

Energetic viability of a polyolefin pyrolysis plant

Gorka Elordi, Miriam Arabiourrutia, Javier Bilbao, Martin Olazar*

Chemical Engineering Department, University of the Basque Country, UPV/EHU, P.O. Box 644-48080, Bilbao, Spain

KEYWORDS: polyolefins, pyrolysis, conical spouted bed reactor, energetic viability, refinery

ABSTRACT: The energetic viability of a polyolefin pyrolysis unit that could be installed in a refinery plant was examined. Thermal pyrolysis at 500 °C and 700 °C, and the catalytic cracking by means of HZSM-5 and HY catalysts were analyzed. The energy requirements for an initial separation of the products by means of distillation towers into four main lumps (gas, gasoline fraction, diesel fraction, and waxes) that could be directly treated in a refinery were calculated as well. An energy balance closure and a sensitivity analysis were also carried out for all cases in order to check the accuracy of the yields of products previously obtained. These results were highly satisfactory for all cases, although the actual heat of combustion might be slightly higher than the values measured experimentally (around 5%). The results of the energetic viability analysis showed that only about 5% of the input mass flow rate is needed to burn to satisfy the energy requirements of the plant. Thus, the heat released in the combustion of the product fraction stream that is in minor proportion in each case showed to be enough.

1. INTRODUCTION

The world's plastic production reached 322 million tonnes in 2015 (thermoplastics, polyurethanes, and other plastics such as thermosets, adhesives, coatings and sealants).¹ Polyolefins (particularly polyethylene and polypropylene) are the largest group of plastics. The pyrolysis process can potentially be used to convert plastics into valuable chemicals and fuels either by thermal pyrolysis²⁻⁶ or catalytic cracking processes.⁶⁻¹⁰

Several technologies have been applied to both thermal and catalytic pyrolysis of waste plastics, such as fixed beds³, rotary kilns¹¹, pyrolysis in molten salts¹², batch reactors¹³⁻¹⁶, but pyrolysis in a fluidized bed reactor is the more widely studied technology at laboratory and pilot plant scale.^{2,5,9,17-21} The conical spouted bed reactor²²⁻²³ is another technology that presents good characteristics for the pyrolysis of these materials. Compared to the bubbling fluidized bed, the conical spouted bed has a lower operating pressure drop (around half) and can handle particles with a wide size or density distribution without segregation.²⁴⁻²⁵ The vigorous contact between phases and the collision between particles in the spout and fountain prevent defluidization problems²⁶, which can take place in the fluidized bed due to the agglomeration of solid particles (sand) coated with fused plastic.²⁷

The viability of thermal and catalytic pyrolysis processes is conditioned by the installation of new industrial units with high fixed asset costs. This viability increases if the valorization is integrated within the operations and processes in a refinery (Waste Refinery or Sustainable Refinery), which helps to pay off the installations, as well as the treatment of the products obtained and posterior commercialization as common (petrochemical) products. In this sense, Tonini et al.,²⁸ carried out a study evaluating the waste refinery as a future solution to obtain material and

energy resources. More recently, Gracida-Alvarez et al.,²⁹ considered municipal solid waste (MSW) to be a promising feedstock for biofuel production through a pyrolysis-based pathway.

In this sense, Williams and Williams³⁰ came to the conclusion that the wax fraction formed from HDPE (which is the main product obtained in the thermal pyrolysis of polyolefins at low temperatures) was an almost pure aliphatic material with no aromatic compounds and could be used as a substitute of petroleum derived feedstock. Arabiourrutia et al.³¹ obtained the same result. Thus, waxes with a boiling point lower than 500 °C are a valuable feedstock for the steam cracking unit combined with conventional naphtha to produce reusable olefins.³² The remaining waxes, with a boiling point higher than 500 °C, can be combined with the usual feed of fluid catalytic cracking (FCC) units to produce gasoline³³⁻³⁵ or they can be upgraded in a hydrocracker.³⁶ Nevertheless, these strategies may require changes in the process conditions of the refinery units and they must be thoroughly analyzed prior to implementation. Donaj et al.³⁷ proposed a concept of feedstock recycling of plastic waste mixtures via pyrolysis. The concept assumes the integration of a fluidized bed reactor into the petrochemical industry. Approximately 25% of olefins can be recovered directly via pyrolysis.

Pyrolysis is an endothermic process so energy requirements in the degradation itself are high. Besides, there are other energy requirements: the fluidization agent and the polyolefinic material fed must be heated from the ambient temperature to the reaction one. These are some of the drawbacks to overcome when the pyrolysis process is scaled up. A fraction of the feed may be separately burned in order to obtain the energy required for the pyrolysis process.³⁸⁻³⁹ Alternatively, the pyrolysis and partial combustion processes may even be carried out simultaneously.⁴⁰ In any case, the combustion of a pyrolysis product has been considered in this article in order to obtain the required energy for the process due to the flexibility and ease of control

that it offers compared to the simultaneous process and to avoid the possible problems related to the combustion of solid materials.

In this work, the energetic viability is analyzed for a polyolefin pyrolysis plant of 1000 kg/h capacity based on a conical spouted bed reactor. The feed is a mixture of LDPE, HDPE and PP in a similar proportion to that they are produced (24, 28, and 48%, respectively). Previously, the pyrolysis of these polyolefins (high density polyethylene, low density polyethylene, and polypropylene) has been studied in a conical spouted bed reactor^{23, 41,42} at laboratory scale. Four different strategies will be analyzed in this study, as are: i) thermal degradation of polyolefins at 500 °C, ii) idem at 700 °C, iii) catalytic cracking of polyolefins on an HZSM-5 zeolite-based catalyst, and iv) idem on an HY zeolite-based catalyst.

One of the advantages of the thermal degradation of polyolefins is the simplicity of the process, as there is no deactivation of the catalyst involved. On the other hand, the high yield of waxes obtained at low temperatures may cause practical issues when handling them due to possible fouling problems unless a proper design is carried out. The temperature of 500 °C has been chosen because this is the minimum one at which the thermal degradation takes place without defluidization problems working in continuous regime. Thus, the energy requirements for the degradation process would be minimum at this lowest temperature. Moreover, the main lump obtained by carrying out the process at 500 °C is that of the waxes, which may be used as feedstock in the fluid catalytic cracking process. The increase in temperature boosts the cracking of these long, mainly paraffinic chains into smaller hydrocarbons, reducing the yield of waxes and increasing those of the diesel fraction, gasoline fraction, and incondensable gases.

The temperature of 700 °C has been chosen because it is the maximum temperature at which the thermal degradation was carried out.²³ Contrary to the experiments carried out at 500 °C, the yield

of waxes was the minimum in the range studied (500-700 °C), whereas that of the incondensable gases (C₄), light olefins and light paraffins reaches the maximum yield. Accordingly, and although the thermal requirements to carry out the process are significantly larger, higher yields of more valuable products, such as light olefins and gasoline fraction, are obtained.

As mentioned before, the catalytic cracking of polyolefins has the drawback of the deactivation of the catalyst, which added to the variability of the feed based on waste products, makes the control of the process a challenging topic. Nevertheless, it allows tailoring the product distribution in order to obtain large yields of high added value products, while still working at low temperatures, that is, with low energy requirements.

Catalytic cracking of polyolefins on the two catalysts was studied at the operating temperature of 500 °C, as the catalyst bed does not undergo defluidization, energy requirements are lower than at higher temperatures, and the product distributions obtained with the two catalysts were interesting. When the HZSM-5 zeolite-based catalyst was used, the main lump was that of light olefins (C₄), especially propylene, with their yields being around 60 and 30 wt.%, respectively. Lower yields of gasoline fraction and light paraffins were obtained, whereas the yield of diesel fraction products was very low and that of waxes almost negligible.⁴¹ Although studies using a β -zeolite catalyst were carried out⁴¹ as well, these data were not used for this study, as the yields obtained using this catalyst were in between those obtained by using the HZSM-5 zeolite-based catalyst and the HY zeolite-based catalyst. Thus, high yields of gasoline fraction and considerable amounts of light olefins were obtained using the HY zeolite-based catalyst, whereas the yields of light paraffins and diesel fraction were low. The yield of waxes was almost negligible, as in the case of the HZSM-5 catalyst.

In all four cases studied, in order to check the energetic viability of the pyrolysis process, the fraction obtained in lower amount, but still considerable (at least around 7 wt.%), was intended to be burned so as to obtain the thermal energy that the overall process requires: heating the raw materials to the reaction temperature, the heat for the pyrolysis process due to its endothermicity, the heat losses in the reactor, and the heat required in the kettles of the distillation towers for separating the reaction products into common product lumps that could easily be treated in a refinery. This option of burning a product-fraction to obtain energy is reported in the literature.⁴³⁻

44

Focusing on the four cases chosen for this study, in the thermal process carried out at 500 °C, the lightest products, the light gases and the gasoline fraction, which account for 7 wt.%, would be destined for burning, whereas at 700 °C, the fraction to be burned would be the heaviest one. Furthermore, this fraction made up of a mixture of the diesel fraction and the waxes may be separated in another distillation tower or in a more complex distillation tower provided by side-product exits and once separated the yield of the waxes might be enough to provide the thermal energy that would be required for the process. If the process were carried out using an HZMS-5 zeolite-based catalyst, the yields of the diesel fraction and that of the waxes are almost zero, and therefore the gasoline fraction (of less interest than light olefins) should be the one used to obtain the energy required. Finally, if the HY zeolite-based catalyst were chosen, the heaviest fraction products would be again those destined for combustion, that is, the diesel fraction and the waxes.

A comparison of the value obtained burning this stream with the energy requirements to carry out the process, which includes the pyrolysis process as well as the posterior separation of the product stream to obtain common refinery product pools, it is possible to deduce whether the whole process is energetically self-sufficient or not. The study of the pyrolysis-product gas stream

separation has been carried out by means of the Pro/II simulation software. In order to do so, different separation systems have been considered.

2. BASIC ASPECTS OF THE PROCESSES

2.1. Conditions and products of pyrolysis. The pyrolysis of HDPE has been carried out in a laboratory scale pyrolysis plant equipped with a conical spouted bed reactor operating in continuous mode. The thermal pyrolysis has been studied at 500-700 °C and the catalytic pyrolysis with HZSM-5 and HY zeolite based catalysts at 500 °C. The pyrolysis plant used, operation conditions, properties of catalysts used and the yields of product-fractions obtained are described in the works previously published.^{23,41} In Table 1 are shown the product-fractions' yields obtained for each case.

Table 1. The yields of product-fractions obtained in the pyrolysis processes.

	Thermal 500 °C	Thermal 700 °C	HZSM-5 500 °C	HY 500 °C
Gas	1.5	39.5	77	33.5
Gasoline	5.5	33	22	55
Diesel	26	15.5	0.6	10
Wax	67	12	0.4	1.5

The yield of the heavy fraction is high in the thermal pyrolysis at low temperatures and decreases as the process is carried out at higher temperatures. On the contrary, the yield of light fractions, such as gas and gasoline, is high at high temperatures and decreases as temperature is decreased.

Nevertheless, in the catalytic pyrolysis the yield of the heavy fraction is almost null, whereas the yield of light olefins in the case of HZSM-5 zeolite-based catalyst and of light gasoline fraction in the case of HY zeolite-based catalyst are the highest ones.⁴¹

2.2. Energy Balance. Energy balance closure has been checked prior to the viability analysis based on the results obtained in the thermal and catalytic pyrolysis of the mentioned polyolefins carried out in a laboratory scale conical spouted bed reactor. A sensitivity analysis of the main parameters that may affect energy balance closure has been conducted in order to identify potential deviations and determine the parameters that have to be measured in more detail. Reaction enthalpies of the pyrolysis processes have been calculated by means of the heats of combustion of the raw materials (the polymers fed into the reactor) and the heats of combustion of the pyrolysis products, according to the following equation:

$$\Delta H_r = \sum \Delta H_{c,react.} - \sum \Delta H_{c,prod.} \quad (1)$$

The heats of combustion of the reactants (HDPE, LDPE, and PP) as well as those of the waxes obtained in the pyrolysis of the polyolefins operating at different temperatures, were measured by means of a calorimetric bomb, *Parr 1356 Oxygen Combustion Bomb Calorimeter*. These heats were 43 and 44 MJ/kg for polyethylenes and polypropylene, respectively. The heats combustion of the waxes obtained at 500, 600 and 700 °C were 35.6, 44.1 and 45.4 MJ/kg, respectively.

The heats of combustion of the pyrolysis products used for the calculation of the reaction enthalpy were taken from the database of the Pro/II simulation software. Given the large amount of components that were identified in the product stream, average combustion heat values have been used in the cases in which there are many isomers with the same carbon atom number and similar chemical structure.

The experimental enthalpies of reaction for the pyrolysis of HDPE, LDPE, and PP were determined by means of a calorimetric analysis in a differential scanning calorimeter, SETARAM DSC 111. The values were 535, 430 and 582 kJ/kg for LDPE, HDPE, and PP, respectively. These values were later used to calculate the heat consumed in the pyrolysis process which were applied both in the energy balance closure and energetic viability analysis. The heats of combustion of the different components are given at ambient temperature and were assumed to be constant. The same applies to the specific heat capacities and the enthalpies of reaction.

2.3. Pyrolysis Product Stream Separation. Simulations of the basic separation of the pyrolysis products were conducted in order to consider the energy requirements for the separation of the pyrolysis products into product lumps that may be used straightforward in a refinery. These simulations were carried out in a Pro/II simulation software and different pieces of equipment were introduced in order to set up the product streams to proper conditions.

Product streams (multicomponent mixtures) separation has been simulated by simplified distillation columns consisting of rectifying and stripping sections. Light and heavy key components were selected for each column, assuming a 99% recovery of them. The minimum amount of theoretical plates were calculated by Fenske's method, and a reflux ratio of 1.2 times the minimum was assumed. The Soave-Redlich-Kwong thermodynamic model was selected to compute the simulation of the separation in these distillation towers, which is suitable for hydrocarbon mixtures and light gases at non-cryogenic temperatures. The fraction of waxes was simulated by assuming a mixture of paraffinic compounds with high carbon atom numbers. The stream that leaves the pyrolysis unit and enters the first separation unit is assumed to be at dew point conditions and atmospheric pressure.

Compressors, pumps, valves, and heat exchangers were introduced into the system in order to adjust the conditions of the different streams to adequate and common operation parameters. Compressors and valves were assumed to be isentropic. Pumps were assumed to have an efficiency of 90%. Finally, water was supposed to be the coolant in the heat exchangers when there was a necessity to cool down product streams.

In order to determine the heat requirements in the kettles of the distillation columns, an extra 10% has been added to the theoretical energy requirement so as to consider the energy losses across the tower wall.

3. RESULTS

3.1. Energy Balance Closure. Table 2 shows the input mass flow rates of LDPE, HDPE and PP for a plastic feed rate of 1000 kg/h, and the heat released during their combustion. These heat values have been calculated by multiplying the input mass flow rate of each material by their heat of combustion. The total amount of heat estimated for the combustion of the raw material in the feed is 43484 MJ/h. Given that the heat of combustion of the three reactants is very similar, the change in their input mass flow rate ratios hardly affects the total heat released during their combustion.

Table 2. Mass Flow Rate of LDPE, HDPE and PP, and Heat Released in their Combustion.

Material	Input mass flow rate (kg h⁻¹)	Heat (MJ h⁻¹)
LDPE	241.2	10371
HDPE	274.6	11807
PP	484.2	21306

The input mass flow rates in LDPE, HDPE, and PP pyrolysis, as well as the heat consumed in their pyrolysis are shown in Table 3. The heat required in the pyrolysis process has been calculated by multiplying the flow rates of each material by their corresponding enthalpies of reaction. The heat that needs to be provided to carry out the pyrolysis process of 1000 kg/h of the assumed polyolefin mixture is about 529 MJ/h. These values show that polyolefin pyrolysis is an endothermic process.

Table 3. Mass Flow rate of LDPE, HDPE, and PP Pyrolysis, and the Heat required for their Pyrolysis.

Material	Input mass flow rate (kg h⁻¹)	Heat (MJ h⁻¹)
LDPE	241.2	128.9
HDPE	274.6	118.0
PP	484.2	281.8

To calculate the heat released in the combustion of the compounds obtained in the pyrolysis processes, the heat of combustion of each compound has been multiplied by the mass flow rate of each of them. Table 4 sets out the heats of combustion of the different product-fractions obtained in their pyrolysis. As observed, the highest heat release values correspond to those fractions with highest yields; that is, the gas fraction when the HZSM-5 zeolite catalyst is used and the wax fraction in the thermal pyrolysis at 500 °C.

Table 4. Heats Released in the Combustion of the Product-fractions Obtained in the Pyrolysis processes (MJ h⁻¹).

	Thermal 500 °C	Thermal 700 °C	HZSM-5 500 °C	HY 500 °C
Gas	676	20110	37304	17891
Gasoline	1525	14082	8841	25112
Diesel	13616	7871	280	4332
Wax	23819	5616	135	338
Total	39635	47679	46560	47673

The enthalpy of reaction is usually calculated using the heats of combustion of the reactants and products, according to eq 1. Given that the major error is introduced in the calculation of the heat released in the combustion of the product-fractions, especially in the combustion of the wax fraction, which is due to low accuracy in the determination of its yield, eq 1 was re-ordered in the following form:

$$\Delta H_r + \Sigma \Delta H_{c,react.} = \Sigma \Delta H_{c,prod.} \quad (2)$$

Accordingly, the heat of combustion of the products was calculated as the sum of the enthalpy of reaction and the heat of combustion of the reactants. The value of this sum is compared with the value calculated for the heats of combustion of the products, and the deviation between both values and the relative deviation (percentage) are calculated. The latter is calculated as the quotient between the deviation value and the value of the enthalpy of reaction plus the sum of the heats of combustion of the reactants.

In Table 5, the heats of combustion of the products and the reactants, as well as the values of absolute and relative deviations for the different pyrolysis processes are shown. The enthalpy of reaction for both the thermal pyrolysis and the catalytic pyrolysis has been considered to be equal, 529 MJ/h, since in both cases the pyrolysis of plastic materials takes place first. In the case of catalytic pyrolysis, thermal degradation takes place followed by the catalytic cracking. Overall, the relative deviation in Table 5 is quite low, with the highest value being of around 10%. This highest value corresponds to the thermal pyrolysis carried out at 500 °C, which is the case in which the yield of waxes obtained is the highest. The explanation of this higher deviation in the energy balance closure in this case lies in the error made in the determination of the wax fraction, since the sticky nature of the material hinders an accurate measurement.

Table 5. Values of Absolute and Relative Deviation in the Calculation of the Product Stream Combustion Heat for the Different Pyrolysis Processes.

Pyrolysis process	$\sum \Delta H_{c,prod}^{\circ}$ (MJ h ⁻¹)	$\sum \Delta H_{c,react}^{\circ}$ (MJ h ⁻¹)	Deviation	% Deviation
500 °C	39635	43484	4378	10
700 °C	47679	43484	-3666	-8
HY	47673	43484	-3660	-8
HZSM-5	46280	43484	-2267	-5

3.2. Sensitivity Analysis. A sensitivity analysis has been carried out to determine the effect of the main parameters on the energy balance closure. The variables that have been analyzed are, on the one hand, the wax and diesel fractions (since the largest errors are made in the determination of these fractions) and, on the other hand, the heat of combustion of the polyolefins and the wax

fraction. The effect of the selected variables on the energy balance in the pyrolysis carried out at 500 °C is shown in Figure 1. The relative deviation is of 10% in this case (Table 5).

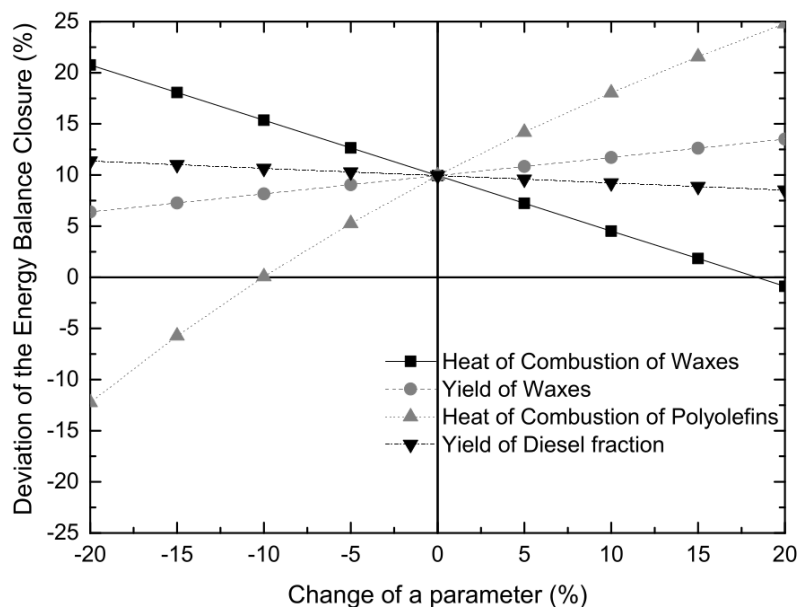


Figure 1. Effect of each variable on the energy balance for the pyrolysis carried out at 500 °C.

Figure 1 shows that the yields of the diesel and wax fractions have little effect on the deviation percentage, so the errors made in the determination of their yields would have low significance in terms of energy balance closure. Nevertheless, an increase in one of these yields involves a decrease in the yields of the remaining fractions. Thus, the effect on the energy balance closure varies depending on the heat of combustion of the fraction whose yield increases or decreases. Besides, it is observed that the heat of combustion of the wax fraction has a significant effect on the energy balance. Thus, as the value of the heat of combustion of the waxes is decreased, the energy balance closure deviation increases linearly and vice versa. The most sensitive variable is the heat of combustion of the feed. In this case, the decrease in this parameter also lowers the deviation of the energy balance closure. The inverse behaviour observed for the heat of combustion

of these variables is explained by the fact that one corresponds to the feed and the other one to the products.

The Figure 1 also lets us determine the percentage by which these variables should be modified, in an isolated mode, in order to erase the deviation in the energy balance closure. Thus, a 10% decrease in the heat of combustion of the polyolefins or a 17% increase in the heat of combustion of the waxes would result in no deviation. The actual situation is surely a sum of errors, in which the yields of the fractions obtained, the heats of combustion assumed for the yields of minor compounds, the experimental determination of combustion heats and reaction enthalpies and the simplifications assumed in order to carry out the calculation, all sum up increasing the uncertainty of the result. In any case, the deviations observed in the energy balance closure could be considered low and the sensitivity analysis allows us to identify the parameters that have to be determined more precisely in order to decrease the uncertainty.

Figures 2, 3 and 4 show the deviations obtained in the thermal pyrolysis at 700 °C, and in the catalytic pyrolysis on HZSM-5 zeolite based catalyst and on HY zeolite based catalyst, respectively. In all these figures the pivot-point is a negative deviation percentage as they correspond to the values shown in Table 5.

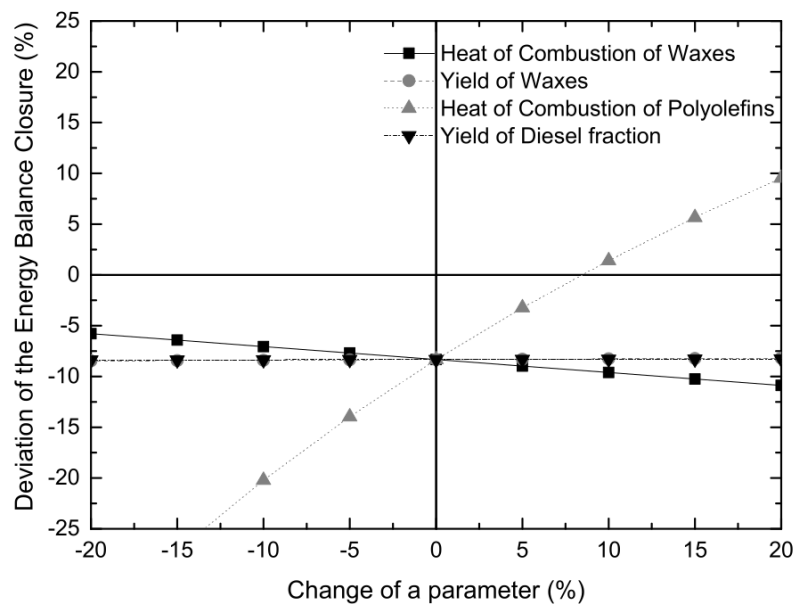


Figure 2. Effect of each variable on the energy balance for the pyrolysis carried out at 700 °C.

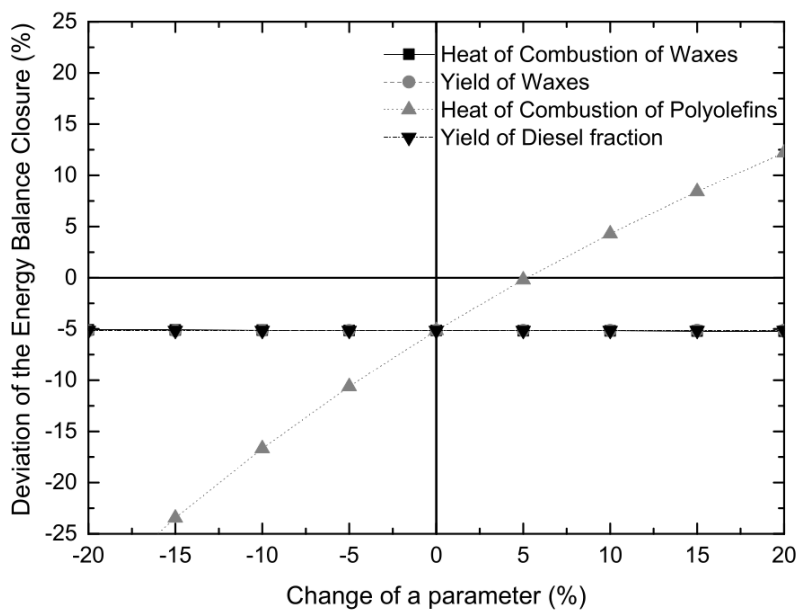


Figure 3. Effect of each variable on the energy balance for the catalytic pyrolysis carried out on HZSM-5 zeolite catalyst.

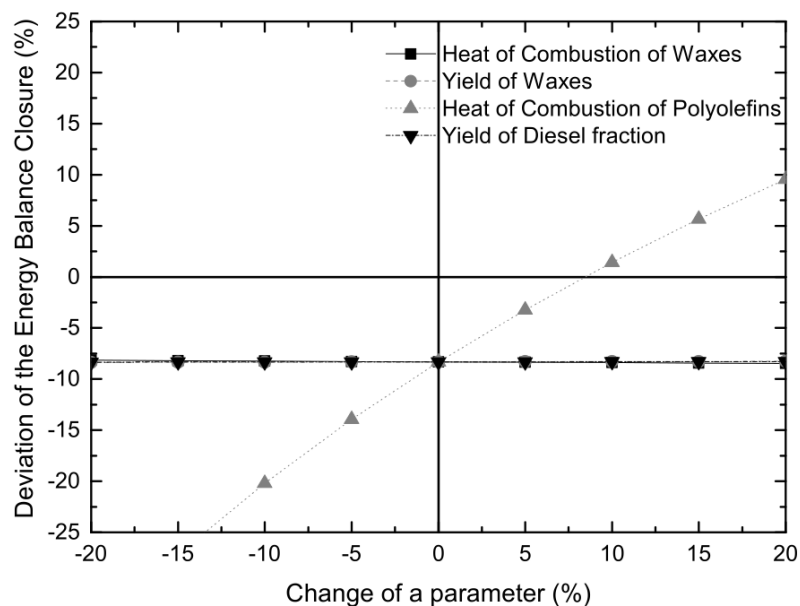


Figure 4. Effect of each variable on the energy balance for the catalytic pyrolysis carried out on HY zeolite catalyst.

According to these figures, the heat of combustion of the reactants is the unique variable that significantly affects the energy balance closure. The low yields of waxes and diesel fraction products obtained in all these cases explain the little effect of all these parameters, as well as that of the combustion heat of the waxes. Overall, analyzing Figures 1 to 4 as a whole, it can be concluded that the actual heat of combustion might be slightly higher than the values measured experimentally (around 5%), with the energy balance closure being in all cases highly satisfactory. Furthermore, for the thermal pyrolysis carried out at 500 °C, the yield and the heat of combustion obtained for the waxes might present a slight deviation (around 10%). The difficulty of measuring both parameters, due to the extremely sticky nature of the waxes and their possible contamination by other pyrolysis products, might be the reason behind this variability. It can be concluded that,

in all cases, if the values measured or determined are within $\pm 10\%$ of the real ones, the procedure described for the energy balance may be applied with high confidence.

3.3. Product Stream Separation. The separation of the products obtained in the four strategies considered has been simulated using the software Pro II. This section deals with the details on which the simulation was based and the results obtained.

3.3.1. Pyrolysis at 500 °C. The separation system proposed for the integration of the pyrolysis process in a refinery plant is shown in Figure 5. It consists of two distillation columns (rectification-stripping columns with a reboiler and a condenser), 5 heat exchangers, 1 pump, 1 expansion unit and 1 expansion valve. The pyrolysis reactor output stream is adjusted to the temperature and pressure of the first distillation column (bubble point temperature at atmospheric pressure). Gas and gasoline fraction products exit from the top of the column, whereas the diesel and wax fraction products exit from the bottom of the column. The components making up the latter two heavy fractions are separated in a second distillation column once the stream goes through a heat exchanger (to cool it down) and an expansion valve (to decrease pressure to 0.1 atm). The diesel fraction products exit from the top of this second column and the wax fraction products exit from the bottom of the column. The temperature and pressure of the output streams of both columns are adjusted by means of valves and heat exchangers so that they could be merged with ordinary refinery streams. All the heat exchangers used for cooling are designed using water as the refrigerating fluid.

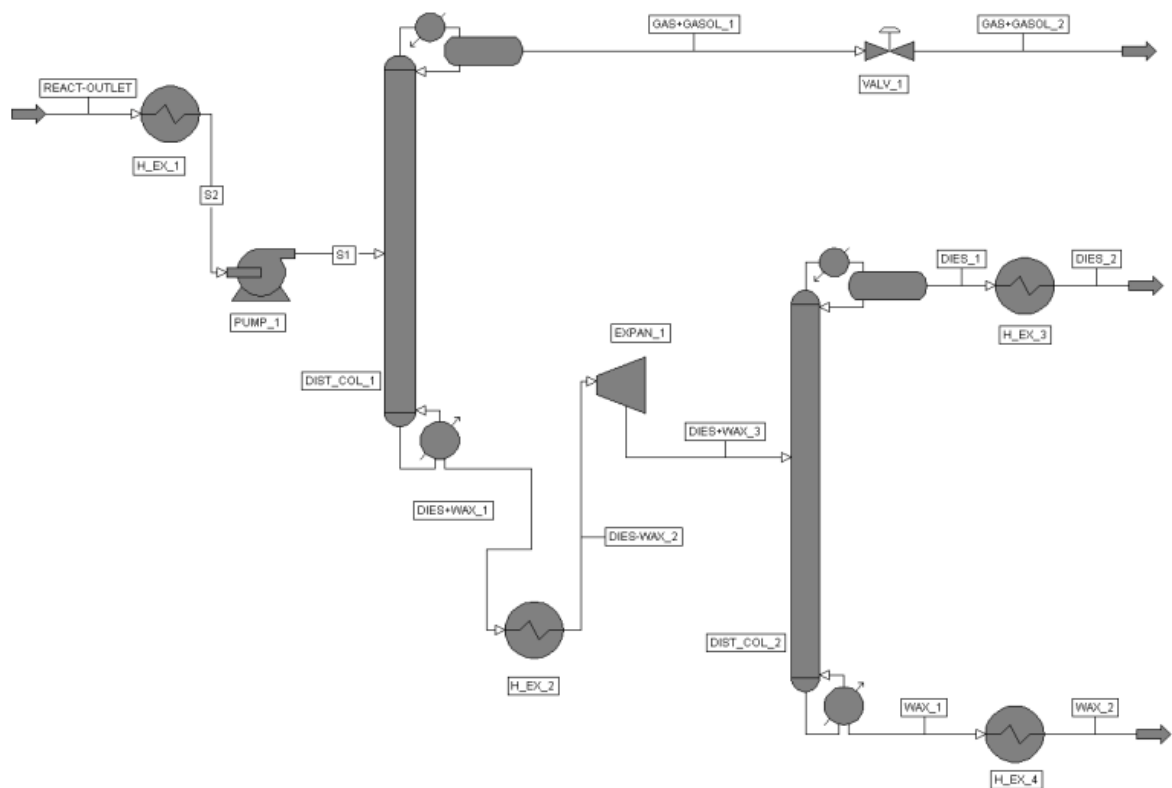


Figure 5. Flow chart of the separation system for the products obtained in the thermal pyrolysis at 500 °C.

The temperatures, pressures, and mass flow rates obtained for the output streams of the distillation towers are shown in Table 6. The temperature and pressure values have been adjusted to the conditions of the refinery streams. The mass flow rate values have been provided by the simulation program. The second distillation column, Table 6, operates at vacuum conditions, 0.1 atm, in order to facilitate the separation of heavy compounds at lower temperatures. The basic characteristics of the two distillation columns are shown in Table 7. The heat that must be provided in the reboiler and the heat that is released in the condenser are quite similar in both columns. The input and output temperatures and pressures together with the energy needs of the pieces of equipment used in the separation system are shown in Table 8.

Table 6. Temperature, Pressure, and Mass Flow Rates of the output Streams.

Output stream	Temperature (°C)	Pressure (atm)	Mass flow rate (kg/h)
Gas + Gasoline	118	1	70
Diesel	80	0.1	260
Wax	95	0.1	670

Table 7. Characteristics of the System Columns.

Column	Number of stages	Feeding stage	Energy needs (MJ h⁻¹)	
			Condenser	Reboiler
Column 1	62	16	-113	183
Column 2	18	8	-125	126

Table 8. Characteristics of the Pieces of Equipment of the Separation System Proposed.

Equipment	Temperature (°C)		Pressure (atm)		Energy required (MJ h⁻¹)
	Input	Output	Input	Output	
Pump	302	302	1	2	20.2
Valve	118	118	2	1	-
Expansion unit	280	255	2	0.1	-6.60
Heat exch. 1	408	302	1	1	-488
Heat exch. 2	337	280	2	2	-173
Heat exch. 3	164	80	0.1	0.1	-60.7
Heat exch. 4	323	95	0.1	0.1	-425

3.3.2. *Pyrolysis at 700 °C.* In this case, the separation system consists again of two distillation columns and there are three output streams. Nevertheless, as the yield of the gas fraction is high in this case, the gas fraction products are separated from the rest of the products in the first column, whereas the gasoline fraction products are separated from diesel and wax fraction products (bottom stream) in the second column.

3.3.3. *Catalytic Pyrolysis on HZSM-5 Zeolite Catalyst.* The separation system proposed is quite different in this case. It consists of only one distillation column. Since the yields of diesel and wax fraction obtained in the reaction are very low, their previous separation in another unit is considered. Thus, only gas and gasoline fraction separation by distillation has been considered in the separation system. As a consequence, there is only one distillation column in this separation system, where the incondensable gases are removed from the top of the column and the gasoline fraction products from the bottom. These streams have been adjusted to the conditions of the corresponding refinery streams using valves and heat exchangers to obtain appropriate temperatures and pressures. Thus, the gas stream that leaves the reactor and enters the column is cooled down and compressed to achieve optimal entrance conditions.

3.3.4. *Catalytic Pyrolysis on HY Zeolite Catalyst.* In this case, the separation system consists of two distillation columns and there are three output streams. The gas and gasoline fraction products exit from the top of the first column and the diesel/wax fraction products from the bottom. The gas and gasoline fractions are separated later on in a second column. The temperatures, pressures, and mass flow rates of the output streams for the thermal pyrolysis at 700 °C, the catalytic pyrolysis on HZSM-5 catalyst and HY catalyst are shown in Table 9.

Table 9. Temperature, Pressure, and Mass Flow Rate of output Streams in the Separation Systems for the Thermal (700 °C) and Catalytic Pyrolysis Processes.

Pyrolysis process	Output stream	Temperature (°C)	Pressure (atm)	Mass flow rate (kg/h)
Thermal, 700 °C	Gas	25	5	395
	Gasoline	45	1	330
	Diesel+wax	248	1	275
HZSM-5 Catalyst	Gas	20	1	770
	Gasoline	20	1	220
HY catalyst	Gas	25	5	335
	Gasoline	45	1	550
	Diesel+wax	248	1	115

In the case of the HZSM-5 zeolite catalyst, the exit flow does not account for 1000 kg/h, because the diesel fraction and the wax fraction, 1 wt.% of the feed (10 kg/h), are assumed to be previously separated. The characteristics of the distillation columns for the thermal pyrolysis at 700 °C and the catalytic pyrolysis processes are shown in Table 10.

Table 10. Characteristics of the Distillation Columns in the Separation Systems for the Thermal (700 °C) and Catalytic Pyrolysis Processes.

Pyrolysis process	Column	Number of stages	Feeding stage	Energy needs (MJ h ⁻¹)	
				Condenser	Reboiler
Thermal, 700 °C	Column 1	53	35	-125	361
	Column 2	86	26	-154	158
HZSM-5 Catalyst	Column 1	28	16	-177	156
HY Catalyst	Column 1	34	28	-54	36
	Column 2	23	12	-132	153

3.4. The estimation of the energy requirements of the process. Calculations will be made to check whether burning one of the side-product streams (the one obtained in a lower amount) satisfies or not the energy requirements of the whole process. In previous sections, the energy requirements for the pyrolysis process and for the separation systems (heating the raw-materials to the reaction temperature, the endothermicity of the reaction, and the heat required to carry out the distillation processes) were determined.

The stream obtained in lower amount has been assumed to be the one that is burnt in all four cases so as to satisfy energy requirements. In the thermal pyrolysis carried out at 500 °C, the gas/gasoline stream (7 wt.% yield) exiting from the top of the first distillation column has been chosen; in the thermal pyrolysis carried out at 700 °C, the diesel/wax fraction products, 27.5 wt.%, exited from the bottom of the second distillation column; in the catalytic pyrolysis on HZSM-5 zeolite catalyst, the gasoline fraction, 22 wt.%, exited from the bottom of the only distillation

column of the system (the yields of the diesel and wax fractions obtained were too low); and in the catalytic pyrolysis on HY zeolite catalyst, the diesel/wax fraction, 11.5 wt.%, removed from the bottom of the first distillation column. Thus, using the heat of combustion of the compounds in these fractions, the total heat obtained by their combustion has been calculated, as previously shown in Table 4.

The energy required to heat the polyolefin mixture from ambient temperature (20 °C) to reaction temperature (500 or 700 °C) has been considered. In order to do so, a mean specific heat capacity of 2122 J/kg K for the three polyolefins has been assumed. The need to heat the fluidizing gas to the reaction temperature has not been considered, given that, in an industrial scale plant, the exhaust gas obtained in the combustion of low yield product streams is at a high temperature and is ideal for this purpose. An extra 10% has been added to the heat required in the reboilers of the distillation columns in order to consider possible heat losses in the columns. Table 11 sets out all the details involving energy requirements and the energy obtained by combustion in the four strategies analyzed.

Table 11. Energy requirements, energy obtained by combustion of an output stream, % of the input mass flow rate used for combustion, and % of combustion heat used for the energy requirements.

Pyrolysis process	Energy requirements (MJ/h)	Energy obtained by combustion (MJ/h)	Input mass flow rate (%)	Heat used (%)		
Thermal 500 °C	Boiler heating					
	Column 1	201				
	Column 2	139				
	Reactant heating	1019	Gas + Gasoline fraction	2200	7	86
	Reaction heat	529				
Total	1888					
Thermal 700 °C	Boiler heating					
	Column 1	397				
	Column 2	174				
	Reactant heating	1443	Diesel + Wax fraction	13487	27.5	19
	Reaction heat	529				
Total	2543					
Catalytic HZSM-5 catalyst	Boiler heating					
	Column 1	172				
	Reactant heating	1019	Gasoline fraction	8841	22	20
	Reaction heat	529				
Total	1720					
Catalytic HY catalyst	Boiler heating					
	Column 1	40				
	Column 2	168				
	Reactant heating	1019	Diesel + Wax fraction	4670	11.5	38
	Reaction heat	529				
Total	1756					

As observed, the energy requirements of the pyrolysis plant are lower in all cases than the energy obtained in the combustion of the minor fraction obtained. In the case of thermal pyrolysis at 500 °C, both values are quite similar. However, in all the other cases, the heat obtained from the combustion of the byproduct stream is substantially higher than the energy required, especially in the thermal pyrolysis at 700 °C and the catalytic pyrolysis on the HZSM-5 zeolite catalyst, as the heat obtained in the combustion of the residual fraction is five times higher than the energy required. This result is a consequence of the considerable yield of the residual fraction in both cases, more than 20 wt.% of the total, but obviously, not all of it would have to be used for combustion. Considering all four strategies, around 5-6 wt.% of the material fed has to be destined for combustion in order to consider the process viable from an energy perspective.

In view of these results, it can be confirmed that the heat of combustion of the outlet streams obtained in a lower amount would be enough to satisfy the energy requirements of the pyrolysis plant and its separation unit and, moreover, there would be an excess of energy that could be used for other applications.

In conclusion, the pyrolysis process followed by the posterior separation of the products obtained into streams that might be directly used in a refinery would be energetically viable. It should be noted that the inclusion of the proposed processes in a refinery would improve their economic viability, as there are alternative sources of energy available in a refinery. The combustion of secondary interest streams, products of other refinery units, could provide the required energy for pyrolysis. Moreover, the cost of the separation of the products would be lower in this case by using the existing infrastructure of the refineries and the composition of the products would be easier to adhere to the market demands compared to a specific unit of pyrolysis and

separation. Additionally, the selection among the four strategies proposed would be conditioned by the economic interest of the refinery, establishing either gasoline or light olefins as the priority products. Thus, initiatives such as the incorporation into the commercial gasoline pool of the polyolefin pyrolysis gasoline product, without sulphur content and with low quantities of aromatic compounds, or the co-feeding of the polyolefin pyrolysis waxes with VGO into the fluid catalytic cracking (FCC) unit, have great economic potential (hard to evaluate without production data).

4. CONCLUSIONS

The fast pyrolysis of polyolefins, separated from the plastic wastes, is an easy and versatile process where the selective production of olefins, gasoline, or waxes may be achieved by means of the selection of the operation temperature and that of the catalyst. As it has been proved in this study, the energy to carry out the pyrolysis and posterior separation of the products of the four alternative processes that have been analyzed, can be obtained by the combustion of the minority product fraction, and so, of less commercial interest, of each process. Thus, it can be concluded that the polyolefin pyrolysis and the posterior separation process of the products is energetically viable. Hence, only about 5% of the input mass flow rate is needed to burn to satisfy the energy requirements.

In view of these results, the option to incorporate a pyrolysis unit including a separation system to obtain typical product-streams of a refinery is viable from an energy perspective. This inclusion may provide an answer to the necessity of waste plastic management and furthermore, the refinery would contribute to the recycling of oil derived products and thus, to the intensification of its upgrading. In addition, the use of installations that are already written off would ease the optimum upgrading and commercialization of the pyrolysis product streams.

AUTHOR INFORMATION

Corresponding Author

*Gorka Elordi. Email: gorka.elordi@ehu.eus

ORCID:

Gorka Elordi: 0000-0001-7902-263X

ACKNOWLEDGMENT

This work was carried out with the financial support from the Ministry of Economy and Competitiveness of the Spanish Government (CTQ2016-75535-R (AEI/FEDER, UE)) and the Basque Government (IT748-13).

5. REFERENCES

- (1) An analysis of European plastic production, demand and waste data. *Plastics Europe-Plastics-the Facts 2016*, 2016. www.plasticseurope.org/Document/plastics-the-facts-2016.aspx
- (2) Williams, P. T.; Williams, E. A. *J. Anal. Appl. Pyrol.* **1999**, *51*, 107-126.
- (3) Achilias, D. S.; Roupakias, C.; Megalokonomosa, P.; Lappas, A. A.; Antonakou, E. V. *J. Hazard. Mater.* **2007**, *149*, 536-542.
- (4) Kaminsky, W.; Predel, M.; Sadiki, A. *Polym. Degrad. Stab.* **2004**, *85*, 1045-1050.
- (5) Berrueco, C.; Mastral, F. J.; Esperanza, E.; Ceamanos, J. *Energy Fuels*, **2002**, *16*, 1148-1153.
- (6) Miskolczi, N.; Bartha, L.; Deak, G. *J. Anal. Appl. Pyrol.* **2004**, *72*, 235-242.
- (7) Aguado, J.; Serrano, D. P.; Escola, J. M.; Garagorri, E.; Fernandez, J. A. *Polym. Degrad. Stab.* **2000**, *69*, 11-16.
- (8) Shoucheng, D.; Valla, J. A.; Parnas, R. S.; Bollas, G. M., *ACS Sust. Chem. Eng.* **2016**, *4*, 2852-2860.
- (9) Mastral, J. F.; Berrueco, C.; Gea, M.; Ceamanos, J. *Polym. Degrad. Stab.* **2006**, *91*, 3330-3338.

(10) Kim, B. S.; Kim, Y. M.; Lee, H. W.; Jae, J.; Kim, D. H.; Jung, S. C.; Watanabe, C., Park, Y. K. *ACS Sust. Chem. Eng.* **2016**, *4*, 1354-1363.

(11) Hornung, A.; Seifert, H. Rotary kiln pyrolysis of polymers containing heteroatoms. In *Feedstock Recycling and Pyrolysis of Waste Plastics. Converting Waste Plastic into Diesel and other Fuels*. Scheirs J.; Kaminsky, W. Eds.; John Wiley & Sons Ltd: West Sussex, UK, 2006; pp 549-567.

(12) Slowinski, K.; Stelmachowski, M. Thermal degradation of plastics and waste rubber in the molten metal bed reactor. *Proc. ECOpole*. **2008**, *2*, 385-391.

(13) Ng, S. H.; Seoud, H.; Stanciulescu, M.; Sugimoto, Y. *Energy Fuels*. **1995**, *9*, 735-742.

(14) Seo, Y.; Lee, K.; Shin, D. *J. Anal. Appl. Pyrol.* **2003**, *70*, 383-398.

(15) Van Grieken, R.; Serrano, D.P.; Aguado, J.; García, R.; Rojo, C. *J. Anal. Appl. Pyrol.* **2001**, *58*, 127-142.

(16) Miskolczi, N.; Bartha, L.; Deák, G.; Jóver, B.; Kalló, D. *J. Anal. Appl. Pyrol.* **2004**, *72*, 235-242.

(17) Mastral, J. F.; Berrueco, C.; Ceamanos, J. *J. Anal. Appl. Pyrol.* **2007**, *80*, 427-438.

(18) Mastellone, M. L.; Perugini, F.; Ponte, M.; Arena, U. *Polym. Degrad. Stab.* **2002**, *76*, 479-487.

(19) Hernandez, M. R.; Gomez, A.; Garcia, A. N.; Agullo, J.; Marcilla, A. *Appl. Catal. A*. **2007**, *317*, 183-194.

(20) Williams, E. A.; Williams, P. T. *J. Anal. Appl. Pyrol.* **1997**, *40-41*, 347-363.

(21) Conesa, J. A.; Font, R.; Marcilla, A.; Caballero, J.A. *J. Anal. Appl. Pyrol.* **1997**, *40-41*, 419-431.

(22) Aguado, R.; Prieto, R.; San José, M. J.; Alvarez, S.; Olazar, M.; Bilbao, J. *Chem. Eng. Process.* **2005**, *44*, 231-235.

(23) Elordi, G.; Olazar, M.; Lopez, G.; Artetxe, M.; Bilbao, J. *Ind. Eng. Chem. Res.* **2011**, *50*, 6650-6659.

(24) Olazar, M.; San José, M. J.; Peñas, F. J.; Aguayo, A. T.; Bilbao, J. *Ind. Eng. Chem. Res.* **1993**, *32*, 2826-2834.

(25) San José, M. J.; Olazar, M.; Peñas, F. J.; Bilbao, J. *Ind. Eng. Chem. Res.* **1994**, *33*, 1838-1844.

- (26) Aguado, R.; Prieto, R.; San José, M. J.; Alvarez, S.; Olazar, M.; Bilbao, J. *Chem. Eng. Process.* **2005**, *44*, 231-235.
- (27) Arena, U.; Mastellone, M. L. *Chem. Eng. Sci.* **2000**, *55*, 2849-2860.
- (28) Tonini, D.; Martinez-Sanchez, V.; Astrup T. F. *Environ. Sci. Technol.* **2013**, *47*, 8962-8969.
- (29) Gracida-Alvarez, U. R.; Keenan, L. M.; Sacramento-Rivero, J. C.; Shonnard, D. R. *ACS Sust. Chem. Eng.* **2016**, *4*, 5972-5978.
- (30) Williams, P. T.; Williams, E. A.; *J. Anal. Appl. Pyrol.* **1999**, *51*, 107-126.
- (31) Arabiourrutia, M.; Elordi, G.; Lopez, G.; Borsella, E.; Bilbao, J.; Olazar, M. *J. Anal. Appl. Pyrol.* **2012**, *94*, 230-237.
- (32) Hájekova, E.; Bajus, M. *J. Anal. Appl. Pyrol.* **2005**, *74*, 270-281.
- (33) Fernández, M. L.; Lacalle, A.; Bilbao, J.; Arandes, J. M.; De la Puente, G.; Sedran, U. *Energy Fuels* **2002**, *16*, 615-621.
- (34) Devard, A.; De la Puente, G.; Sedran, U. *Fuel Process. Technol.* **2009**, *90*, 51-55.
- (35) Arandes, J. M.; Torre, I.; Castaño, P.; Olazar, M.; Bilbao, J. *Energy Fuels* **2007**, *21*, 561-569.
- (36) Kirkwood, K. C.; Leng, S.A.; Sims, D. W. Polymer cracking, US Patent 5,364,995. 1992.
- (37) Donaj, P. J.; Kaminsky, W.; Buzeto, F.; Yang, W. *Waste Manage.* **2012**, *32*, 840-846.
- (38) Leckner, B. Atmospheric (non-circulating) fluidized bed (FB) combustion. In *Fluidized bed Technologies for near-zero Emission Combustion and Gasification*. Scala, F., Ed.; Woodhead Publishing Books, Cambridge, UK, 2013; pp 641-668.
- (39) Leckner, B. *Waste Manage.* **2015**, *37*, 13-25.
- (40) Mastral, F. J.; Esperanza, E.; Berrueco, C.; Juste, M.; Ceamanos, J. *J. Anal. Appl. Pyrol.* **2003**, *70*, 1-17.
- (41) Elordi, G.; Olazar, M.; Lopez, G.; Amutio, M.; Artetxe, M.; Aguado, R.; Bilbao J. *J. Anal. Appl. Pyrol.* **2009**, *85*, 345-351.
- (42) Elordi, G.; Olazar, M.; Lopez, G.; Artetxe, M.; Aguado, R.; Bilbao, J. *Ind. Eng. Chem. Res.* **2011**, *50*, 6061-6070.
- (43) Bosmans, A.; Vanderreydt, I.; Geysen, D.; Helsen, L. *J. Cleaner Prod.* **2013**, *55*, 10-23.
- (44) Luo, S.; Feng, Y. *Energy Convers. Manage.* **2017**, *136*, 27-35.