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# Recycling of plastic waste using flash pyrolysis – Effect of mixture composition

S. KLAIMY<sup>1, 2</sup>, J.-F. LAMONIER<sup>2</sup>, M. CASSETTA<sup>1</sup>, S. HEYMANS<sup>3</sup>, S. DUQUESNE<sup>1\*</sup>

- ◆ <sup>1</sup> Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France
- ◆ <sup>2</sup> Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
- ◆ <sup>3</sup>NeoEco, Zone commerciale, 1 Rue de la Source, 59320 Hallennes-lez-Haubourdin, France

\* [sophie.duquesne@ensc-lille.fr](mailto:sophie.duquesne@ensc-lille.fr)

## **Abstract**

Recovery of plastic waste is becoming crucial since the amount of such waste increases continuously. The objective of this study is to investigate the potential of the pyrolysis technique for the recovery of plastic waste. In that frame, the influence of temperature (550°C or 600°C) on the pyrolysis of pure polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyethylene terephthalate (PET) was first studied. It is shown that whatever the type of polymer, aromatic compounds are mainly formed and could reach 55wt.-% of the oil fraction for PP and 31wt.-% for PE at 550°C. In a second step, a PP/PE mixture and a model mixture representative of the packaging plastic waste stream were pyrolyzed to investigate the influence of a combination of polymers on the proportions and composition of the different fractions. The pyrolysis of the polymer mixtures shows that, even if the aromatic compounds formed are similar to those obtained for the virgin polymers, the proportion of aromatic compounds is much more important than when the polymers are pyrolyzed alone. Indeed, mixing PE with PP at a 50/50 ratio does not affect the amount of liquid, gas and solid fractions but leads to the formation of a higher quantity of xylene (39 wt.-%) at 550°C. The combination of the plastics in the model mixture has also led to a decrease of the amount of waxy compounds. Furthermore, it was shown that a higher amount of aromatics than expected was formed. As a conclusion, this study demonstrates that pyrolysis is an effective technique to recover plastic waste as aromatic compounds for the petroleum industry. In the specific conditions used in this study (proposed model mixture and pyrolysis conditions), it will favor the idea that sorting is not needed to recover plastic waste through pyrolysis since aromatics formation is favored when the stream is composed of a mixture of polymers.

**Keywords:** Flash Pyrolysis, Plastic Waste, Model Mixture.

## 1. Introduction

Europe is a major plastic consumer and produces around 20% of the plastic in the world [1]. Such materials provide a fundamental contribution to our society due to their wide range of applications [2] in various sectors such as food packaging, textile, automotive, electrical and electronic equipment... Packaging represents around 40% of the plastic consumption including mainly polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyethylene terephthalate (PET). The increasing use of plastics has led to an increase of plastic waste for which different end of life scenarios can be considered. Among them, landfill consumes a lot of space and can cause serious environmental problems. On the other hand, plastic waste incineration does not constitute a long-term solution because of greenhouse gases emission. Moreover, it has a very bad image due to potential risk of toxic gases release such as dioxins, even if those aspects are under control nowadays. Finally, mechanical recycling represents an interesting way to recover plastic waste even if the need for sorting leads to an increased cost of recovered materials [3][4][5]. Moreover, many multi-materials are used in the packaging industry that cannot be separated and thus valorized. Finally, in France, selective collection of plastics actually concerns bottles (PET) and other plastic containers (PE and PP). The gradual extension of sorting instructions to all plastic types (packaging films, bags, polyester trays, etc.) [6] should lead to new mixtures of plastic waste that will need valorization. In this context, alternative ways to recover plastic waste as mixture have to be developed and chemical recycling through the pyrolysis technique appears as an attractive solution [7].

Pyrolysis appears to be a promising way to recover plastics since it could transform polymers into liquid fuel or valuable products [8-11]. The pyrolysis of polyolefins leads to the formation of a complex mixture composed of alkanes, alkenes and aromatics. Pyrolysis consists in cracking molecules in absence of oxygen at a temperature between 300 and 900°C in order to obtain liquid, gas and solid fractions. Many parameters affect the pyrolysis and among them, the temperature can be considered as the most important variable in the process. It is generally accepted that low temperatures of pyrolysis favor liquid phase formation and the production of long hydrocarbon chains. By increasing the temperature, the amount of liquid fraction decreases while that of gas increases. Small chains are formed due to breaking of C-C bonds [12]. Flash pyrolysis is distinguished from the other pyrolysis technics by its relatively higher heating rate and lower retention time [13]. It favors the formation of low molecular weight products whereas low heating rate pyrolysis will be used when a higher solid fraction is wanted.

A number of studies have been carried out to investigate the pyrolysis products of PE. As an example, Uddin [14] studied the decomposition of different types of polyethylene and showed that the pyrolysis of HDPE at 430°C produces 58.4 wt.-% of liquid, 26.3 wt.-% of waxy compounds, 6.3wt.-% of gas and 9 wt.-% of residue whereas that of LDPE produces 75.6wt.-% of liquid, 8.7wt.-% of waxy compounds, 8.7 wt.-% of gas and 7.5wt.-% of residue also at the same temperature. . The thermal pyrolysis of PE leads to the formation of wax instead of oil. Wax consists of long linear hydrocarbons chains (> C20) which solidify at room temperature [15]. As the yield of liquid and gas fractions is more important for LDPE, the study of Uddin [14] shows that thermal pyrolysis is easier for LDPE than for HDPE. In another study [16], the pyrolysis of low density polyethylene (LDPE) in a pilot-plant scale internally circulating fluidized bed was carried out and it was shown that more than 90wt.-% of the gas fraction mainly composed of polyolefins can be obtained. At the opposite, Scott et al. [17] demonstrate that considering fast pyrolysis of linear low density polyethylene (LLDPE), the condensate (liquid and wax) can reach more than 30wt.-% depending on the experimental conditions. Those results thus demonstrate the importance of the experimental conditions considering recovery of plastic waste through pyrolysis. As far as polypropylene is concerned, Jin et al. investigates the pyrolysis of polypropylene (PP) in a vertical falling film reactor [18]. They show that, depending on the temperature the recovered oil fraction can varied from 74.4 wt% to 53.5 wt% and is mainly composed of alkenes and naphtenes, aromatics and alkanes are also evolved but in a lower amount. On the other hand, according to R. Miandad et *al.*, the pyrolysis of PP produces 42wt.-% of oil, 54.6wt.-% of gas and 3.5wt.-% of solid residue at 450°C [19]. In this study, a batch reactor using 10°C/min heating ramp was used. The difference in fraction yields can thus be attributed to the type of reactor used and this parameter is crucial considering the fraction yield of pyrolysis products as well as their composition. PS, being composed of an aromatic side chain, decomposes at low temperature following a depolymerisation process presenting a low activation energy [20]. Therefore, considering PP, PE and PS, the degradation of PS is the fastest followed by that of PP and finally that of PE [21] and the pyrolysis of PS can be performed at a lower temperature than that of PE. The pyrolysis of PET was only studied by very few authors [22-24]. Cepeliogullar and Putun [25] observed that the liquid oil yield (23.1wt%) was less important than that of the gaseous products (76.9wt%) when pyrolysis is carried out at 500°C with a 10°C/min heating rate while no solid residue is remaining. The main component was benzoic acid which accounts for around 50wt.-%. Fakhrohoseini and Dastanian [24] also studied the pyrolysis of PET in the same conditions (temperature and heating rate). The liquid yield was 39.9wt%, 52.1wt% for the gas fraction and a 9.0wt% solid residue was obtained.

Even if the pyrolysis of pure polymers has been widely investigated, that of plastic mixtures is less reported. Kaminsky *et al.* studied the pyrolysis of a plastic mixture composed of 75wt.-% of PP and PE and 25wt.-% of PS at 730°C. The amount of liquid oil was 48.4wt.-% [26]. The mixture of PP, PE, PS and PET (40/20/20/20) coming from disposable plates, grocery bags and cups leads after pyrolysis to 40wt.-% of liquid oil, while gases and char yields represent respectively 42 and 18wt.-% [19]. In those studies, the objective of the recovered oil was to obtain fuel and low attention was paid to clearly establish and study the interaction between the polymers considering the composition of the oil phase.

In this context, the aim of this study is to investigate the flash pyrolysis of packaging plastic waste. In a first step, the composition of a model mixture representative of the packaging plastic waste stream collected in French municipal solid waste (MSW) was established, taking into account literature data and through the analysis of the composition of post-consumer plastic waste. In a second step, flash pyrolysis is carried out on pure PP, PE, PS and PET in order to quantify the different pyrolysis fractions. Then, the composition of liquid oil, which is the main fraction of interest, is determined by GC-MS. Finally, the pyrolysis of a PP/PE mixture and of the model mixture is performed to study the influence of combinations of different polymers on the pyrolysis products formed.

## **2. Experimental**

### **2.1. Materials**

Polypropylene pellets with a density of 0.906g/cm<sup>3</sup> were obtained from Nutripack (Flines les Râches, France). A linear low density polyethylene (Eltex® PF6220AE) used in food packaging with a density of 0.919 g/cm<sup>3</sup> was obtained from Wipak (Bousbecque, France). Polystyrene pellets were obtained from Sigma Aldrich. Polyethylene terephthalate pellets (SABIC POLYESTER TC 196) were obtained from SABIC. PP, PE, PS and PET were used for pyrolysis experiments. A solid recovery fuel sample (SRF) shredded into small pieces was obtained from Baudelet (Blaringhem, France) to determine the composition of the model mixture.

### **2.2. Determination of the model mixture**

The determination of the composition of a model mixture (called “model mixture” (MM)) representative of the plastic composition of municipal solid waste (MSW) in France that is poorly valorized, including the evolution of the selective collection policy is crucial to carry out such a study. Two studies coming from the literature as well as an experimental determination of the composition of a solid recovery fuel sample collected in North of France were used to determine this model mixture.

The first study concerns plastic waste coming from the sorting centers and was carried out by Valorplast. Based on those data, assumptions were made to evaluate the percentage of each polymer in the model mixture (Table 2). PET was not taken into account in the calculation since PET bottles are usually well sorted and valorized in France. Then, only PP, PE, PS and PET (not coming from the bottles) were considered in the calculation (PVC and multi-materials were not included). Finally, the percentage of PE/PP in the bottles and flasks corresponds to the selective collection of plastics from MSW in France with 75% of PE and 25% of PP in the PP/PE mixture since PE is largely more used than PP.

This study leads to a first model mixture composed of 27wt.-% PP, 47wt.-% PE (including HDPE, LDPE and LLDPE), 14wt.-% PS and 12wt.-% PET.

Table 2 : Quantity of plastics (in tonnes) used according to the study of ValorPlast

	PP	PE	PS	PET	Total amount of polymer
bottles	33712	101137	0	0	134849
trays	100800	21600	75600	61200	259200
films	8400	120400	0	0	128800
Total weight	142912	243137	75600	61200	522849
Composition from Valorplast data (wt.-% )	<b>27</b>	<b>47</b>	<b>14</b>	<b>12</b>	

The second study was carried out by ADEME [28]. In 2015, ADEME studied the quantity of waste produced in France and its composition. In the report [29], only the uncollected plastic waste was considered (Table 3) as they represent the type of plastic waste directly concerned by the extension of sorting instructions. From the analysis of ADEME data, the composition of the mixture is: 32wt.-% of PP, 42wt.-% of PE, 11 wt.-% of PS and 15wt.-% of PET.

Table 3 : Quantity of plastics (in kTonnes) used according to the study of ADEME [25]

	PP	PE (HDPE and LDPE)	PS	PET	Total
Total solid waste	650	1 150	200	420	2420
Collected amount to be recycled	160	500	30	180	870
Potential amount of plastic to be recovered	490	650	170	240	1550
Composition from ADEME data (wt.-%)	<b>32</b>	<b>42</b>	<b>11</b>	<b>15</b>	<b>100</b>

The third study was based on experimental considerations. The composition of a solid recovery fuel (SRF) obtained from Baudalet environment (North of France) was determined. To determine the plastic composition, paper, cardboard and wood were first removed manually. Then, the flotation method was used to separate the different polymers according to their density. The SRF sample (about 20g) containing different types of plastics is placed in a beaker containing water (3L). According to the densities of these plastics (Figure 1), PE and PP will float on the surface whereas the other plastics will sink downward. Polyolefins are further separated using a solution containing 57.9% of ethanol. PS and PET, remaining at the bottom of the water solution, are separated using a solution containing 12 wt-% of NaCl. The samples are then dried, weighted and analyzed by FTIR in order to verify the nature of the plastic material.

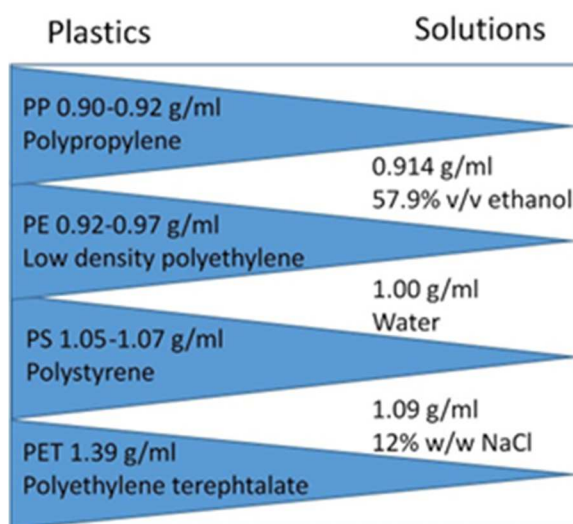


Figure 1 : Densities of plastic materials

To ensure the homogeneity of the results, each analysis was repeated three times. Results are summarized in Table 4. From those data, it was thus possible to determine the SRF sample plastic composition: 32% of PP, 24% of PE, 17% of PS and 27% of PET.

Table 4: Determination of the SFR sample composition (in %)

Analysis	PP	PE	PS	PET
1	33	19	16	32
2	30	29	18	23
3	34	23	18	25

<b>Average wt-%</b>	<b>32</b>	<b>24</b>	<b>17</b>	<b>27</b>
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Table 5 gathers the different data obtained from the three studies. First, it can be seen that the amount of PP and PS are comparable for the three studies. On the contrary, the amount of PET determined in the SFR sample is much more important (around twice as much important) than those obtained from Valorplast and ADEME studies. This discrepancy can be explained by the heterogeneity of the SFR composition. Moreover, in the first two studies, recycled PET was not taken into account in the calculations. So, the amount of PET calculated from literature data is more representative of the real percentage found in the French MSW stream and is thus taken into account to determine the composition of the model mixture (MM). Consequently, the amount of PE in the MM will also be determined from the first two studies.

Finally, from these different studies (Table 5), the composition of the model mixture is defined as, 30wt.-% of PP, 45wt.-% of PE, 10wt.-% of PS and 15wt.-% of PET.

*Table 5: Comparison of the polymeric compositions determined from the 3 previous studies (Tables 2 to 4)*

Study	PP (wt.-%)	PE (wt.-%)	PS (wt.-%)	PET(wt.-%)
Composition from Valorplast data	27	47	14	12
Composition from ADEME data	32	42	11	15
Composition from SFR sample	32	24	17	27
<b>Model mixture composition</b>	<b>30</b>	<b>45</b>	<b>10</b>	<b>15</b>

### 2.3. Thermogravimetric analyses

Thermogravimetric analyses (TGA) were carried out to study the thermal decomposition of single and mixed polymers. The analyses were carried out by heating 8 to 10 mg of polymer samples from 25 to 800°C at a 100°C/min heating rate under nitrogen flow (40 ml/min) using a TG 209 F1 LIBRA apparatus. In order to compare the experimental curves to the expected ones, calculated curves were obtained in the case of mixture of polymers by a linear combination of the TGA curves of the virgin polymers weighted by their amount in the mixture. As a consequence, for PP/PE and for the model mixture (MM) that will be detailed in part 3, those curves were determined as follows:  
 $TGA_{\text{calculated PP/PE wt\% (PP/PE)}} = 0.5 \times TGA_{\text{experimental PP wt\% (50\% PP)}} + 0.5 \times TGA_{\text{experimental PE wt\% (50\% PE)}}$ ,  
 $TGA_{\text{calculated MM wt\% (MM)}} = 0.3 \times TGA_{\text{experimental PP wt\% (30\%PP)}} + 0.45 \times TGA_{\text{experimental PE wt\% (45\%PE)}} + 0.1 \times TGA_{\text{experimental PS wt\% (10\%PS)}} + 0.15 \times TGA_{\text{experimental PET wt\% (15\%PET)}}$ .

### 2.4. Pyrolysis equipment and experimental conditions



The laboratory set-up for pyrolysis process investigation is mainly composed of a pyrolysis furnace containing the reactor and a liquid condensation system. The pyrolysis furnace is a CARBOLITE CERGO 30-3000°C and the condensation system is composed of two condensation baths soaked in liquid nitrogen. A schematic representation of the pyrolysis reactor is given in Figure 2. The reactor is made of stainless steel with a length of 700 mm and a diameter of 60.3 mm. As flash pyrolysis is considered in this study. Prior to the start of the experiment, the sample carrier is placed in the cooling coil possessing a 152 mm length and a 25 mm diameter and which is coupled to a water shiller ( LAUDA ECO SILVER) to maintain a constant temperature of 20°C. When the equilibrium temperature is reached in the reactor, the sample carrier allows introducing directly the sample into the center of the furnace at the pyrolysis temperature. It permits a rapid increase of the temperature of the sample and a flash pyrolysis can thus be considered.

The experimental protocol is defined as follows: 1g of polymer is placed in the sample carrier located in the cooling coil. The reactor is then purged with a nitrogen flow at 5L/min for 5 minutes and an oxygen analyzer controls the absence of oxygen in the furnace. The nitrogen flow is then fixed at 200ml/min for the whole experiment. Once the furnace is purged and the desired temperature equilibrated, the sample is rapidly introduced into the reactor thanks to the sample carrier. The reaction time is fixed at 40 minutes. This time corresponds to the time required for the complete pyrolysis of the polymers (considering modification of temperatures and polymer types). At the end of the experiment, the liquid phase, corresponding to the vapors trapped thanks to two condensation baths, and the solid residue are weighed; the waxy compounds located at the end of the reactor (prior to the condensation bath) are also collected and weighed. The gas yield is calculated by subtracting the liquid, the wax and the residue content from the initial polymer weight. The liquid fraction contains molecules containing from 6 to 25C. Each experiment is repeated at least twice to ensure the repeatability of the pyrolysis pilot experiments. The results presented in this paper correspond to the average data. It was determined data are obtained with an experimental error of 3wt.-%.

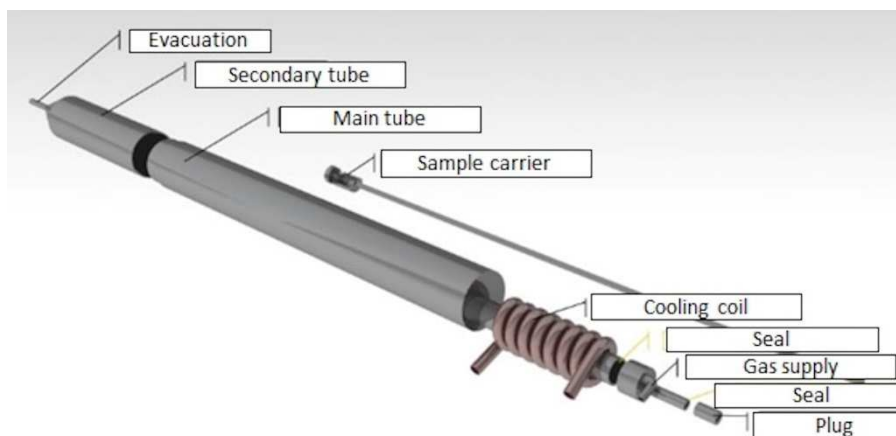


Figure 2: Home-made reactor used for the flash pyrolysis

## 2.5. Liquid phase analysis

The chemical composition of pyrolysis liquid oils i.e. the liquid phase was determined by GC-MS. The GC-MS equipment used was a Thermo Scientific focus GC equipped with a TG-5MS capillary column (15 m long, 0.25 mm diameter and 0.25  $\mu\text{m}$  film thickness) and a DSQII MS. The program used is described in Table 1. Chromatographic peaks were recognized by Replib and Mainlib library based on their retention times using standard compounds. The percentages of the peaks were calculated from total ion chromatogram (TIC) peak area. The composition of the liquid phase reported in this paper is as a consequence semi-quantitative. Such an approach allow a comparison of the data obtained between each other. Since the objective of the paper is to establish the influence of the composition of the stream on the pyrolysis products, such an approach is well adapted.

Table 1 : GC-MS protocol

Column	TG5-MS
Carrier gas	He
Carrier gas flow	1ml/min
Initial temperature/ initial time	40°C/15min
Heating rate	0.5°C/min
Final temperature/ final time	160°C/ 15min
Injection temperature	300°C
Injection volume	split (10:1)
split flow	10ml/min
Transfer line	300°C

### 3. Results and discussions

#### 3.1. Determination of the Model mixture composition

#### 3.2. Thermal pyrolysis of virgin polymers

##### 1.2.1 Thermogravimetric analyses

Figure 3 shows the thermal decomposition of the single polymer (PP, PE, PS and PET) obtained by TGA in the conditions of the flash pyrolysis ( $N_2$ ,  $100\text{ K}\cdot\text{min}^{-1}$ ). Considering a 50% weight loss for all polymers, the ranking according to the decomposition temperature is as follows: PS ( $457^\circ\text{C}$ ) < PET ( $470^\circ\text{C}$ ) < PP ( $487^\circ\text{C}$ ) < PE ( $505^\circ\text{C}$ ). Other authors observed this behavior. Demirbas showed that the decomposition of PS is faster than PP and PE and attributes that to the macromolecular structure of polymers and pyrolysis mechanism[30]. According to S.M. Al-Salem, the ranking of the decomposition of these polymers is the same as for our study [31]. A Lopez et al who studied the influence of time and temperature on pyrolysis of plastic wastes showed that the temperature at which decomposition is maximum of PE is the highest ( $500^\circ\text{C}$ ) followed by PP ( $475^\circ\text{C}$ ), PET ( $460^\circ\text{C}$ ) and PS ( $425^\circ\text{C}$ )[32]. Fanfan Xu et al studied also the degradation of PP and LDPE at  $100\text{K}/\text{min}$  and showed that the maximum weight loss was observed at  $491^\circ\text{C}$  and at  $508^\circ\text{C}$  for LDPE\_[33]. It must be emphasized that PET is not completely degraded in our experimental conditions since 7.2 wt% of residue remains. Several authors have already observed this phenomenon [22][34]. They consider that an interlinking reaction between the decomposed products can form stabilized products that can increase the amount of residue [35].

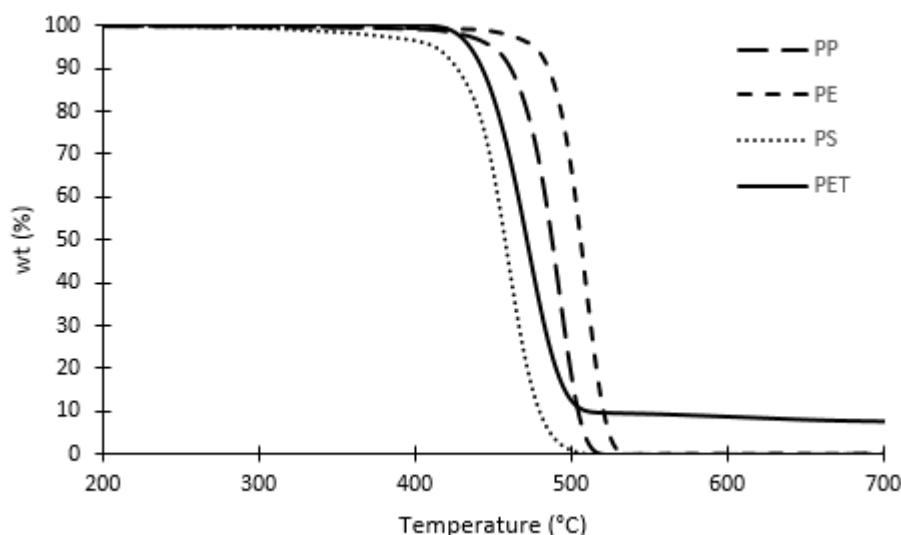


Figure 3 : TGA of the pure plastic materials

##### 1.2.2 Influence of the pyrolysis temperature

Thermal pyrolysis of the same virgin polymers (PP, PE, PS and PET) was investigated at 550 and 600°C. The yield of liquid, wax, gas and residue for both temperatures and for the different polymers are presented in Figure 4.

The amount of each fraction (liquid, wax/viscous liquid, gas and residue), formed during the pyrolysis, changes according to the nature of the polymer and to the pyrolysis temperature. As previously observed in TGA experiments, no residue remains at the end of the experiment except for PET with around 12 wt.-% of residue for both pyrolysis temperatures (Figure 4).

In the case of PP, when the pyrolysis temperature increases from 550°C to 600°C, the amount of liquid increases from 31 to 37wt.-%. This can be related to the decrease of the amount of waxy compounds from 8 to 2wt.-% since the yield of gas is similar for both temperatures. This result is in good agreement with literature studies that generally demonstrate that a temperature increase promotes the cracking of C-C bonds and thus leads to hydrocarbons with shorter carbon chains [36,37].

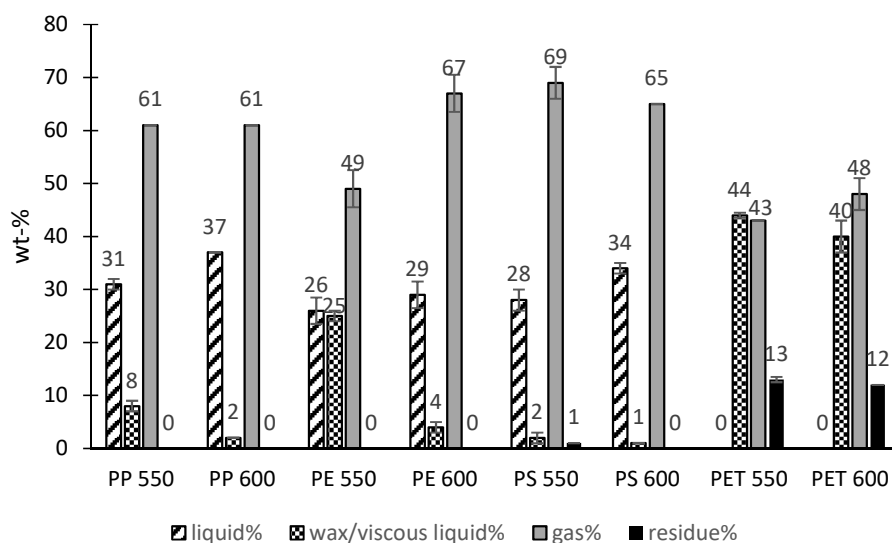


Figure 4: Effect of the temperature on the pyrolysis fractions yield (liquid, wax, gas and residue) of PP, PE, PS and PET carried out at 550°C and 600°C

For PE, increasing the pyrolysis temperature decreases notably the yield of wax from 25wt.-% at 550°C to 4wt.-% at 600°C. Wax is formed due to random chain scission of straight long carbon chains of PE. As for PP, the temperature increase affects the degradation of PE and lighter molecular weight compounds are formed [15]. It can however be observed that in the case of PP, the cracking of waxy compounds leads to the formation of liquid whereas in the case of PE, it contributes to increase the



Figure 5 : The degradation mechanism for thermal pyrolysis of PE [13]

The literature demonstrates that for a given pyrolysis temperature, the gas yield should be superior for PP than for PE. However, in our study, the pyrolysis at 600°C leads to 61wt.-% and 66wt.-% of gas respectively for PP and PE. In the case of PP, it can be supposed that the formation of smaller chains that can interact together to form longer chain of hydrocarbons is favored, leading to an increase in the amount of condensable gases when the conversion is complete and when the residence time is relatively high. Thus, the amount of gases is similar for both temperatures (550°C and 600°C) for PP whereas this amount increases largely for PE.

In the case of PS, the amount of liquid increases slightly from 28 to 34wt.-% when the temperature increases and the yield of gas decreases from 70 to 65wt.-%. These results are surprising and opposite to those of Karaduman *et al.* who showed that the flash pyrolysis of polystyrene leads to a decrease of the liquid phase from 25 to 21wt.-% and of the solid phase from 40 to 34wt.-% whereas an increase of the gas phase from 35 to 45wt.-% is observed at 825 and 875°C respectively [13]. Among all the studied polymers, PS pyrolysis should lead to the maximum conversion into liquid oil due to its simple decomposition process [19]: thermal degradation of PS is mainly a depolymerisation process and a high fraction of styrene is produced. However, the amount of liquid is smaller than expected because of the relatively significant losses during pyrolysis due to the reactor shape and the presence of cold spots where the gases can condense before reaching the condensation system. This phenomenon was not observed during the pyrolysis of the other polymers because the degradation of PS takes place much faster and thus the nitrogen flow inside the reactor is not high enough to allow the evacuation of the degradation gases as they are formed. Thus, the residence time of the degradation products is too high, leading to the condensation of some gases in the cold spots.

Finally, PET pyrolysis was carried out using 0.3 g of polymer instead of 1 g due to the high production of residue that can overflow the spoon of the reactor and can stick to the walls. From the pyrolysis at 550°C, 44% of pale yellow particles were collected in the condensation baths and were thus considered as viscous liquid and this fraction will be further analyzed by GC-MS. Increasing the temperature do not affect the yield of viscous liquid and gas taking into consideration the standard deviation. Whatever the temperature (550 or 600°C), around 12wt.-% of residue remain at the end of the pyrolysis process, far more than for PP, PE and PS. These results are similar to those of Fakhroseini *et al.* who studied the pyrolysis of PET at 500°C. They obtained approximately 40 wt% of liquid oil, 52 wt% of gas and 9 wt.% of solid residue [24]. As mentioned at the end of the introduction, the fraction of interest is the liquid phase. Thus the next step concerns the determination of the composition of the liquid phase.

### 1.2.3 Composition of liquid phase obtained from thermal pyrolysis of virgin polymers

Figure 6 shows the composition of the liquid fraction according to the carbon number distribution for the two considered pyrolysis temperatures of the different polymers.

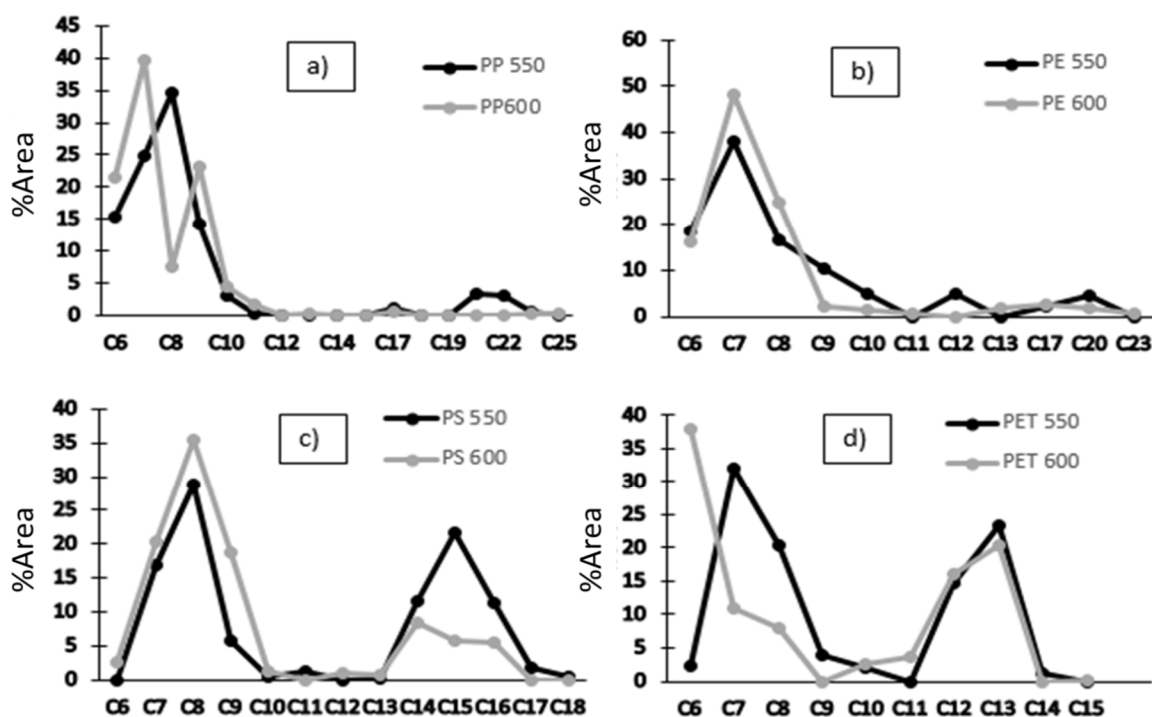


Figure 6: Carbon number distribution of oil derived from thermal pyrolysis at 550 and 600°C of a) PP; b) PE; c) PS; d) PET

At 550°C, a distribution from C<sub>6</sub> to C<sub>25</sub> with a maximum fraction between C<sub>6</sub> and C<sub>9</sub> is obtained for PP (Figure 6a). Increasing the pyrolysis temperature increases the amount of C<sub>6</sub> and C<sub>7</sub> from 15 to 21% and from 24 to 39% respectively. At the same time, the yield of C<sub>8</sub> decreases from 35 to 8%. As previously discussed, the cracking of the C-C bonds is favored when the pyrolysis temperature increases, leading to the formation of lighter hydrocarbons. The liquid fraction analyzed using GC-MS contains many compounds and the main ones are listed in Table 6. The liquid oil contains mainly alkenes and cycloalkenes (1,3 cyclohexadiene, 2,4 dimethyl 1,4 pentadiene, 4,4 dimethylcyclopentene) and aromatics (benzene, toluene and p-xylene). The total amount of alkenes and cycloalkenes decreases (30 and 28% at 550 and 600°C respectively) while increasing the temperature whereas the amount of aromatics increases (55 and 61 % at 550 and 600°C respectively). The formation of aromatics in the pyrolysis of polyolefin is accomplished through a Diels-Alder reaction followed by a dehydrogenation. This reaction is favored at higher temperatures [38].

Table 6: Major compounds formed in the liquid phase obtained from PP pyrolysis

Compounds	% at 550°C	% at 600°C
Benzene (C <sub>6</sub> H <sub>6</sub> )	6	11
1,3 cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	10	9
Toluene (C <sub>7</sub> H <sub>8</sub> )	19	25
2,4 dimethyl 1,4 pentadiene (C <sub>7</sub> H <sub>12</sub> )	6	2
4,4 dimethylcyclopentene (C <sub>7</sub> H <sub>12</sub> )	0	6
p-xylene (C <sub>8</sub> H <sub>10</sub> )	31	4
propylbenzene (C <sub>9</sub> H <sub>12</sub> )	0	10
1,2,4 trimethylbenzene (C <sub>9</sub> H <sub>12</sub> )	0	5

Considering PE (Figure 6b and Table 7), the distribution range of carbon number is almost the same as the one observed for PP. C<sub>7</sub> compounds are mainly produced whatever the pyrolysis temperature (550 or 600°C). Increasing the temperature increases the amount of C<sub>7</sub> and C<sub>8</sub> from 37 to 48% and from 16 to 24% respectively. The amount of aromatic compounds formed during PE pyrolysis is lower for PP (31% at 550°C versus 55% for PP). The formation of aromatic compounds may arise from the intramolecular abstraction of an hydrogen atom to give a stable aromatic ring [39]. The easier formation of propene in the pyrolysis of polypropylene may take part in the Diels–Alder reaction favoring the aromatization [36]. The formation of benzene, toluene and xylene during PP and PE pyrolysis was already reported by R. Miandad *et al.* [19]. They also observed that the amount of aromatics is more important for PP pyrolysis. On the other hand, it could be noted that this high amount of aromatics is not always observed in the literature reporting the pyrolysis of polyolefins such as for example [18]. It thus demonstrate that the pyrolysis condition are crucial considering the oil composition obtained from pyrolysis.

Table 7: Major compounds formed in the liquid phase obtained from PE pyrolysis

Compounds	% at 550°C	% at 600°C
Benzene (C <sub>6</sub> H <sub>6</sub> )	5	8
1,3 cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	9	3
Toluene (C <sub>7</sub> H <sub>8</sub> )	16	4
1,3 cycloheptadiene (C <sub>7</sub> H <sub>10</sub> )	7	3
4,4dimethylcyclopentene (C <sub>7</sub> H <sub>12</sub> )	5	32



The thermal pyrolysis of PS leads to the formation of C<sub>6</sub>-C<sub>18</sub> range of carbon number (Figure 6c) with two major peaks: the first one between C<sub>7</sub> and C<sub>9</sub> and the second one between C<sub>13</sub> and C<sub>17</sub>. It can be observed that the amount of light molecules increases when the reaction temperature is raised while the amount of heavier molecules decreases significantly. In fact, the second peak, corresponding to dimers, decreases when the temperature increases. The composition of the liquid fraction obtained from thermal decomposition of PS at different temperatures is shown in Table 8. Only aromatic compounds are detected. Styrene, that can be easily formed from the degradation of PS, represents the main compound with 27.0 and 35.6% at 550 and 600°C respectively. Shah and Jan [40] also reported that increasing the temperature leads to an increase in the production of styrene. On the contrary, according to Demirbas *et al* [30], using temperatures higher than 500°C decreases the production of styrene. The amount of toluene and styrene increases with temperature whereas the amount of diphenylethane and 1,3 diphenylpropane decreases. These results are in agreement with literature works [13][41] [42]. Yirong Liu *et al* [42] studied the thermal pyrolysis of PS in a fluidized bed reactor at various temperatures and observed that PS is cracked to form lighter hydrocarbons when the temperature increases from 450 to 600°C.

Table 8: Major compounds formed in the liquid phase obtained from PS pyrolysis

Compounds	% at 550°C	% at 600°C
Toluene (C <sub>7</sub> H <sub>8</sub> )	17	20
Styrene (C <sub>8</sub> H <sub>8</sub> )	27	36
Methylstyrene (C <sub>9</sub> H <sub>12</sub> )	6	12
1,2,4 trimethylbenzene (C <sub>9</sub> H <sub>12</sub> )	0	6
Diphenylethane (C <sub>14</sub> H <sub>14</sub> )	12	5
α-methylbibenzyl (C <sub>15</sub> H <sub>16</sub> )	5	1
1,3 diphenylpropane (C <sub>15</sub> H <sub>16</sub> )	13	5
1,2,3,4 tetrahydro 2 phenyl naphthalene (C <sub>16</sub> H <sub>16</sub> )	11	5

Finally, in the case of PET, a carbon number distribution from C<sub>6</sub> to C<sub>15</sub> with two maximum peaks for C<sub>7</sub> and C<sub>13</sub> is observed at 550°C. Increasing the temperature decreases the yield of C<sub>7</sub>-C<sub>8</sub> from 53 to 19% and increases C<sub>6</sub> yield from 2 to 38%. As shown in Table 9, this peak corresponds to the formation of benzene whose amount increases significantly with temperature while the amount of benzoic acid derivatives decreases sharply from 46 at 550 to 11% at 600°C.

Table 9: Major compounds formed in the liquid phase obtained from PET pyrolysis

Compounds	% at 550°C	% at 600°C
Benzene (C <sub>6</sub> H <sub>6</sub> )	2	38
benzoic acid (C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> )	32	11
3 methylbenzoicacid (C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> )	14	0
Styrene (C <sub>8</sub> H <sub>8</sub> )	0	7
2,4 dimethylphenylbenzene (C <sub>13</sub> H <sub>12</sub> O)	9	11
2 ethenynaphtalene (C <sub>12</sub> H <sub>10</sub> )	15	16

The thermal pyrolysis experiments performed with the virgin polymers show that the temperature has an important influence on the composition of the liquid phase. Moreover, each kind of polymer has its own degradation mechanism and thus the composition of the liquid oil differs from one polymer to another. The following step is to see if combining various polymers has an influence on the proportion of the different fractions and on the composition of the liquid oil. As PP and PE are the main plastics used in the packaging industry and as these polymers represent 75wt.-% of the total amount in the model mixture, the pyrolysis of a 50/50 PP/PE binary mixture was investigated.

### 3.3. Thermal pyrolysis of PP/PE binary mixture

#### 3.3.1. Thermogravimetric analyses

TGA experiments were performed for the mixture 50/50 PP/PE in order to see if there is any interactions between these two polymers than can affect the degradation temperature of the mixture (Figure 7). This mixture was selected since PP and PE represent the main constituents of municipal solid waste and also of MM. As it can be seen, the experimental curve tend to degrade faster than the calculated one. The presence of PP in the mixture has led to degrade the PE at a lower temperature. As a result, the maximum degradation temperature shifted to a lower value (499°C) as appears in the DTG curve. These results can conclude that there is an interaction between PP and PE.

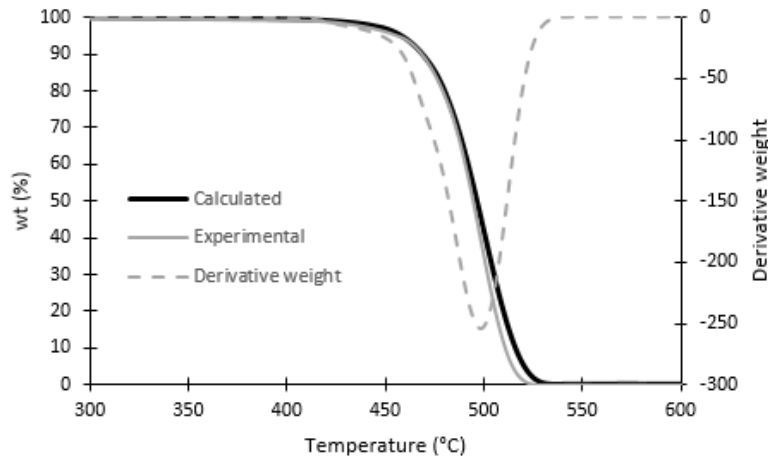


Figure 7 : TG and DTG for PP/PE mixture compared to TG calculated curve for 50%PP+50%PE

### 3.3.2. Fractions yield

The yields of liquid, gas, wax and residue obtained at 550 and 600°C from the thermal pyrolysis of PP/PE mixture are presented in Figure 8. The yield of liquid and gas increases from 29 to 32wt.-% and from 59 to 67wt.-% respectively when the temperature increases from 550 to 600°C. At the same time, the amount of waxy compounds decreases from 12 to 1 wt.-%. These data have been compared with those theoretically obtained by a linear combination of the virgin PP and PE yields, considering a 50/50 ratio (Figure 8). It can be observed that there is a difference between experimental and calculated value where the amount of wax reaches 17% for calculated value versus 12% for the experimental one. For the gas phase, its amount reaches 55% for calculated value versus 59 % for the experimental value. This behavior prove that the combination of PP and PE has an influence on the pyrolysis fractions. This result was previously explained by thermogravimetric analyses that shows that the mixture of these polymers can lead to an easier degradation and thus a higher amount of gas is obtained.

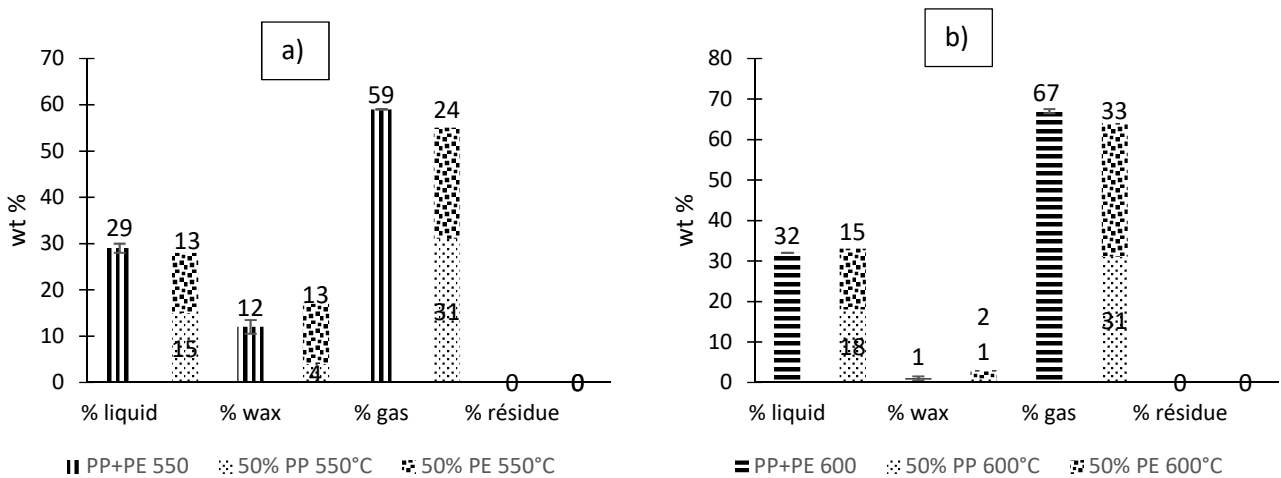


Figure 8: Amount of the different pyrolysis fractions for the PP/PE mixture: comparison between experimental results and calculated ones (by linear combination) at 550 a) and 600°C b)

### 3.3.3. Composition of the liquid phase for PP/PE binary mixture

Figure 9 presents the carbon number distribution corresponding to the pyrolysis oil for the 50/50 PP/PE binary mixture. When the temperature is increased from 550°C to 600°C, an increase in the C<sub>6</sub> component and a decrease in the C<sub>8</sub>-C<sub>9</sub> amount is observed. Compared to the theoretical values calculated from the pyrolysis of virgin polymers at 550°C and 600°C, it can be seen that, at 550°C, the maximum peak has shifted from C<sub>7</sub> to the production of C<sub>8</sub> compounds whereas at 600°C, the maximum peak has shifted from C<sub>7</sub> to the formation of C<sub>6</sub> compounds. In order to understand the reason for these results, the composition of the main compounds is given in Table 10.

Pyrolysis of the PP/PE mixture at a 50/50 ratio leads to the formation of 88% of C<sub>6</sub>-C<sub>9</sub> products. Increasing the temperature increases the amount of all C<sub>6</sub>-C<sub>9</sub> products to 92%. Benzene, toluene and xylene (BTX products) are the main compounds formed and account for around 65% of the oil fraction. At 550°C (Table 10), the percentages of benzene (at 550°C) and toluene are in good agreement with the calculated ones obtained by linear combination of the results obtained for the virgin polymers weighted by their content. On the contrary, the amount of benzene at 600°C (14%) is slightly higher than the theoretical value (10%). Furthermore, the amount of xylene is almost twice the theoretical value at 550°C (39 and 20.3% for the experimental and theoretical values respectively) and 7 times more than the theoretical value at 600°C (35 and 6% for the experimental and theoretical values respectively). Thus, even if mixing PP with PE does not really affect the yield of the liquid oil fraction, the composition is different when both polymers are combined. Ciliz *et al* studied also a PP/PE mixture from waste plastics and observed the formation of 32 wt-% of aliphatic compounds while the mono aromatics constitute 30 wt-% [43]. In this study, propylbenzene has reached 16 wt-% while the percentage of toluene and xylene were both 5 wt-%.

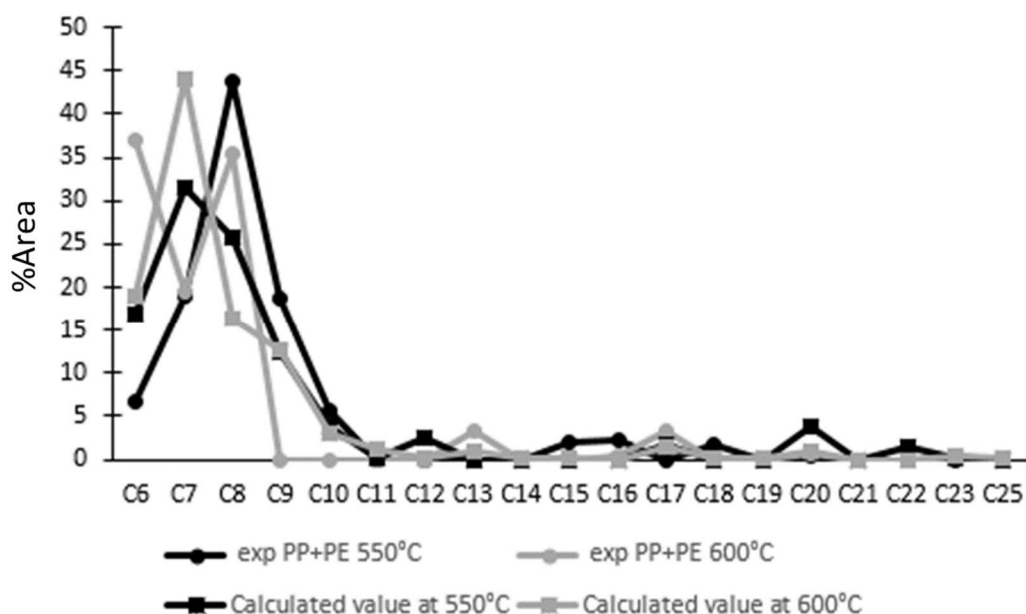


Figure 9: Carbon number distribution of the liquid fraction for the PP/ PE mixture at 550 and 600°C

Table 10: Major compounds formed from the pyrolysis of the PP/PE mixture at 550°C and 600°C (Calculated value are obtained by linear combination of the results obtained for pure polymers weighted by their content i.e. 50% for PE and 50% for PP)

	Exp % at 550°C	Calculated % at 550°C	Exp % at 600°C	Calculated % at 600°C
<b>Benzene</b>	7	5	14	10
<b>Toluene</b>	19	18	14	15
<b>Xylene</b>	39	20	35	6
<b>Total</b>	65	43	64	30

Thus, combining PP and PE in the pyrolysis mixture is of significant advantage for pyrolysis purpose as TGA experiments prove that the decomposition is slightly accelerated when PP and PE are combined. Moreover, this mixture allows obtaining a better selectivity in the composition of the liquid fraction compared to the pure polymers: around 65% of BTX compounds. However, the thermal degradation mechanism is similar for both PP and PE, being a radical mechanism. But, what happens when polymers having potentially a different thermal degradation process are incorporated in the mixture?

The next section is thus devoted to the pyrolysis of the model mixture (MM) composed of PP, PE, PS and PET.

### 3.4. Thermal pyrolysis of the model mixture

#### 3.4.1. Thermogravimetric analyses

The test was carried out for the model mixture MM composed of 30 wt-% of PP, 45 wt-% of PE, 10 wt-% for PS and 15 wt-% of PET and was compared to the calculated curve in order to see the influence of the mixture on the process of the degradation. As it can be seen from Figure 10, the degradation of the model mixture is accelerated where there is 20°C of difference between the two curves. This result shows that adding PS and PET to the mixture even with a small amount has led to a faster degradation than expected. Furthermore, the degradation of the model mixture is extended in a wide degradation temperature span as appears in the derivative weight curve. Therefore, the large peak of degradation can be a combination of peaks of the individual plastics due to the different temperature range. As the degradation of PS is the faster, this decisive step will initiate the reaction of degradation. The radicals formed will be the primary radicals for PP and PP degradation. The mechanism of degradation of the mixture is detailed by Costa et al [44]. This result is the reason of the acceleration of the degradation process of the MM.

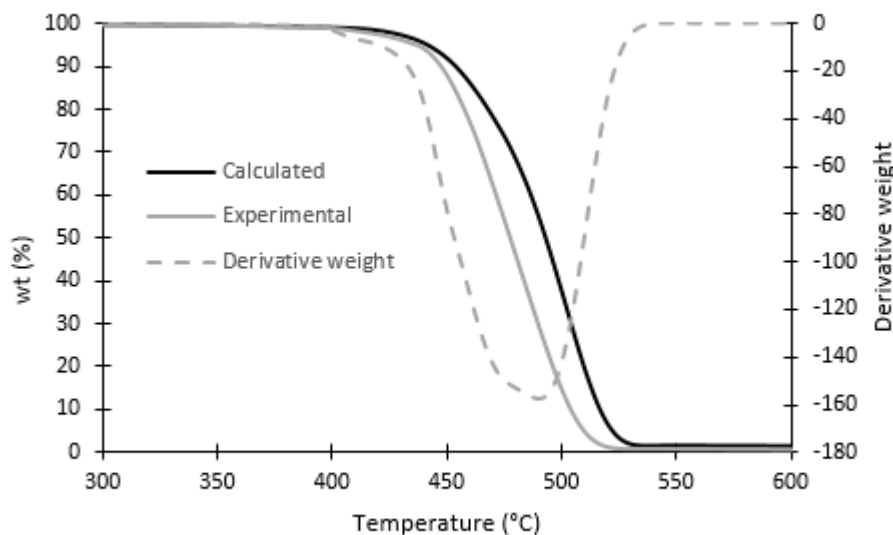


Figure 10 : TG and DTG curves for the MM compared to the calculated curve

#### 3.4.2. Fractions yield

The pyrolysis of the model mixture (30%PP/45%PE/10%PS/15%PET) was carried out and the yields obtained (weight %) for the different fractions are presented in Figure 11. An increase from 26 to

32wt.-% and from 61 to 63 wt.-% of the liquid and gas fraction fraction is observed when the temperature increases from 550°C to 600°C, while the amount of wax decreases from 11 to 3 wt.-%. It is also possible to compare those data with the theoretical yield values calculated by a linear combination of the yields obtained for the virgin polymers (Figure 11). A reduction by half of the amount of wax and an increase of the amounts of liquid and gas are observed compared to the theoretical values. This phenomenon can be attributed to the increase in the number of free radicals when adding PS to the mixture that can accelerate the decomposition of the reaction and thus decrease the amount of waxy compounds [45]. This result is in agreement with TGA curves that proves also the interaction between the polymers and the acceleration of the degradation process. The presence of a residue can mainly be attributed to the presence of PET in the mixture and is supported by TGA experiments that demonstrate the formation of 0.4 wt.-% of residue in the case of the MM.

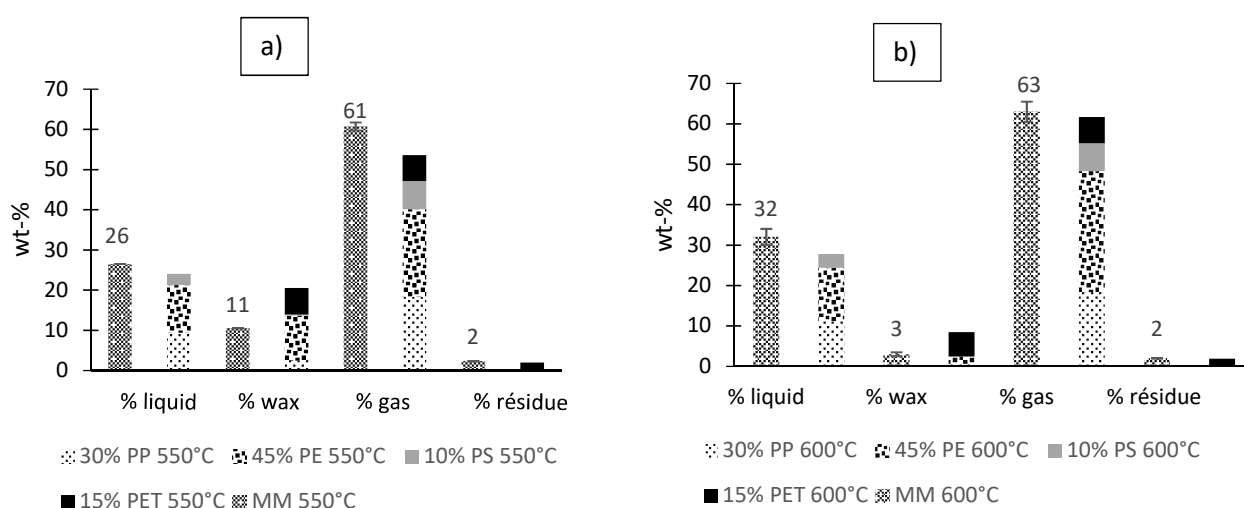


Figure 11: Amount of the different pyrolysis fractions for the MM: comparison between experimental results and calculated ones (by linear combination) at 550 a) and 600°C b)

### 3.4.3. Composition of the liquid phase for the model mixture

Mixing PP, PE, PS and PET leads to a new distribution of the liquid products that do not fit with the theoretical values at 550 and 600°C as shown in Figure 12. The amount of light hydrocarbons is higher than the theoretical values especially for C<sub>6</sub> at 550°C and C<sub>7</sub> at 600°C. Furthermore, the formation of new products that were not detected with virgin polymers occurs at 550°C like 4 methyl 3 penten 2-ol and 1,4 cyclohexadiene (Table 11). Indeed, aromatic compounds represent 59% of the total amount of liquid at 550°C. Surprisingly, increasing the temperature from 550°C to 600°C leads to an increased amount of C<sub>7</sub> fraction, especially the quantity of toluene, from 24 to 61% while the amount of benzene and styrene decreases from 13 to 6 and from 16 to 7% respectively. The pyrolysis

of the PP/PE mixture leads to an amount of xylene twice as important as the theoretical yield whereas the liquid fraction obtained after the pyrolysis of the MM at 600°C is mainly composed of toluene (around 6 times more than the theoretical value). This large amount of toluene could be interesting if the valorization of the liquid fraction is considered.

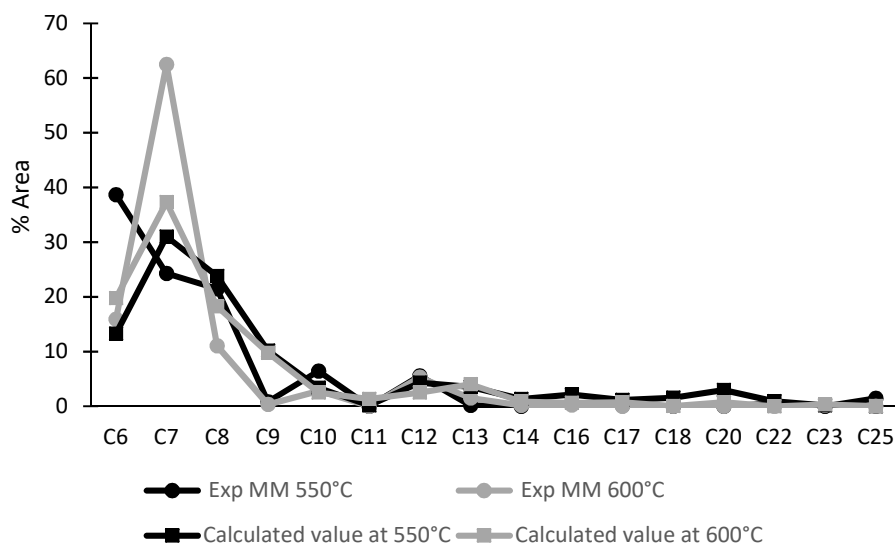


Figure 12: Carbon number distribution of the thermal pyrolysis of the model mixture

Table 11: composition of the liquid phase for the model mixture (Calculated value are obtained by linear combination of the results obtained for pure polymers weighted by their content i.e. 30%PP/45%PE/10%PS/15%PET)

Compounds	PE	PP	PS	PET	Exp % at 550°C	Calculated value at 550°C	Exp % at 600°C	Calculated value at 600°C
Benzene C <sub>6</sub> H <sub>6</sub>	X	X		X	13	4	6	13
1,3 cyclohexadiene C <sub>6</sub> H <sub>8</sub>	X	X			8	7	5	4
1,4 cyclohexadiene C <sub>6</sub> H <sub>8</sub>					5	0	2	0
4 methyl 3 penten-2-ol C <sub>4</sub> H <sub>12</sub> O					9	0	0	0
Toluene C <sub>7</sub> H <sub>8</sub>	X	X	X	X	24	15	61	11
Styrene C <sub>8</sub> H <sub>8</sub>			X	X*	16	3	7	5
p-xylene C <sub>8</sub> H <sub>10</sub>	X	X			5	14	4	5

X: Presence in the liquid fraction X\*: only at 600°C

#### 4. Conclusion



The main objective of this study was to evaluate the effect of mixture composition on the pyrolysis oil yield and composition. For that, in a first part, a model mixture composition was determined in order to establish a mixture representative of the plastic waste in France. Then, the virgin plastics were pyrolyzed at 550 and 600°C. It was shown that the pyrolysis of PP, PE, PS and PET leads to the formation of C<sub>6</sub>-C<sub>25</sub> hydrocarbons in the pyrolysis oil. This oil is mainly composed of aromatic compounds (BTX and Styrene). Liquid oil from PP pyrolysis contains benzene, toluene and xylene as major compounds at 550 and 600°C. PE produces also aromatics and the major compounds are toluene and xylene at 550°C and 4,4 dimethylcyclopentene and xylene at 600°C. PS pyrolysis leads to the formation of styrene (27 and 34%) at 550 and 600°C. In the case of PET, it was shown that benzoic acid derivatives are mainly formed at 550°C. The study of the pyrolysis products obtained in the case of mixture of polymer (PP/PE and model mixture) shows that, even if aromatics compounds are also obtained similarly to the results obtained for virgin polymers, the ratio between the aromatics compounds varies when the polymers are pyrolyzed alone or in the case of a mixture. Indeed, mixing PE with PP at a ratio of 50/50 does not affect the amount of the liquid, gas and solid phase but it leads to form a high quantity of xylene at 550°C where the amount is twice the theoretical value. For the model mixture, it was observed that adding PS and PET to PP and PE leads to obtain 61% of toluene which is six times more than the theoretical value. These results are promising for valorizing the liquid phase especially for a mixture of plastic that is representative of the waste in France. Thus, this study demonstrates that pyrolysis is an effective technique to recover plastic waste. In particular, aromatics compounds can be obtained and recovered in the petroleum industry.

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