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Operating Conditions for the Pyrolysis of Poly-(ethylene terephthalate) in a Conical Spouted-Bed Reactor

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Continuous pyrolysis of poly-(ethylene terephthalate) (PET) was performed in a conical spouted-bed reactor. This reactor is especially suitable for this process, because of its excellent hydrodynamic behavior and its versatility. An optimization of the operating conditions has been performed to avoid particle agglomeration and defluidization, given that these are serious problems that hinder plastic waste pyrolysis. Moreover, the influence of temperature in the pyrolysis product distribution was studied in the range of 500–600 °C. PET pyrolysis led to a high yield of gas fraction, a low amount of liquids, a significant yield of solid fraction, and a solid residue that remained in the reactor coating sand particles. The main products obtained are carbon monoxide, carbon dioxide, benzoic acid, and acetaldehyde.

1. Introduction

The use of different types of plastics has greatly increased in recent years, and the disposal of plastic waste has become a major environmental issue. Nowadays, poly-(ethylene terephthalate) (PET) is the plastic with the highest growth in consumption and an annual increase of 10% is expected by the year 2010 in Europe.¹ PET is used for many different applications, mainly in packaging in the food industry and in the manufacture of beverage bottles. The high consumption of this type of plastic is a serious environmental problem, because of the fact that most of the plastic waste produced is deposited in landfills or treated in incinerators. Therefore, alternative methods of plastics recycling should be developed, which may be physical or chemical methods. PET physical recycling includes collection, separation, digestion, granulation of polymer waste, and recirculation into production.² Several chemical recycling methods have been studied: solvolysis with water, methanol, and glycol, and degradation or cracking, where raw materials such as terephthalic acid and ethylene glycol, or other valuable products can be recovered.¹

Thermal degradation of used plastic could be a good alternative to present plastic-upgrading processes and, consequently, used plastic could become a valuable source of chemicals, as well as gas and liquid fuels. The pyrolysis of poly-(ethylene terephthalate) yields a gas that consists of carbon dioxide and carbon monoxide, a small amount of liquids, a significant solid fraction, and a residue.³ The thermal stability of PET is rather high, so volatile emissions start at 300 °C,^{4,5} with the primary formation of cyclic oligomers, and at 300–400 °C, the main products of pyrolysis are acetaldehyde and anhydride-containing oligomers.⁵ Although the devolatilization process starts at 300 °C, the pyrolysis of PET occurs within a limited temperature range (400–550 °C), in which the main fraction of the plastic is decomposed, and the solid continues smoothly decomposing at higher temperatures.⁶ The main products of PET pyrolysis are (apart from carbon dioxide and carbon monoxide) oxygenated compounds, such as benzoic acid, terephthalic acid, aldehydes, acetophenone, dioxolanes, diacetyl benzene, etc.;^{7–10} however, at high temperatures (>700 °C), there is an important amount of polycyclic aromatics.^{10–12}

Furthermore, the solid residue can be treated to obtain a high-value carbon-adsorptive material by several treatments.^{13–15}

The pyrolysis of poly-(ethylene terephthalate) has been performed in the literature mainly in fixed-bed reactors,^{1–3,9–11} as well as in thermogravimetric analyzers,^{6,15} to study the kinetics;^{4,16} however, fluidized beds have not been commonly used.⁸ The major difficulty in the pyrolysis of plastics is the energy supply required, because of their poor thermal conductivity.⁷ Therefore, a suitable pyrolysis reactor is essential, to ensure good heat transfer. Fluidized beds have extensively been used in plastics pyrolysis,^{17–19} but large-scale operation in this reactor presents problems of defluidization, because of particle agglomeration that is caused by the fusion of particles coated with plastic.²⁰ PET pyrolysis presents a significant risk of defluidization in fluidized beds, which is caused by the formation of agglomerates composed of sand and a sticky solid residue. At the initial stage of the reaction, the melted plastic forms aggregates with the sand (sand particles stuck on the surface of the molten plastic). Simultaneous to polymer cracking, aggregates composed of a sticky carbon residue and sand particles are formed, which may join together to form bigger aggregates and cause difficulties in the fluidization and, finally, bed collapse.²⁰

In this paper, a conical spouted-bed reactor has been used for the pyrolysis of poly-(ethylene terephthalate) at different temperatures. Spouted beds with fully conical geometry combine the features of cylindrical spouted beds (such as the capacity for handling coarse particles, small pressure drop, cyclic movement of the particles, and so on) with those inherent to their geometry, such as stable operation in a wide range of gas flow rates.²¹ This versatility in the gas flow rate allows for the handling of particles of irregular texture, fine particles, and those with a wide size distribution, and sticky solids, whose treatment is difficult, using other gas–solid contact regimes.^{22–24} Moreover, operation can be conducted with short gas residence times (as low as milliseconds) in the dilute spouted bed.²⁵

Therefore, the cyclic movement of sand particles allows for their uniform coating with melted plastic, and the high velocity of the particles avoids their agglomeration, as has been proven in polyolefin pyrolysis under conditions of maximum particle stickiness.²⁶ The good performance of this reactor for handling polyolefins and polystyrene has been verified in the thermal and

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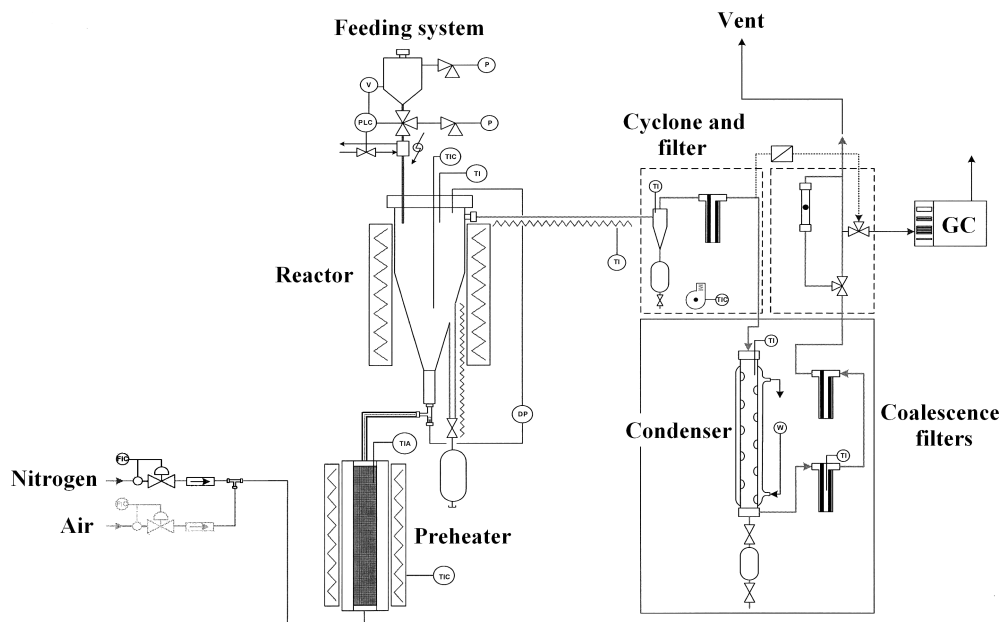


Figure 1. Scheme of the pyrolysis pilot plant.

catalytic pyrolysis that has been performed in previous studies.^{25–28}

2. Experimental Section

2.1. Equipment. The continuous pyrolysis unit used in this study is shown in Figure 1. The unit has been improved based on the experience acquired in a cold unit, as well as in the pyrolysis of biomass,²⁹ tires,³⁰ and plastic wastes.^{25–28} The main component of the unit is the spouted-bed reactor, which consists of a lower conical section and an upper cylindrical section. The total height of the reactor is 34 cm, the height of the conical section is 20.5 cm, and the angle of the conical section is 28°. The diameter of the cylindrical section is 12.3 cm, the bottom diameter is 2 cm, and the gas inlet diameter is 1 cm. These dimensions guarantee bed stability over a wide range of operating conditions.

The plastic feeding system allows for the continuous operation of the pyrolysis pilot plant. This system consists of a hopper connected to a pneumatically actuated valve, which measures out the solid and is able to feed up to 300 g/h of plastic. The nitrogen flow is controlled by means of a mass flow meter (up to 30 L/min) and heated to the reaction temperature using a preheater with an internal cartridge. The pyrolysis products leave the reactor through a thermostatted pipe to an insulated high-efficiency cyclone and a filter (located in a thermostatted chamber), to remove the fine particles of the gaseous stream. The stream leaving the chamber is condensed in a double-shell condenser and two coalescence filters, where the liquids and solids are separated from the gases.

The mass balance is closed using the information obtained by burning the solid residue that is coating the sand at the end of the continuous run and by monitoring the product stream using gas chromatography (GC) and Micro GC. In the first case, data are provided on the yield of condensable plus noncondensable products, which is obtained by subtracting the yield of residue from the total amount of plastic fed into the reactor.

The quantification of the individual products formed in the thermal degradation of PET has been conducted by monitoring the product stream using a GC system (Agilent Model 6890) equipped with a flame ionization detector (FID) and a Micro

GC system connected to a mass spectrometer (Agilent Model 5975B). This required a sophisticated analytical procedure to be set up and tuned. Thus, a sample of the product stream has been taken downstream from both the reactor and cyclone, diluted with an inert carrier (nitrogen), and then injected into the GC by means of a thermostatted line maintained at 250 °C. This temperature is required to avoid the condensation of the heavier products in the transfer line and, consequently, to monitor all the volatile products formed in the reaction. Furthermore, once the condensable products have been retained in the condenser and filter, the noncondensable products have been monitored using a Micro GC system. Samples have been taken at least five times under the same conditions, and the calculated mass flow rate of the volatile stream is of the same order (within 8% error) as that obtained by subtracting the solid residue from the total plastic fed into the reactor.

A calibration has been performed to obtain the response factors of the FID device to oxygenate compounds. Note that, unlike hydrocarbons, the FID response to oxygenate compounds is not proportional to their mass.

Moreover, the pyrolysis products are identified using a mass spectrometer (Shimadzu Model GC-MS-QP2010S). The analysis of the light products is performed by means of a Micro GC system connected to a mass spectrometer (Agilent Model 5975B).

PET was provided by Artenius PET Brand Seda Group (Spain). The plastic pellets have dimensions of 3 mm × 2.5 mm × 2 mm, and, given the good performance of the conical spouted-bed reactor, no size reduction is required to feed them into the reactor.

2.2. Experimental Procedure. The pyrolysis of PET was performed under several conditions, with the objective of determining the optimum ranges to avoid bed defluidization. The effect of pyrolysis temperature, sand particle diameter, bed mass, plastic feed rate, and gas flow rate has been studied.

Once the optimum hydrodynamic conditions for stable operation have been delimited, a study has been conducted on the effect of temperature on the continuous pyrolysis of PET. The experiments have been conducted at 500, 550, and 600 °C. The continuous feed rate of PET was 1.5 g/min, and

the bed was initially composed of 100 g of sand (0.63–1.18 mm in size). A high nitrogen flow rate (28 L/min)—twice that corresponding to the minimum spouting velocity—was used to avoid defluidization problems and ensure good mixing in the bed.

3. Results

3.1. Stable Operation Conditions. Several parameters have been studied to set the adequate operating conditions to perform poly-(ethylene terephthalate) pyrolysis without bed defluidization, including the PET feed rate, nitrogen flow rate, bed height, bed material size, and temperature.

One of the factors causing defluidization is the poor heat transfer of the plastic materials, which gives way to severe temperature gradients inside the plastic particle. Thus, whereas the surface of the particles is being pyrolyzing, inside temperatures are much lower and pyrolysis is hindered. Furthermore, melted plastic forms aggregates with sand and these can grow to generate bigger ones and, subsequently, cause defluidization. Moreover, when big aggregates are formed, the melted plastic is subjected to repolymerization reactions that give way to the formation of a carbon material, and heat transfer is even worse under these conditions. This carbon material is highly stable at the pyrolysis temperature and holds the big aggregates together, which causes permanent defluidization. Combustion is the best and easiest solution to eliminate this material and recover the spouting regime. Nevertheless, conical spouted beds are well-known for their gas flow rate versatility,³¹ which may be increased from the state of spouting to that of dilute spouting. This means that large-scale operation with high gas flow rates is possible with higher PET flow rates, processed with the same ratio of bed mass to plastic flow rate. Moreover, the conical spouted-bed reactor is able to handle the sand polymer aggregates under vigorous solid movement conditions, because of the possibility to operate with solid mixtures without segregation³² and, consequently, avoid defluidization.

Different experiments have been conducted using PET feed rates (Q_{PET}), ranging from 0.5 g/min to 3 g/min at 500 °C and using 100 g of sand. In the runs with feed rates higher than 1.5 g/min, poor particle circulation was observed subsequent to a few minutes of operation, leading to a complete defluidization of the bed. Nevertheless, spouting is not affected and the pyrolysis process is satisfactorily conducted when the feed rate is lower than this value. Defluidization occurred because the size of the sand and pyrolyzed plastic aggregates was so large that the bed was completely collapsed, similar to that which occurs in fluidized beds for much lower PET flow rates.²⁰

Furthermore, the effect of bed height (or bed weight, W_{bed}) was studied in the range of 50–150 g of sand by feeding 1.5 g/min of polymer. The main conclusion is that a bed of 100 g is the minimum required to avoid defluidization with the PET flow rate used. Therefore, at 500 °C (the lowest temperature used in this study) and using a relatively coarse sand (0.63–1.18 mm), the critical value of the $W_{\text{bed}}/Q_{\text{PET}}$ ratio to ensure a suitable bed performance is 4000 s.

The gas flow rate used in the pyrolysis is an important parameter for suitable spouting behavior. Runs have been conducted using flow rates in the range of 1.2–2.5 times greater than those corresponding to the minimum velocity, which is 3.6 m/s with 100 g of sand at 500 °C. It is observed that turbulence with a velocity 1.2 greater than that corresponding to the minimum is not vigorous enough to guarantee the correct operation and bed collapse is the result. Nevertheless, raising the gas velocity to twice that corresponding to the minimum

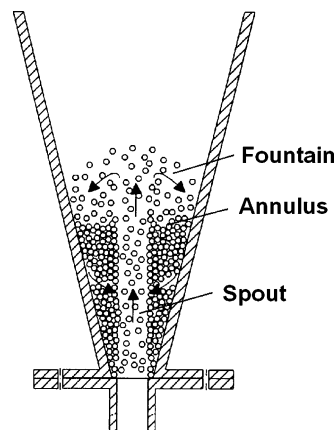


Figure 2. Solid cyclic movement in a conical spouted bed.

resulted in a more vigorous movement and improved heat transfer to the plastic, thus avoiding bed defluidization. This is an interesting result, given that increasing gas velocity in fluidized beds does not lead to significant improvement in the fluidization of the aggregates.²⁰ Thus, although gas velocity is increased in fluidized beds, particle velocity is hardly changed, because most of the excess gas rises through the bed in the bubble phase. Nevertheless, particle velocity in conical spouted beds is strongly dependent on gas velocity. Figure 2 shows the solid cyclic movement in a conical spouted bed, which is greatly enhanced by increasing gas velocity. Especially remarkable is the role played by the spout region, given that this zone has an extremely vigorous solid movement and high gas velocities, which are conditions that allow for breaking up the sand-melted plastic aggregates, making possible a stable operation in the pyrolysis of plastics.

The effect of the bed material size was studied using two types of sand: a fine sand (0.3–0.63 mm in size) and a coarse sand (0.63–1.18 mm in size). In both cases, the temperature was 500 °C, the amount of sand was 100 g, and the nitrogen flow rate was twice that which corresponds to the minimum spouting velocity. When the fine sand was used, bed defluidization occurs, unless very low PET flow rates (below 0.5 g/min) are fed into the reactor. However, when the coarse sand was used, aggregates were not formed (for PET flow rates of <1.5 g/min), because a more vigorous movement allows for a good covering of sand particles with melted plastic and, consequently, a faster plastic degradation is possible. In this case, a thin layer of pyrolytic residue is deposited on the sand particle surface. Figure 3 shows a comparison between two pictures corresponding to the sand before the pyrolysis process (Figure 3a) and the sand extracted subsequent to 1 h of operation (Figure 3b). As observed, the sand is completely covered by an uniform layer of carbonaceous residue. This material is highly stable under pyrolysis conditions and is not sticky, so does not compromise continuous operation. Moreover, it is hard and, despite the vigorous movement in a conical spouted-bed reactor, it does not undergo attrition. Regarding the thickness of the residue layer, it increases as the run time is increased. This implies that particles become large when continuous operation is conducted for a long time. Nevertheless, conical spouted beds can operate with particles as large as the inlet diameter, which is another advantage over the fluidized bed. Operation will have to be stopped to burn the residue, and we have shown that the residue can be burnt at 500 °C. Consequently, the best option for scaling up the plant and for energy integration is to burn this residue.

With regard to bed temperature, when operating at temperatures below 500 °C, fluidizing problems were unavoidable and

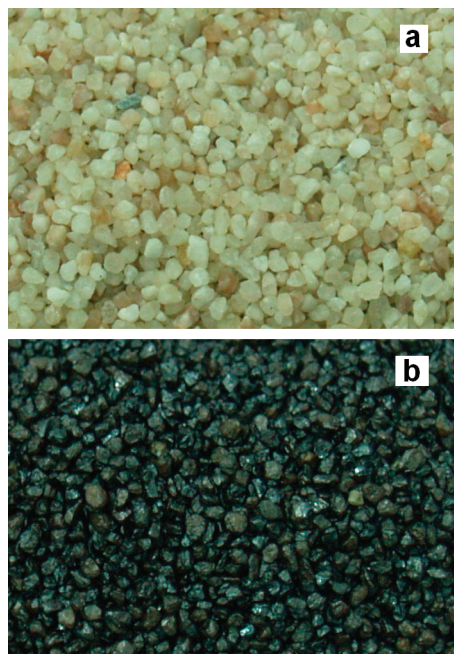


Figure 3. Photographs of the sand (a) before and (b) after the PET pyrolysis process, conducted at 500 °C.

defluidization occurred within a few minutes of operation. Nevertheless, at 500 °C, with coarse sand, a flow rate of nitrogen that is twice that corresponding to the minimum velocity, and PET flow rates of <1.5 g/min, a correct fluidization is ensured, but a significant amount of solid residue (7% PET fed) remains in the reactor that is coating the sand (Figure 3). A similar situation was observed by Arena and Mastellone in a fluidized bed when the temperature was increased to 650 °C.²⁰ Finally, when pyrolysis was conducted at 550 and 600 °C, the amount of this solid residue was dramatically reduced to 3% and 2%; in fact, the sand after the pyrolysis process does not have the same dark color obtained at 500 °C, which is due to the much-lower amount of solid residue deposited on its surface. This decrease in residue deposition is due to the increase in reaction rate when the temperature is increased. In fact, the pyrolysis reaction is much faster than the PET repolymerization that causes the formation of stable carbon material and covers the sand particles. Consequently, pyrolysis is more efficient at high temperatures and the result is the reduction of the solid residue.

3.2. Influence of Temperature on PET Pyrolysis Product Distribution. Continuous pyrolysis of PET has been performed for 1 h at three different temperatures and under suitable operating conditions to avoid defluidization. Thus, the bed was composed of 100 g of coarse sand (0.63–1.18 mm), the nitrogen gas flow rate was twice that corresponding to the minimum spouting velocity, and the PET flow rate was 1.5 g/min. Pyrolysis products have been divided into four different lumps: gas fraction, liquid fraction, solid fraction, and the solid residue remaining in the reactor. The main products obtained at the three temperatures are the gases (mainly carbon monoxide and carbon dioxide) and the solid fraction. The liquid yield is low and is embedded in the solid. The solid is collected mainly in the condenser and filter; however, because of its sticky nature, it is also retained in the pipes from the thermostatted chamber to the condenser. The appearance of the solid is that of a whitish powder, mainly composed of organic acids and other oxygenates.

The effect of temperature on the yield of the different lumps is shown in Figure 4.

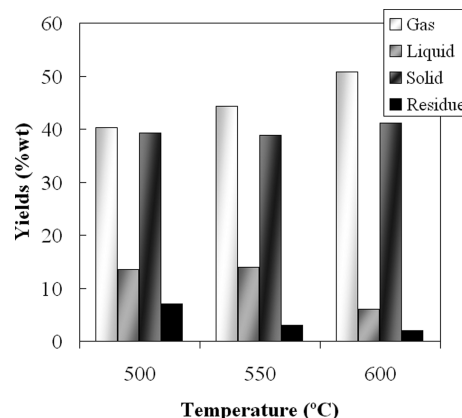


Figure 4. Influence of pyrolysis temperature on the yield of different fractions.

Table 1. Gas Fraction Yields at 500, 550, and 600 °C

compound	Yield (wt %)		
	500 °C	550 °C	600 °C
CO	9.88	17.90	14.21
CO ₂	29.28	23.89	31.08
ethylene	3.09	3.53	3.35
propene	0.37	0.06	0.22
cyclobutene	0.16	0.22	0.24
total	42.78	45.60	49.10

As expected, an increase in temperature leads to an increase in the gas fraction, which is due to the more severe thermal cracking. Moreover, a reduction in the solid residue remaining in the reactor is observed, from 7% at 500 °C to 2% at 600 °C. The yield of solid fraction is hardly affected by temperature, showing a slight increase when the temperature is increased to 600 °C. The amount of liquid in PET pyrolysis is low (13% at 500 °C) and decreases with temperature to 6% at 600 °C. Yoshioka et al.⁷ obtained a large amount of gases and solids by operating in a fluidized-bed reactor. In fact, they observed that the amount of the solid residue remaining in the reactor was higher (11% at 630 °C), probably because of poor fluidization. The yield of liquid fraction obtained by these authors is lower than in our reactor (4% at 630 °C).

The yields of the different components in the gas fraction obtained at the three temperatures studied are shown in Table 1.

The gas fraction is mainly composed of carbon monoxide and carbon dioxide, both formed by decarboxylation reactions in the thermal degradation of the polymer. The C₁–C₄ yield is very low for the three temperatures studied, and its nature is olefinic, with ethylene being the main component.

As observed in Table 2, the yield of liquid fraction remains essentially constant when the temperature is increased from 500 °C to 550 °C, but it is much lower when a temperature of 600 °C is reached. The main product in the liquid fraction is acetaldehyde, which is the most important product at the initial stage of PET pyrolysis, especially at the lower temperatures.⁵ The high amount of this compound at 500 and 550 °C is probably due to the short residence time of pyrolysis products in the conical spouted-bed reactor. At 600 °C, the yield of acetaldehyde undergoes a severe reduction, because of thermal cracking. Furthermore, although the main products are oxygenates, the amount of aromatic hydrocarbons is slightly increased when temperature is increased to 600 °C, because of decarboxylation and aromatization reactions.

Table 2. Liquid Fraction Yields at 500, 550, and 600 °C

compound	Yield (wt %)		
	500 °C	550 °C	600 °C
acetaldehyde	11.11	11.06	3.35
acetone	0.14	0.43	0.24
2-propenal	0.03	0.49	0.21
furane	0.06	0.05	0.11
benzene	1.04	0.81	0.87
toluene	0.10	0.11	0.24
2,3-dimethyl-2-pentene	0.04	0.05	0.10
4-hydroxy-4-methyl-2-pentanone	0.25	0.48	0.83
styrene	0.00	0.00	0.06
ethylbenzene	0.00	0.03	0.03
benzaldehyde	0.05	0.04	0.22
total	12.82	13.54	6.25

Table 3. Yields of the Solid Fraction Components at 500, 550, and 600 °C

compound	Yield (wt %)		
	500 °C	550 °C	600 °C
phenol	0.02	0.00	0.00
acetophenone	0.12	0.56	3.64
benzoic acid	26.98	21.91	15.12
naphthalene	0.00	0.13	0.14
3-phenyl-2-propenal	0.30	0.26	0.46
1-(3-methylphenyl)-ethanone	0.79	0.14	0.20
4-methylbenzoic acid	0.10	0.00	0.56
hydroxyethylbenzoate	0.21	0.00	0.00
4-phenyl-3-buten-2-one	0.00	0.00	0.64
1-(4-ethylphenyl)-ethanone	0.00	0.00	0.27
1-phenyl-1,2-propanodione	0.00	0.00	0.04
1-(2,5-dimethylphenyl)-ethanone	0.00	0.00	0.07
4-vinylbenzoic acid	0.00	0.00	0.98
benzoylformic acid	2.55	6.89	3.66
biphenyl	0.41	0.12	0.42
2,3-dihydro-3,3-dimethyl-1H-inden-1-one	0.00	0.00	0.14
1-[4-(1-methylethenyl)phenyl]-ethanone	0.00	0.00	0.21
1,1'-(1,3-phenylene)bis-ethanone	0.00	0.65	1.39
4-propylacetophenone	0.00	0.00	0.05
1,1'-(1,4-phenylene)bis-ethanone	0.00	0.00	0.08
<i>o</i> -diacetylbenzene	0.00	0.11	2.62
benzoacetic acid	0.00	0.04	0.29
<i>o</i> -acetylbenzoic acid	0.00	0.00	4.67
<i>p</i> -acetylbenzoic acid	0.00	0.00	1.02
vinyl-3-phenyl-2-propenoate	0.35	0.76	0.63
[1,1'-biphenyl]-4-carboxaldehyde	0.00	0.00	0.39
2-hydroxy-2-methoxy-1H-indene-1,3(2H)-dione	3.62	5.04	2.63
1-[1,1'-biphenyl]-3-yl-1-ethanone	0.00	0.00	0.03
1-[1,1'-biphenyl]-4-yl-1-ethanone	0.00	0.00	0.11
4-(hydroxyacetyl)-1,1'-biphenyl	0.00	0.00	0.03
4,5-dimethylphthalic acid	0.00	0.00	0.14
total	35.46	36.59	40.61
unidentified C₅+	1.93	1.24	2.03

Finally, Table 3 shows the evolution with temperature of the yields of the solid fraction components. As observed, almost all components are oxygenates.

The main product in the pyrolysis of PET, apart from carbon monoxide and carbon dioxide, is benzoic acid, whose yield is reduced to a large extent when temperature is increased to 600 °C. Yoshioka et al.⁷ observed a similar trend, but it is not as pronounced as that observed in our case. Thus, they observed a 25% reduction in the yield of benzoic acid from 510 °C to 630 °C. In our case, the reduction from 500 °C to 550 °C is 18% and from 500 °C to 600 °C is 44%. The other significant products in the solid fraction are benzoylformic acid and a substituted oxygenate indene (2-hydroxy-2-methoxy-1H-indene-1,3(2H)-dione), both reaching a maximum at 550 °C (6.89% and 5.04%, respectively). At 600 °C, the pyrolysis process leads to a wider product distribution in the solid fraction, which is composed of heavier products. This is due to the important effect

of temperature on the cracking and secondary reactions. The exception is acetophenone, whose yield considerably increases at 600 °C.

4. Conclusions

The conical spouted-bed reactor is a suitable technology for poly(ethylene terephthalate) (PET) pyrolysis, because of its excellent performance, with regard to heat-transfer rates and bed turbulence. Operating under adequate conditions, defluidization problems are totally avoided and the pyrolytic solid residue is deposited on the sand particle surface, instead of forming sand-pyrolyzed plastic aggregates. These conditions correspond to a value of bed mass to PET flow rate ratio ($W_{\text{bed}}/Q_{\text{PET}}$) higher than 4000 s, the use of coarse sand (above 0.63–1.18 mm in size), a high gas velocity (more than twice that corresponding to the minimum fluidization velocity), and temperatures above 500 °C.

The pyrolysis of PET leads to a high amount of gas and solid fractions. A solid residue remains in the reactor, coating the sand; however, its yield is dramatically reduced when the temperature is increased. The main pyrolysis products obtained are carbon monoxide, carbon dioxide, benzoic acid, acetaldehyde, and other oxygenate compounds. An increase in temperature to 600 °C results in the formation of heavier oxygenated compounds.

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