INTRODUCTION

The high demand for fuel and energy at the national and international levels, the scarcity of oil sources and the increase in the prices of fuels obtained from oil have begun to motivate various researchers to seek different alternative sources of energy in order to reduce the high commands the resources that are available. On the other hand, the scientists presents a serious problem in the disposal of solid waste, which is beginning to have a high environmental impact. Some studies show that the accumulation of plastics tends to be close to 25.8 million tons in Europe (Al-Salem et al., 2017). All this must be solved through practices which help to solve or, failing that, minimize all these problems in the best economic and environmental conditions. In the last two decades, various studies have focused and concentrated their efforts on developing technologies which allow the reuse or recycling of waste into energy sources, within the technologies is the thermochemical degradation better known as pyrolysis. This technique is a recycling alternative for materials or products that are not easily recycled through traditional methods. The process is responsible for degrading the components of larger molecular size into products of lower molecular weight such as liquids, gases and coal (Calderón Sáenz, 2016; Kalargaris et al., 2017a, 2017b, 2018; Mianadad et al., 2017; Miskolczi et al., 2009; Ratio & Engine, 2021).

Thermochemical degradation can be slow or fast considering the residence times of the process. Authors have investigated this process to different types of plastics such as: tire waste (Islam et al., 2004; Ucar et al., 2005), waste electronic equipment, and other waste from different products or devices (Dou et al., 2007; Elordi et al., 2009; Garforth et al., 1998; Islam et al., 2004; Kodera et al., 2006; Lin et al., 2010; Miskolczi et al., 2009; Murphy et al., 2012; Scott et al., 1990; Yoon et al., 1999). The plastics included are:
polystyrene (Lin et al., 2010; Scott et al., 1990; Yoon et al., 1999), poly(vinyl chloride) (Lin et al., 2010; Scott et al., 1990), polyethylene (PE) (Elordi et al., 2009; Garforth et al., 1998; Lin et al., 2010; Scott et al., 1990; Yoon et al., 1999) poly(vinyl chloride and polypropylene (Ali et al., 2011; Cardona & Corma, 2000; Kim & Kim, 2004; Miskolczi et al., 2009). The physical-chemical characteristics of the liquid product recovered from the pyrolysis process have characteristics similar to those of traditional fuels such as density, viscosity and calorific value. These recovered liquid hydrocarbons can be used as fuel for combustion engines or thermal machines without generating any problem in the devices (Kalargaris et al., 2017a, 2017b, 2018; Miskolczi et al., 2009; Ratio & Engine, 2021).

The products obtained depend mainly on the type of waste, according to its composition and its physical and chemical characteristics (Othman et al., 2008). Other applications that are given to the liquids obtained from the pyrolysis process are in the use of motor generators, diesel engines, heaters, turbines, ovens, among others (Bridgewater, 2012). On the other hand, it has been studied that most of the compounds obtained tend to be volatile, which can be recovered and processed into liquid products for later application in other processes. This work aims to collect and contrast different studies reported in the literature about the thermochemical degradation of polyethylene terephthalate (PET) as well as to exemplify a general overview of its degradation mechanism.

Table 1 shows the proximal analyzes of different plastic resins – it allows determining what number of volatile compounds can be recovered when degraded.

### Recycling methods

Most of the polymers are processed from oil, and it is for this reason that their recycling is of the utmost importance through thermochemical processes. They can be converted into petrochemical hydrocarbons again, although some compounds such as mixed plastics, hard plastics and elastomers cannot be pelletized and recycled using traditional methods, and can only be recycled through thermochemical degradation of macromolecules into lower weight molecules.

Recycling methods according to Al-Salem et al. (2017) are listed as follows:

- **Primary recycling**: where the plastic undergoes a grinding process and is reintroduced to heating to be reprocessed within the production line.
- **Secondary recycling**: it is similar to primary recycling, except that the plastic waste is poured into an extruder and mixed with virgin

### Table 1. Proximal and elemental analysis of plastics

<table>
<thead>
<tr>
<th>Type of plastics</th>
<th>Plastics type marks</th>
<th>Moisture (wt%)</th>
<th>Fixed carbon (wt%)</th>
<th>Volatile (wt%)</th>
<th>Ash (wt%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene terephthalate (PET)</td>
<td></td>
<td>0.46</td>
<td>7.77</td>
<td>91.75</td>
<td>0.02</td>
<td>Zannikos et al., 2013</td>
</tr>
<tr>
<td>High-density polyethylene (HDPE)</td>
<td></td>
<td>0.61</td>
<td>13.17</td>
<td>86.83</td>
<td>0.00</td>
<td>Heikkinen et al., 2004</td>
</tr>
<tr>
<td>Polyvinylchloride (PVC)</td>
<td></td>
<td>0.80</td>
<td>6.30</td>
<td>93.70</td>
<td>0.00</td>
<td>Heikkinen et al., 2004</td>
</tr>
<tr>
<td>Low-density polyethylene (LDPE)</td>
<td></td>
<td>0.74</td>
<td>5.19</td>
<td>94.82</td>
<td>0.00</td>
<td>Heikkinen et al., 2004</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td></td>
<td>0.30</td>
<td>0.00</td>
<td>99.70</td>
<td>0.00</td>
<td>Park et al., 2012</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td></td>
<td>0.18</td>
<td>0.16</td>
<td>97.85</td>
<td>1.99</td>
<td>Heikkinen et al., 2004</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td></td>
<td>0.25</td>
<td>0.12</td>
<td>99.63</td>
<td>0.00</td>
<td>Parthasarathy &amp; arayanan, 2014</td>
</tr>
<tr>
<td>Acrylonitrile butadiene styrene (ABS)</td>
<td></td>
<td>0.30</td>
<td>0.20</td>
<td>99.50</td>
<td>0.00</td>
<td>Park et al., 2012</td>
</tr>
<tr>
<td>Polyamide (PA) or Nylons</td>
<td></td>
<td>0.10</td>
<td>0.04</td>
<td>98.87</td>
<td>0.99</td>
<td>Jung et al., 2010</td>
</tr>
<tr>
<td>Polybutylene terephthalate (PBT)</td>
<td></td>
<td>0.16</td>
<td>2.88</td>
<td>97.12</td>
<td>0.00</td>
<td>Heikkinen et al., 2004</td>
</tr>
</tbody>
</table>
material, which significantly reduces production costs.

- Tertiary recycling: this method deals with the chemical alteration in the structure of the polymer and is reformed in a chemical or thermo-chemical way, the purpose of this method is to recover valuable compounds that can be reused to produce various products.
- Energy recovery: this method is about recovering steam, electrical energy or heat through the combustion of plastic waste (Fig. 1).

THERMOCHEMICAL DEGRADATION OF PET

Properties and global demand for polyethylene terephthalate

Polyethylene terephthalate (PET) has become one of the plastics with the highest demand for the food packaging and packaging area, being mostly carbonated beverages such as soft drinks, mineral water, juices, soft drinks, among other products. In another of its industrial and commercial uses are electrical insulators, labels, magnetic tapes and photographic films (Çepelioğullar and Pütün, 2013).

PET belongs to the group of thermoplastic polymers and is a polyester synthesized from terephthalate acid and a diol, commonly ethylene glycol. PET is a ubiquitous thermoplastic polymer used from everyday household objects to sophisticated engineering applications. Due to its great resistance to water and humidity, it is widely used in the manufacture of plastic bottles for soft drinks (Al-Salem et al., 2017).

The temperature that PET can tolerate without reaching deformation and without degrading is higher than that of other polymeric materials, its melting point is 260 °C. PET has significant mechanical strength, toughness and thermal resistance up to 150–175 °C. Crystallized PET has good resistance to temperatures up to 230 °C. Its chemical, hydrolytic and solvent resistance constitute some of the qualities due to the rigidity of the polymeric chains of PET. Due to its excellent wrinkle resistance and good abrasion resistance, this polymer can be treated with crosslinking resins to impart permanent wash and wear properties (Venkatachalam et al., 2012).

Polyethylene terephthalate (PET) consists of a pair of aromatic rings with a short aliphatic chain, a rigid molecule when compared to other aliphatic polymers such as polyolefin or polyamide. The crystalline structure that forms PET is unique and corresponds to a triclinic unit, its crystallization speed is slow due to the limited movement of its chains that prevent the growth of crystals at temperatures greater than 200 °C. This slow crystallization gives rise to amorphous zones with high clarity that are very common in the manufacture of bottles, thin films and packaging materials (Figure 2) (Venkatachalam et al., 2012).

According to the Plastics Europe (2019) approximately 359 million tons of plastics are generated in the world and 7.7% refers to PET, that is, 27,653 million annual tons of polyethylene terephthalate, its main sector being the area of

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Recycling of plastics based on the recovery of municipal solid waste.
containers and packaging. Due to its applications, PET tends to have a very short life and a very high disposal rate. On the other hand, on the subject of recycling, it is reported that only 32.5% is recovered and of this, 24.9% ends up in landfills due to the technical and economic difficulties that recycling plastics represents (Sharma et al., 2014).

**Thermal and catalytic degradation**

The thermal degradation mechanism is mainly to decompose and separate terephthalic acid and benzoic acid, then benzoic acid enters the decarboxylation stage forming acetophenone. Artetxe et al. (2010) identified benzoic acid and acetylbenzoic acid as the most abundant in the products of thermal degradation at 600 °C, they observed that higher temperatures increased the yields of acetophenone at high temperatures.

The addition of catalysts in the pyrolysis of synthetic polymers improve deoxygenation reactions, ZSM-5 has been used effectively for these purposes, reducing the amount of acids contained in the products, however, it increases the amount of polyaromatic hydrocarbons (PAHs) and carbon resulting in a low amount of liquid and high amounts of carbon and gases (Elordi et al., 2009). On the other hand, catalysts such as calcium oxide (CaO) have been studied to improve the quality of the pyrolytic liquid, as shown in Figure 3, degradation in the presence of CaO tends to degrade aromatic acids into aromatic hydrocarbons, since the selectivity tends to release OHs from polyaromatic compounds (Yoshioka et al., 2005).

The thermochemical degradation or pyrolysis of PET has been studied by various researchers analyzing the products obtained from its degradation. One of the existing problems in its decomposition by means of heat is the tendency to release compounds such as benzoic acid, which has corrosive and oxidative properties, which is why most of the reported studies have focused on studying pyrolysis using catalysts.
Vijayakumar and Fink (1982) assess the pyrolysis of polyethylene terephthalate and polybutylene terephthalate at a temperature of 400 °C in a vacuum at a pressure of 1 Pa. The products were identified by chromatography and mass spectrometry and were found to contain highly volatile compounds as shown in the Table 1 as they are; acetaldehyde, benzene, toluene, styrene, and ethylbenzene. On the other hand, the less volatile products contained benzoic acid, terephthalic acid, mono-vinyl esters and higher oligomers.

In another study conducted by Martin-Gullón et al. (Martín-Gullón et al., 2001) the thermal decomposition kinetics of polyethylene terephthalate residues was evaluated. This was carried out under strict conditions where different proportions of oxygen were evaluated by thermogravimetry between temperatures of 25 to 800 °C. The composition of the gas was analyzed and it was found to contain an appreciable amount of poly aromatic hydrocarbons (PAH). From the results obtained, it was observed that polyethylene terephthalate has a high thermo-stability, the first mixture of hydrocarbons was obtained at a temperature of approximately 250 °C and its decomposition did not begin until 400 °C. The solid decomposed rapidly in a range of 420 to 477 °C, around 90% decomposition, the process was finished.

Under pyrolytic conditions almost 70% of the material decomposed into light and semi-volatile compounds. At least more than 45 wt.% of the PET degraded to CO/CO₂, and about 4 wt.% of the yield in light hydrocarbons, where the 2.8 wt.% corresponds to methane. A high emission of benzene near 11 wt.% was noted, while the yield of toluene presented a moderate value of 2.5 wt.%.

Several of the compounds obtained are highly toxic, especially CO/CO₂, followed by benzene, toluene, and methane.

Yoshioka et al. (2004) carry out a thermo-chemical degradation in the presence of calcium hydroxide (CaOH)₂ as a catalyst, they used a quartz reactor at a temperature of 700 °C, different ratios of PET/catalyst 1:0, 1:1, 1: 3, 1:5 and 1:10. The highest liquid yield was obtained in the ratio of 1:10, approximately 45.51 wt.%, and the highest percentage of residues was at a ratio of 1:1 with approximately 36.10 wt.%. The highest gas yield was obtained at a ratio of 1:5 with an average of 37.02 wt.%. The products were quantitatively analyzed by GC-MS, FID, GC-TCD and a large proportion of benzene was found in the liquid product, close to 35.85 wt.% at a 1:10 ratio, and in the gaseous product, close to 37.02 wt.% at a 1:1 ratio. 5, found carbon monoxide, carbon dioxide, methane, ethylene, hydrogen, ethane.

Sarker et al. (2011) studied the catalytic pyrolysis of polyethylene terephthalate, using calcium hydroxide (CaOH)₂ as a catalyst. The tests were carried out in a round bottom boiling flask with 40 g of PET and 80 g CaOH, at a temperature of 405 °C. Different degradation products were obtained, 14.25 wt.% liquid yield, 12.5 wt.% gas, 51.6% residues (carbon, catalyst) and 21.75 wt.% water. The liquid product was analyzed by gas chromatography and compounds such as benzene (C₆H₆), heptacosane (C₃₇H₇₆) and benzene-ethamine-3 were detected.

In another study carried out by Kumagai et al. (2015), make a comparison between different catalysts (CaO, CaOH) in order to observe the yields of the different products. For this, 0.5 g of PET was used with a catalyst ratio of 1:1, in a vertical tube reactor at a temperature of 600 °C. From the experiment it was obtained that the highest gaseous yield was obtained with CaO, close to 25.2 wt.%, in terms of liquid yield an approximate of 37.7 wt.% was achieved and approximately 19.9 wt.% as residue. The chemical found in the highest proportion was benzene.

Dhahak et al. (2019) evaluates the thermal pyrolysis of PET, they used PET powder, the samples were 0.5 g and used different temperatures (410, 430, 450 and 480 °C), with residence time of 120, 90, 60, 60, respectively, the ramp heating rate was set at 5 °C/min. The gaseous products were analyzed and CO₂ and CO were found, mostly, and to a lesser extent ethylene and benzene. In the waxy products, the one with the greatest presence was benzoic acid.

Park et al. (2020) performs catalytic pyrolysis in the presence of carbon-based palladium, in a Pd/PET ratio of 0.01 to 0.05, a tubular furnace was used in a temperature range of 400–700 °C, the gaseous yields obtained at a concentration of catalyst of 0.01 were close to 43% and for 0.05 they increased to 49%, the liquid yield was 39% and had a decrease to 33%, and for the carbonaceous residue it was from 18% to 19%. Compounds such as: 2-naphthalencarboxylic acid, fluorenone, triphenylene, biphenyl-4-carboxylic acid, p-terphenyl and o-terphenyl were found in the liquid.

Another study carried out by Li et al. (2021), the catalytic pyrolysis of PET in the presence of zeolite type (A4) is studied, the tests were carried out in a fluidized bed semi-batch type reactor with
15 g of material at a temperature of 500 °C for 20 minutes. The products obtained from the degradation were gas, wax, tar and carbon. It was observed that the presence of this catalyst increased the gaseous yield from 35 to 43 wt.%, the tar improved the yield from 23 to 26.5 wt.%, on the other hand, the coal decreased from 20 to 18.5 wt.% and finally the waxes were reduced from 22 to 12 wt.% compared to thermal pyrolysis. The compounds found within the gaseous products were CO, H\textsubscript{2}, C\textsubscript{3}H\textsubscript{8}, C\textsubscript{2}H\textsubscript{6}, CH\textsubscript{4} and CO\textsubscript{2}, with methane being one of the largest with 35.61 wt.% and CO\textsubscript{2} with the lowest composition with 1.78 wt.%.

**Experimental schemes**

In this section, the different types of reactors used in the pyrolysis of polyethylene terephthalate are discussed, since it is one of the most important components, due to the fact that several studies show significant differences in the processes. Claudinho and Ariza (2017) around-bottomed flask placed on a heating mantle was used as a reactor. The flask was connected to a recirculating glass condenser and the liquid product was recovered in a two-necked flask (Figure 4).

Hang et al. (2020) carry out thermal and catalytic pyrolysis in a horizontal tubular quartz reactor in an inert atmosphere with nitrogen (N\textsubscript{2}). The reactor was loaded with polyethylene terephthalate (PET) and the catalyst was put on the walls of the reactor; the nitrogen flow was 200 ml/min for 10 minutes to eliminate the oxygen inside the tube. For the recovery of the condensable products, a condenser with ethanol recirculation at -5 °C was used. The products were recovered in a ball flask immersed in salted ice (Figure 5).

Kongsupapkul et al. (2017) study pyrolysis in a batch type reactor with a condenser of gaseous products and different sampling points (Figure 6). The reactor was heated in an electric furnace and the reaction temperature in the pyrolysis zone was measured. In another study carried out by Kumagai et al. (2015) an electrically heated vertical tube reactor equipped with a steam generator was used, the liquid products were collected in two condensers cooled by water and liquid nitrogen. The gaseous products were collected in a gas bag. Helium was used as inert gas with a flow rate of 50 ml/min (Figure 7).

**Table 2.** Concentrated information on the pyrolysis of polyethylene terephthalate (PET)

<table>
<thead>
<tr>
<th>References</th>
<th>Plastic / catalyst type</th>
<th>Reactor</th>
<th>Process parameters</th>
<th>Liquid wt.%</th>
<th>Products</th>
<th>Solid wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vijayakumar &amp; Fink, 1982</td>
<td>PET</td>
<td>-</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Martín-Gullón et al., 2001</td>
<td>PET</td>
<td>-</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Yoshioka, Grause et al., 2004</td>
<td>PET/CaOH\textsubscript{2}</td>
<td>quartz reactor</td>
<td>700</td>
<td>34-45</td>
<td>23-37</td>
<td>21-36</td>
</tr>
<tr>
<td>Yoshioka et al., 2005</td>
<td>PET/CaOH\textsubscript{2}</td>
<td>quartz reactor</td>
<td>700, 30</td>
<td>9.7-36</td>
<td>34-38</td>
<td>6.6-26</td>
</tr>
<tr>
<td>Sarker et al., 2011</td>
<td>PET/ CaOH\textsubscript{2}</td>
<td>ball flask</td>
<td>405</td>
<td>14.25</td>
<td>12.5</td>
<td>51.6</td>
</tr>
<tr>
<td>Kumagai et al., 2015</td>
<td>PET/ CaO, CaOH\textsubscript{2}</td>
<td>vertical tube reactor</td>
<td>600</td>
<td>37.7</td>
<td>25.2</td>
<td>19.9</td>
</tr>
<tr>
<td>Kongsupapkul et al., 2017</td>
<td>PET/MgO-ZSM-23-Zeolite</td>
<td>batch reactor</td>
<td>440, 60</td>
<td>20</td>
<td>76</td>
<td>4</td>
</tr>
<tr>
<td>Dhahak et al., 2019</td>
<td>PET</td>
<td>-</td>
<td>410, 430, 120, 90, 450, 480</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Park et al., 2020</td>
<td>PET/Pd</td>
<td>tube furnace</td>
<td>400-700</td>
<td>39-33</td>
<td>43-49</td>
<td>18-19</td>
</tr>
<tr>
<td>Pet &amp; Chloride, 2020</td>
<td>PET/NaCl</td>
<td>tube reactor</td>
<td>450-600</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Li et al., 2021</td>
<td>PET/ Zeolite (A4)</td>
<td>fluidized bed semibatch</td>
<td>500</td>
<td>22-12</td>
<td>35-43</td>
<td>coal (20-18.5), tar (23-26.5)</td>
</tr>
</tbody>
</table>
Yoshioka et al. (2005) used a quartz reactor with a diameter of 16 mm, helium was used as an inert gas with a flow of 50 ml/min. For the recovery of the products, traps cooled by water and liquid nitrogen were used. The gaseous products were recovered in a bag (Figure 8).

Yoshioka et al. (2004) used an experimental setup based on a quartz and wool reactor, the sample was placed inside the reactor and the reactor was filled with helium as inert gas at a flow rate of 50 ml/min, the liquid products were recovered through two traps, one trap cooled with ethanol and the other with liquid nitrogen, as for the non-condensable gases, they were recovered in a bag for gases (Figure 9).

According to the studies reported by various authors, there are different experimental schemes, among the simplest such as the implementations made with a ball flask and a heating mantle. The simplicity of this process allows easy experimentation at the laboratory level, the scaling of this scheme would be almost impossible or very complex due to the container used as a reactor. On a medium scale, batch or batch type reactors are usually...
interesting, this due to the ease in their operation and in their assembly. The disadvantage of this scheme is the scalability which becomes more complex and the energy cost is usually very high due to the heating to be done for each batch. At an industrial level, fluidized bed reactors are usually the most interesting.

**PRODUCTS OBTAINED**

The products generally obtained from the thermochemical degradation of PET tend to vary according to the type of catalyst used. Table 3 lists the compounds according to what has been reported in some studies and the catalysts used.
of the areas of opportunity is the improvement in the separation of the various products in order to use them separately.

**CONCLUSIONS**

Polyethylene terephthalate is a thermoplastic that, unlike polyethylene, maintains a cyclic group within its chains, offering an improvement in the rigidity and mechanical resistance of the material. Due to the cyclic group, Benzene, which is one of the most reported products, is used industrially as a solvent, and as an intermediate starting material in the synthesis of various chemicals. Another of its potential uses is as a gasoline additive, since products are made with it, such as ethylbenzene, cumene and cyclohexane. Other products in gaseous form such as hydrogen, methane, ethane and ethene, are used in the industrial branch in different processes, for example in the area of refrigeration.

The thermal degradation of PET offers a wide range of compounds with high added value. One of the areas of opportunity is the improvement in the separation of the various products in order to use them separately.
the thermochemical degradation of this plastic turns out to be more complex, unlike polypropylene or polyethylene, either high or low, to be degraded requires high amounts of energy or the use of catalysts which help improve reactions of decomposition, and thereby avoid the formation of benzoic and terephthalic crystals. Based on this, several authors have chosen to study the catalytic pyrolysis of this material and have reported various compounds obtained from its degradation.

The products obtained show the potential to be used in various industrial sectors, one of the compounds with the highest value is benzene, which is used for the synthesis of other molecules with high added value. Studies also report aromatic compounds such as styrene and toluene. used in the production of octane improvers, cumenes, cyclohexenes, among others.

The recycling of PET through its thermochemical degradation has the potential to be used as an alternative for those wastes that have been contaminated, or that have not been recycled mechanically or traditionally. This allows compounds to be recovered and re-entered into the commercial chain, reducing its final disposal in landfills or the environment.

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REFERENCES


