatures (600–650°C), the C_6 – C_7 and C_{10} – C_{11} lumps are the most abundant, increasing their yield from around 3 to 5 wt%; and at higher temperatures the lighter lumps (C_3 , C_4 , and C_7) are the most abundant (7–9 wt%) as a consequence of the cracking reactions that take place. With respect to the nature of the compounds, the olefins are by far the most abundant compounds, followed by the paraffins.

In the diesel fraction, (C_{12} – C_{20}), at 500°C, the C_{18} – C_{20} lumps are the most abundant; at 600°C, the yields of these lumps decrease while that of C_{12} – C_{13} increase; and at 700°C, the yields of C_{18} – C_{20} lumps decrease again but their yield is the most abundant, around 2 wt%.

As seen in **Figure 4**, among all the fractions, waxes are those of the highest yield, is obtained except at 700°C. These waxes are collected mostly in the coalescence filter (**Figure 2**). This

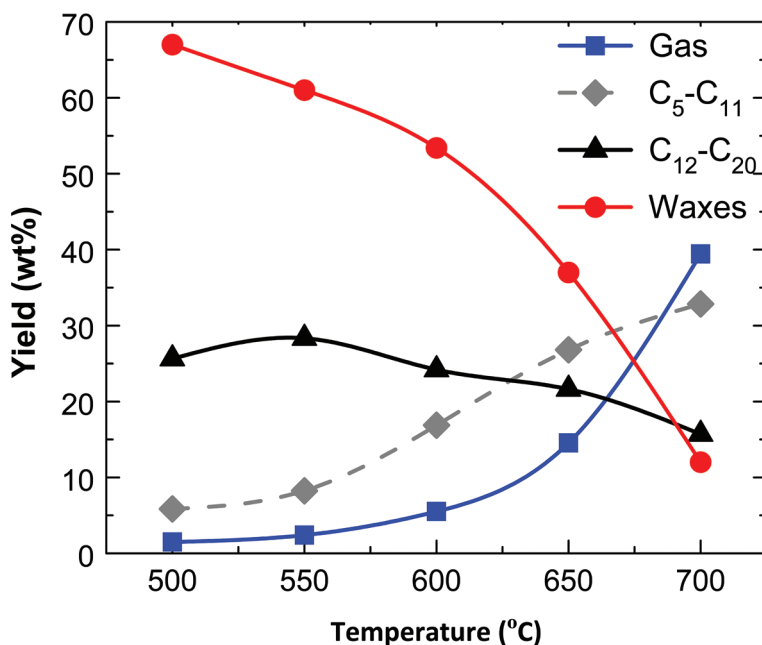


Figure 4. Yields of products obtained (wt %) at 500–700°C temperature range.

fraction is formed by hydrocarbons of long chains which are paraffinic and olefinic in nature, the latter being more abundant at higher temperatures. The characteristic gas-solid contact of this reactor is especially suitable for selectively obtaining waxes due to the high linear velocity of the gas, the vigorous gas-solid contact, and the low residence time of the gas in the reactor [23]. These characteristics allow the production of waxes at low temperatures and minimize the secondary reactions of wax transformation.

The yields of waxes obtained from the HDPE pyrolysis are similar to those obtained from the LDPE pyrolysis, while the yields obtained from the PP pyrolysis are higher, especially at low temperatures [24]. This result can be explained as a consequence of the more branched structure of polypropylene, compared to that of polyethylenes. At low temperatures such as 450 and 500°C, cracking takes place firstly in the branched chain of PP, and the cracking of the principal chain is minimal due to the very short residence times resulting from the contact method used for wax production.

In thermal degradation process that was carried out in a batch reactor at 450°C, Hájeková and Bajus [25] also obtained a higher mass yield of the oil/wax from PP than from LDPE, 87.8% as opposed to 75%. The yield of waxes obtained for polyethylene pyrolysis is lower than that reported by Predel and Kaminsky [26] in a fluidized bed reactor at 510°C, which is between 85 and 88 wt% when polyolefins are continuously fed into the reactor. Nevertheless, it is higher than the value of 71 wt% obtained by Chaala et al. [27], by vacuum pyrolysis carried out at 450°C and 20 kPa in a batch reactor.

3.1.1. Characterization of waxes

The waxes obtained in the pyrolysis of polyolefins are classified as “synthetic waxes,” and they are an alternative to those obtained from petroleum products.

A simulated distillation analysis, an FTIR analysis, and a heating value measurement were carried out.

3.1.1.1. Simulated distillation

In order to analyse the possible inclusion of waxes as part of the feed of the Fluid Catalytic Cracking (FCC) unit of a refinery, a simulated distillation analysis was carried out in order to know the temperature interval at which the waxes boil. The simulated distillation curves obtained are shown in **Figure 5** [22].

As it is observed, gasoline and diesel fractions are dissolved in the waxes. Based on the paraffin standard used, the two fractions have been quantified (delimited by the discontinuous line in the figures): (i) light waxes, C_{21} – C_{40} , corresponding to compounds with a boiling points between 343 and 525°C and (ii) heavy waxes or the remaining fraction, with higher boiling temperatures. It should be noted that 343°C is considered as the minimum temperature to define the range of heavy cycle oil (HCO) fraction.

Predel and Kaminsky [26] delimited the light wax fraction in the 300–500°C range (corresponding to C_{17} – C_{36} compounds). It was observed that, as the reaction temperature was

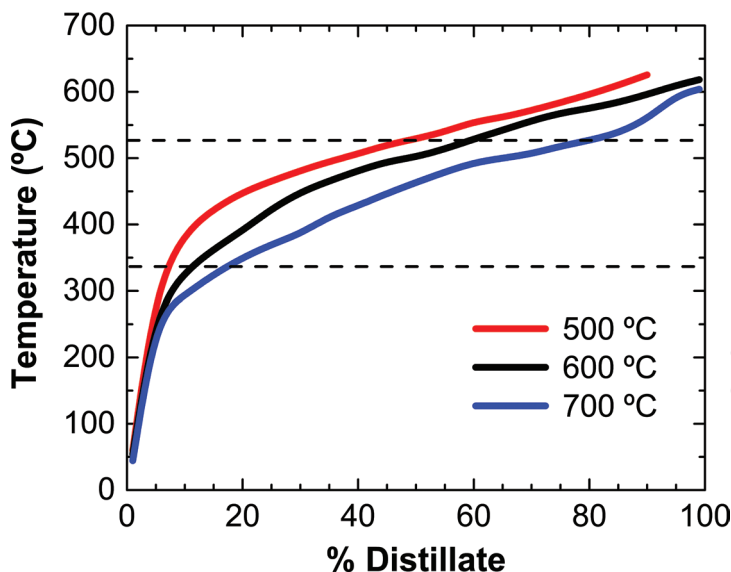


Figure 5. Simulated distillation curves for waxes.

increased, the content of the light fraction compounds (C_{20} –) that were dissolved in the waxes increased as well: 7, 12, and 19 wt % for 500, 600, and 700°C, respectively. Waxes with a boiling point lower than 500°C are a valuable feedstock for a steam cracking unit combined with conventional naphtha to produce reusable olefins [25]. The remaining waxes, with a boiling point higher than 500°C, can be combined with the usual feeding of catalytic cracking (FCC) units to produce gasoline, or they can be upgraded in a hydrocracker [27]. This latter strategy has good industry perspectives with the goal of meeting the demand for new feeds in refineries.

3.1.1.2. Fourier Transform Infrared spectrophotometry (FTIR) analysis

An FTIR analysis was carried out to determine the type of bonds that appears in the waxes and to demonstrate its paraffinic and olefinic nature. The FTIR spectra is shown in **Figure 6**.

The peaks that correspond to paraffinic bonds are the following: the characteristic symmetric and asymmetric stretching bands of C–H bonds corresponding to $-CH_2-$ groups at 2855 and 2920 cm^{-1} [28] are similar to the bonds of the same group in commercial waxes [29]. Likewise, the double peak at 725 cm^{-1} corresponds to the skeletal vibration of these groups. The shoulders observed at 2960 and 2900 cm^{-1} correspond to the $-CH_3$ terminal group bonds, although in the case of commercial waxes, these shoulders are more pronounced, which is evidence that the waxes obtained in this chapter are lesser branched chains than those found in commercial waxes. Other bands corresponding to aliphatic chains appear at 1386 and 1471 cm^{-1} and are due to methyl and methylene groups' deformation vibrations.

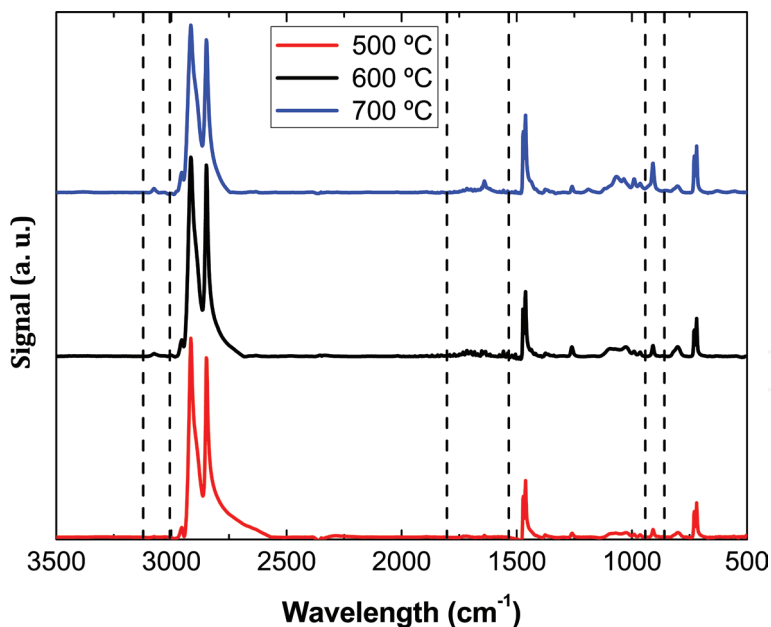


Figure 6. FTIR spectra of the waxes obtained.

The peaks which demonstrate the presence of olefinic bonds are the following: the bands at 1646 and 1725 cm^{-1} are due to the stretching of C=C bonds, which confirms the presence of olefins. Another significant difference between commercial waxes is the more pronounced olefinic nature of pyrolysis waxes, which is explained by the formation of C=C groups by the radical degradation mechanisms. This olefinic nature is confirmed by the bands at 910 and 995 cm^{-1} , which correspond to the R-CH=CH₂ group [29]. The olefinic nature is clearly observed in the waxes obtained at 700°C.

3.1.1.3. Heating value

The higher heating value has been measured in a calorimetric bomb. The values obtained for the waxes collected at 500, 600, and 700°C are 35.6, 44.1, and 45.4 MJ/kg, respectively. The values for the waxes obtained at 500 and 600°C are comparable to the original polyolefins and not much lower than the values corresponding to gasoline and natural gas. Thus, the direct combustion of the waxes to obtain energy is an alternative to pyrolysis, in case the use of waxes as raw materials to obtain fuels or chemical products would not be of commercial interest.

3.1.2. Application of waxes

The waxes can be used to prepare new materials and as feed in the FCC units of the refineries.

3.1.2.1. *New materials*

The waxes obtained in the pyrolysis of polyolefins may substitute those obtained in the Fischer-Tropsch synthesis in order to mix them with asphalt, producing WMA (warm mix asphalt). This mixture can be used to prepare asphalt at lower temperatures minimizing the environmental problems associated with the emission of volatiles and moreover, improving the resistance to fatigue and stiffness due to its peculiar crystalline structure [30].

They can be used to prepare reinforced plastics with natural fibres [31]. They can also be used as binders in the preparation of composites (as WC-TiC-Co carbide) by the means of moulding, improving its mechanical properties [32]. Furthermore, they can be used for metal coating, in this way, decreasing the infrared emissivity of metals (as a consequence of high transparency and low emissivity of waxes) and reducing the aging of metal.

Waxes have a high fusion latent heat, and this property can be useful for incorporating them into construction materials, and by means of encapsulation techniques, in textile materials.

3.1.2.2. *Feed for the Fluid Catalytic Cracking (FCC) unit of a refinery*

As waxes are not composed of many aromatic compounds and do not contain heteroatomic compounds (S, N, metals), they are an acceptable feed for the FCC unit of a refinery, either in their pure form, dissolved in the usual feed of FCC units, or dissolved in alternative ones.

Arandes et al. [33] studied the cracking of waxes in an FCC simulator unit (riser). The waxes were previously obtained in the pyrolysis carried out in a conical spouted bed reactor like the one described in section 2.1. They also mixed the waxes (20 wt%) with the standard FCC unit feed and vacuum gas oil (VGO) to analyse their effect on the yields and on the composition of the products obtained. The experiments were carried out in the 500–550°C range, with a catalyst/feed weight ratio of 5.5, and with a contact time value between 3 and 12 s. The catalyst used was an equilibrated commercial catalyst based on an HY zeolite.

The degree of conversions obtained by using these feeds follows this order: waxes > mixture > VGO. These results were explained as a consequence of the olefinic nature of the waxes (as opposed to the aromatic content of VGO, around 40%), which is more favourable for cracking.

With respect to the yields of the products obtained, at 550°C, the gasoline fraction was the one with the higher yield, around 40 wt% when waxes were fed purely, followed by the waxes and the VGO-mixture feed and by the VGO-pure feed.

3.2. Catalytic pyrolysis

The use of the catalysts in the conical spouted bed reactor changes the distribution of products obtained in pyrolysis and permits the increase of selectivity towards products of high interest as olefins, gasoline, or diesel fractions.

Elordi et al. [34] studied the effect of an HZSM-5 zeolite catalyst placed *in-situ* in the pyrolysis reactor on the product distribution carried out at 450–570°C. They used 30 g of catalyst in the

bed in the form of pellets with a particle diameter between 0.6 and 1.2 mm. HDPE was fed at a flow rate of 1 g/min into a bed of 30 g of catalyst. The products were lumped into the following fractions: (C_2 – C_4) olefins, light alkanes (C_4 –), non-aromatics (C_5 – C_{11}), single-ring aromatic (C_{12} – C_{20}) fractions, and waxes (C_{21+}). The evolution of different fraction yields in relation to the quantity of HDPE fed at 500°C are shown in **Figure 7**.

The main differences obtained with respect to pyrolysis without catalyst are the very high yield of olefins and the very low yield of the C_{12} – C_{20} fraction and waxes. These results are a consequences of the cracking reactions promoted by the catalyst that leads to obtaining lighter products. The results also show the low deactivation of the catalyst behaviour as HDPE is fed.

In the case of LDPE and PP, the results have been quite similar.

The use of other catalysts modifies the distribution of products obtained in pyrolysis. Elordi et al. [35] studied the effect of H β and HY zeolite catalysts on product distribution. The yields of different product-fractions obtained with H β zeolite catalyst and HY zeolite catalyst, respectively, at 500°C are shown in **Figures 8** and **9**. Using a H β zeolite catalyst, the non-aromatic C_5 – C_{11} fraction is the one with the highest yield, followed by the light olefin fraction (around 47 wt.% and 35 wt%, respectively). Using a HY zeolite catalyst, the non-aromatic C_5 – C_{11} fraction (around 45 wt%) is also the main fraction, followed again by light olefins (around 22 wt%). In this case, the yield of C_{11+} fraction is higher than that obtained using the HZSM-5 and the H β zeolite catalysts, around 10 wt%, and this yield increases with time. Contrary to what occurs with the HZSM-5 zeolite catalyst, with H β and HY zeolite catalysts, the yield of wax increases with time due to the deactivation that both catalysts undergo.

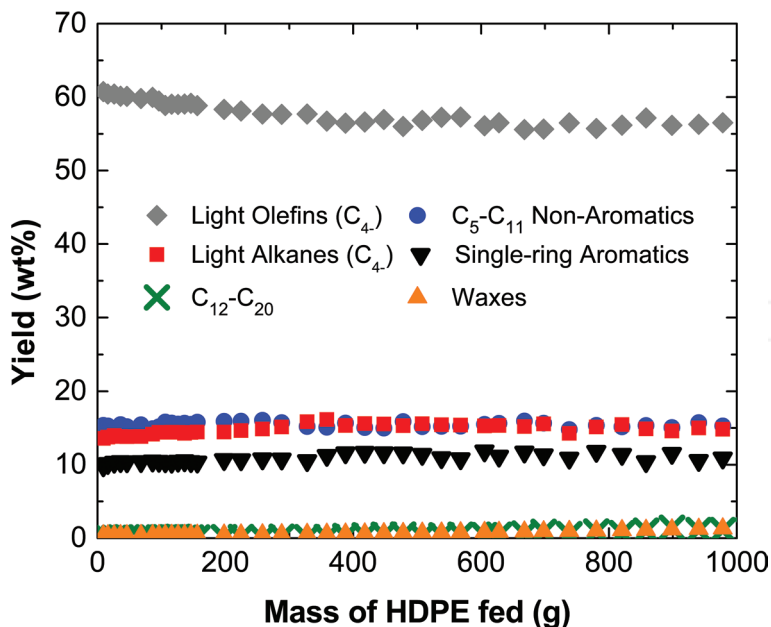


Figure 7. Evolution of product fraction yield with the quantity of HDPE fed at 500°C.

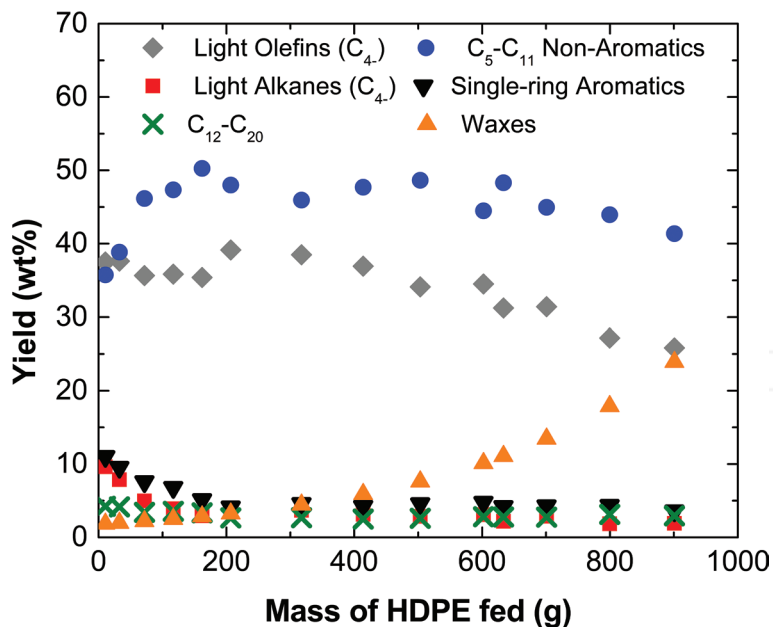


Figure 8. Yields of fractions throughout time using the H β zeolite catalyst.

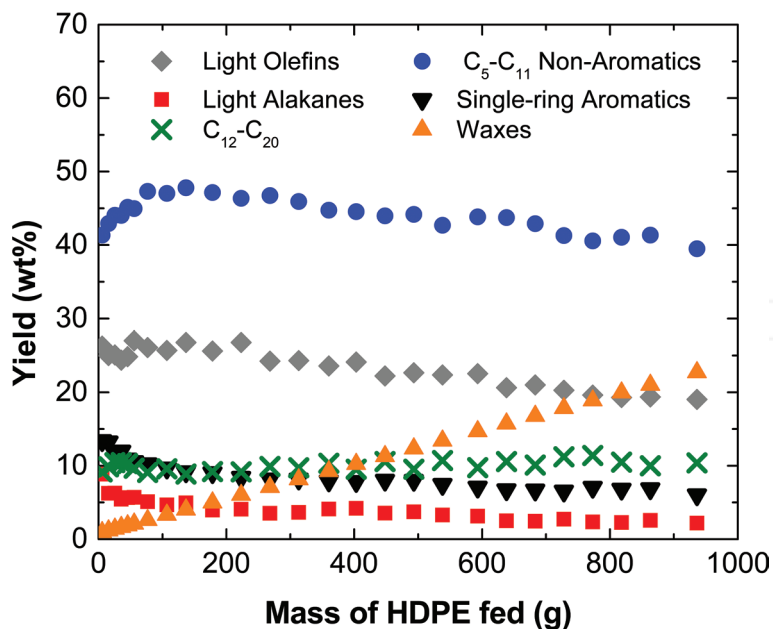


Figure 9. Yields of fractions throughout time using the HY zeolite catalyst.

This different fraction distribution is a consequence of the pore size and the acid strength of each catalyst. Thus, the HZSM-5 zeolite, which has the lowest pore size, 5.5 Å, related to the shape selectivity of this zeolite, gives way to the highest yield of light olefins, whereas the lowest yields are obtained with the HY zeolite catalyst. In the same way, the yields of non-aromatic C_5 – C_{11} and C_{11+} fractions are higher when using the catalyst with a larger pore size (HY zeolite). The high acid strength of the HZSM-5 zeolite is related to the higher yield of single-ring aromatics obtained with this zeolite.

Olazar et al. [36] obtained 8 wt% of gaseous fraction, 22 wt% of C_5 – C_9 fraction, and 69 wt% of C_{10+} fraction (diesel fraction) at 475°C, using a commercial FCC catalyst based on a HY zeolite active phase (30 g), after a severe steaming was applied to the catalysts. These results are a consequences of the decrease in acidity that the catalyst undergoes in the aforementioned treatment.

3.3. Other applications

Another option to modify the product distribution consists of carrying out the reforming of volatiles formed in the pyrolysis by means of a second reactor. Artetxe et al. [37] carried out the pyrolysis of HDPE in a conical spouted bed reactor at 500°C (using 50 g of sand), and the volatiles formed were passed through a second fixed bed reactor, where an HZSM-5 zeolite catalyst (8 g), heated at 500°C, was placed. The conditions used were appropriate to obtain a high yield of olefins, around 58% wt%, similar to that obtained when placing the catalyst in-situ, although with a lower catalyst space time.

Another application that might be used combined with the pyrolysis of HDPE, gives production hydrogen yield [38]. The volatiles formed in the pyrolysis, using steam as a fluidization agent, are reformed in a fixed bed reactor, placed in line using an Ni commercial catalyst. The pyrolysis was carried out at 500°C and the reforming at 700°C. They observed that steam is inert at 500°C since the products obtained are very similar to those obtained using N_2 . Moreover, the use of steam in the first reactor simplifies the pyrolysis-reforming process. The H_2 yield obtained was 81.5% with respect to the stoichiometric one, which results in 34 g H_2 per 100 g HDPE fed into the reactor.

Barbarias et al. [39] studied the same process, but using a fluidized bed reactor to carry out the reforming of the volatiles formed in the pyrolysis step. They obtained a H_2 yield of 92.5% with respect to the stoichiometric one, which results in 38 g H_2 per 100 g HDPE fed. This higher yield compared to that obtained in a fixed bed reactor is attributed to the better mixing of the catalyst particles, higher temperature of isothermicity in the bed, and the gasification of the coke formed during the reaction promoted by the fluidized bed reactor.

4. Conclusion

The conical spouted bed reactor is adequate to carry out the pyrolysis process and catalytic pyrolysis of polyolefins. There is not any problem of bed defluidization using plastic materials

that melt and cover the sand particles of the bed at a temperature at around 500°C due to the vigorous cyclic movements of the particles.

In the pyrolysis process without the catalyst, the wax is the fraction obtained in a higher yield at low temperatures, being around 67 wt% in weight at 500°C. This wax can be used to prepare new materials like asphalt at lower temperatures, reinforced plastics with natural fibres, composites or for metal coating, and can be incorporated into construction materials and into textile materials due to its high fusion latent heat. On other hand, it has good properties to be fed into an FCC unit of a refinery. On the contrary, at higher temperatures, 700°C, the yield of the wax fraction decreases considerably and the gas fraction, formed principally of olefins (ethene, propene and butene), becoming the main fraction, around 40 wt %, as a consequence of the cracking reactions that are favoured by the high temperature.

With respect to catalytic pyrolysis, it significantly modifies the product distribution. Thus, the wax fraction decreases dramatically as a consequence of the cracking reactions that are promoted by the acidic zeolite-based catalysts (HZSM-5, HY, and H β). Thus, olefins constitute the main fraction with the HZSM-5 zeolite catalyst, whereas the non-aromatic C₅–C₁₁ fraction is the main fraction when the HY and H β zeolite catalysts are used.

H₂ may be produced by reforming the volatiles obtained in the pyrolysis of polyolefins with steam. 38 g of H₂ were obtained per 100 g of HDPE fed.

All the product fractions obtained in these processes can be used in refinery units to obtain commercial products such as ethene, propene, butenes, gasoline and diesel, either mixing them with conventional streams of a refinery and/or directly applying some treatments to them.

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References

- [1] Plastics Europe-Plastics-the Facts 2015. An analysis of European plastic production, demand and waste data, [Internet]. 2015. Available from: www.plasticseurope.org/Document/plastics---the-facts-2015.aspx [accessed on 21 November 2016].
- [2] Plastics News 2013. [Internet]. 2013. Available from: www.plasticsnews.com/article/20130909/NEWS/130909948 [accessed on 21 November 2016].

- [3] Mastral JF, Berruero C, Ceamanos J. Theoretical prediction of product distribution of the pyrolysis of high density polyethylene. *Journal of Analytical and Applied Pyrolysis*. 2007;80(2):427-438. doi:10.1016/j.jaap.2006.07.009.
- [4] Siddique R, Khatib J, Kaur I. Use of recycled plastic in concrete: a review. *Waste Management*. 2008;28(10):1835-1852. doi:10.1016/j.wasman.2007.09.011.
- [5] Zucchelli L, Rizzi R. Fuel composition which combusts instantaneously, method and plant therefore. US Patent 7,488,358 B2, Pirelli Ambiente S.p.A. 2009.
- [6] Vasudevan R, Ramalinga Chandra Sekar A, Sundarakannan B, Velkennedy R. A technique to dispose waste plastics in an ecofriendly way-application in construction of flexible pavements. *Construction and Building Materials*. 2012;28(1):311-320. doi:10.1016/j.conbuildmat.2011.08.031.
- [7] Wahid SA, Rawi SM, Desa NM. Utilization of plastic bottle waste in sand bricks. *Journal of Basic and Applied Scientific Research*. 2015;5(1):35-44.
- [8] Suganthi P, Chandrasekar D, Sathish KPK. Utilization of pulverized plastic in cement concrete as fine aggregate. *International Journal of Research in Engineering and Technology*. 2013;2(6):1015-1019.
- [9] Cerruti P, Avolio R, Gentile G, Carfagna C, Persico P, Errico ME, Malinconico M, Avella M. Up-cycling end-of-use materials: highly filled thermoplastic composites obtained by loading waste carbon fiber composite into fluidified recycled polystyrene. *Polymer Composites*. 2014;35(8):1621-1628. doi:10.1002/pc.22815.
- [10] Hugo AM, Scelsi L, Hodzic A, Jones FR, Dwyer-Joyce R. Development of recycled polymer composites for structural applications. *Plastics, Rubber and Composites*. 2011;40(6-7):317-323. doi:10.1179/1743289810Y.0000000008.
- [11] Siddiqui MN, Redhwi HH. Pyrolysis of mixed plastics for the recovery of useful products. *Fuel Processing Technology*. 2009;90:545-552. doi:10.1016/j.fuproc.2009.01.003.
- [12] López A, de Marco I, Caballero BM, Laresgoiti MF, Adrados A. Pyrolysis of municipal solid wastes: influence of raw material composition. *Waste Management*. 2010;30:620-627. doi:10.1016/j.wasman.2009.10.014.
- [13] Liu W, Hu C, Yang Y, Liu S, Tong D, Li G, Zhu, L. Influence of ZSM-5 on the pyrolytic intermediates from the co-pyrolysis of pubescens. *Energy, Conversion and Management*. 2010;51:1025-1032. doi:10.1016/j.enconman.2009.12.005.
- [14] De Marco I, Caballero BM, Cabrero MA, Laresgoiti MF, Torres A, Chomón MJ. Recycling of automobile shredder residues by means of pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 2007;79:403-408. doi:10.1016/j.jaap.2006.12.002.
- [15] Guo Q, Yue X, Wang M, Liu Y. Pyrolysis of scrap printed circuit board plastic particles in a fluidized bed. *Powder Technology*. 2010;198:422-428. doi:10.1016/j.powtec.2009.12.011.
- [16] Kang BS, Kim SG, Kim JS. Thermal degradation of poly(methyl methacrylate) polymers: kinetics and recovery of monomers using a fluidized bed reactor. *Journal of Analytical and Applied Pyrolysis*. 2008;81(1):7-13. doi:10.1016/j.jaap.2007.07.001.

- [17] Na D, Zhang Y, Wang Y. Thermogravimetric analysis and kinetic study on pyrolysis of representative medical waste composition. *Waste Management*. 2008;28:1572-1580. doi:10.1016/j.wasman.2007.05.024.
- [18] Kaminsky W, Schmidt H, Simon CM. Recycling of mixed plastics by pyrolysis in a fluidized bed. *Macromolecular Symposia*. 2000;152:191-199. doi:10.1002/1521-3900(200003)152:1<191::AID-MASY191>3.0.CO;2-2.
- [19] Donaj PJ, Kaminsky W, Buzeto F, Yang W. Pyrolysis of polyolefins for increasing the yield of monomers' recovery. *Waste Management*. 2012;32(5):840-846. doi:10.1016/j.wasman.2011.10.009.
- [20] Aguado R, Prieto R, San José MJ, Alvarez S, Olazar M, Bilbao J. Defluidization modeling of pyrolysis of plastics in a conical spouted bed reactor. *Chemical Engineering and Processing*. 2005;44(2):231-235. doi:10.1016/j.cep.2004.02.016.
- [21] Elordi G., Thermal and catalytic pyrolysis of polyolefins in a conical spouted bed reactor [thesis], University of the Basque Country, Bilbao; 2010.
- [22] Elordi G, Olazar M, Lopez G, Artetxe M, Bilbao J. Product yields and compositions in the continuous pyrolysis of high density polyethylene in a conical spouted bed reactor. *Industrial & Engineering Chemistry Research*. 2011;50:6650-6659. doi:10.1021/ie200186m.
- [23] Olazar M, San José MJ, Izquierdo MA, Ortiz de Salazar A, Bilbao J. Effect of operating conditions on solid velocity in the spout, annulus and fountain of spouted beds. *Chemical Engineering Science*. 2001;56:3585-3594.
- [24] Arabiourrutia M, Elordi G, Lopez G, Borsella E, Bilbao J, Olazar M. Characterization of the waxes obtained by the pyrolysis of polyolefin plastics in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*. 2012;94:230-237. doi:10.1016/j.jaap.2011.12.012.
- [25] Hájeková E, Bajus M. Recycling of low-density polyethylene and polypropylene via copyrolysis of polyalkene oil/waxes with naphta: product distribution and coke formation. *Journal of Analytical and Applied Pyrolysis*. 2005;74:270-281. doi:10.1016/j.jaap.2004.11.016.
- [26] Predel M, Kaminsky W. Pyrolysis of mixed polyolefins in a fluidized-bed reactor and on a pyro-GC/MS to yield aliphatic waxes. *Polymer Degradation and Stability*. 2000;70:373-385.
- [27] Kirkwood KC, Leng SA, Sims DW. Polymer cracking. US Patent 5,364,995. 1992.
- [28] Vogel A. *Vogel's Textbook of Practical Organic Chemistry*. New York: Longman; 1981.
- [29] Chaala A, Darmstadt H, Roy C. Vacuum pyrolysis of electric cable wastes, *Journal of Analytical and Applied Pyrolysis*. 1997;39:79-96.
- [30] Petit C, Millien A, Canstrari F, Pannunzio V, Virgili A. Experimental study on shear fatigue behavior and stiffness performance of Warm Mix Asphalt by adding synthetic wax. *Construction and Building Materials*. 2012;34:537-544. doi:10.1016/j.conbuildmat.2012.02.010.

- [31] Arrakhiz FZ, El Achaby M, Benmoussa K, Bouhfid R, Essassi EM, Quiss A. Evaluation of mechanical and thermal properties of pine cone fibers reinforced compatibilized polypropylene. *Materials and Design*. 2012;40:528-535. doi:10.1016/j.matdes.2012.04.032.
- [32] Qu X, Gao J, Qin M, Lei C. Application of a wax-based binder in PIM of WC-TiC-Co cemented carbides. *International Journal of Refractory Metals & Hard Materials*. 2005;23:273-277. doi:10.1016/j.ijrmhm.2005.04.006.
- [33] Arandes JM, Torre I, Castaño P, Olazar M, Bilbao J. Catalytic cracking of waxes produced by the fast pyrolyse of polyolefins, *Energy & Fuels*. 2007;21:561-569. doi:10.1021/ef060471s.
- [34] Elordi G, Olazar M, Lopez G, Artetxe M, Bilbao J. Continuous polyolefin cracking on an HZSM-5 zeolite catalyst in a conical spouted bed reactor. *Industrial & Engineering Chemistry Research*. 2011;50:6061-6070. doi:10.1021/ie2002999.
- [35] Elordi G, Olazar M, Lopez G, Amutio M, Artetxe M, Aguado R, Bilbao J. Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*. 2009;85:345-351. doi:10.1016/j.jaap.2008.10.015.
- [36] Olazar M, Lopez G, Amutio M, Elordi G, Aguado R, Bilbao J. Influence of FCC catalyst steaming on HDPE pyrolysis product distribution. *Journal of Analytical and Applied Pyrolysis*. 2009;85:359-365. doi:10.1016/j.jaap.2008.10.016.
- [37] Artetxe M, Lopez G, Amutio M., Elordi G, Bilbao J, Olazar M. Light olefins from HDPE cracking in a two-step thermal and catalytic process. *Chemical Engineering Journal*. 2012;207-208:27-34. doi:10.1016/j.cej.2012.06.105.
- [38] Erkiaga A, Lopez G, Barbarias I, Artetxe M, Amutio M. HDPE pyrolysis-steam reforming in a tandem spouted bed-fixed bed reactor for H₂ production. *Journal of Analytical and Applied Pyrolysis*. 2015;116:34-41. doi:10.1016/j.jaap.2015.10.010.
- [39] Barbarias I, Lopez G, Alvarez J, Artetxe M, Arregi A, Bilbao J, Olazar M. A sequential process for hydrogen production based on continuous HDPE fast pyrolysis and in-line steam reforming. *Chemical Engineering Journal*. 2016;296:191-198. doi:10.1016/j.cej.2016.03.091.