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# Thermochemical recycling of polystyrene by pyrolysis: Importance of the reflux to maximise the production of styrene and BTEX

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**KEY WORDS:** Pyrolysis; Polystyrene; Reflux; Semi-batch reactor; Recovery and waste management; Styrene; BTEX.

## ABSTRACT

Chemical recycling of polystyrene (PS) via pyrolysis is of great importance for both environmental and economical purposes. In this work, a specially designed laboratory semi-batch glass reactor apparatus equipped with a reflux condenser was developed and investigated for the pyrolysis of PS at 480°C with nitrogen as the carrier gas and operating at atmospheric pressure with the main goal of improving the recovery of styrene monomer and BTEX components. A set of experiments were carried out with and without a reflux condenser. The upper temperature of the reflux condenser was between 200°C to 400°C depending on the amount of heat applied to the reflux condenser wall. A comprehensive gas chromatography (GC-MS/FID) coupled with a  $\mu$ -GC-TCD were used to provide an exhaustive characterization of the liquid and gaseous products. The use of reflux influenced the yields of styrene, ethylbenzene and toluene in the liquid output and the C<sub>1</sub>–C<sub>4</sub> content of the gaseous output. The mass fraction of styrene monomer related to the analyzed oil from GC-MS/FID reached a maximum of 81.2 wt% with an optimal reflux temperature of 200 °C, whereas styrene only represented 59.3 wt% when the reflux was not used. The present study illustrates the significant impact of the presence of the reflux on the liquid and gas yields by

maximising the molecules of interest, especially those corresponding to styrene, toluene and ethylbenzene comparably to usual pyrolysis without reflux.

## 1. INTRODUCTION

The worldwide use and production of plastics have grown rapidly over the last few decades. It has been estimated that almost 391 million tonnes of plastics were produced worldwide during the year 2021 [1]. During 2021, the amount of plastic solid wastes produced in Europe reached almost 58 million tonnes and a fourfold increase of the production is expected by 2050 [2] despite the continuous efforts to reduce, re-use, recycle and recover. This is mainly due to the wide application of plastics in the manufacture of packaging for the food industry, as well as in other daily life application [1]. The current most common practice for handling plastic waste are landfill, incineration and remelting. Remelting seems to be easier to achieve, but it can only be applied for pure PS streams without additives and not contaminated [3]–[5], unlike pyrolysis. Landfill and incineration are less preferable due to high cost, low bio-degradability and the possibility of unacceptable and non-regulated emissions. Therefore, these handling methods are generally not accepted as a long-term solution.

Consequently, one of the promising alternatives to landfill and incineration for the treatment of plastic waste such as polyolefins (polypropylene, polyethylene and polystyrene) can be pyrolysis to recover the monomer or other valuable chemicals [3], [6]–[11].

Pyrolysis had received a lot of attention from the scientific community [12]–[15], not only because it is considered as an eco-friendly technology but also because the process can produce liquid oil as fuels and chemicals up to 80 wt.% at an easily reachable temperature of about 500 °C [16] ; the products could be merged in standard petrochemical or petroleum refining industry operation, and the recovered monomer can be used to produce new polymer.

One of the most important and widely used thermoplastic throughout the world is polystyrene (PS) which is cheap, hard, transparent but may be colored by introducing colorants. It is heat resistant, light and, exhibits good strength and durability that make this polymer fit for a variety of applications such as car parts and tires, food packaging, paper coating and carpet backing, electrical appliances, thermal insulation and composites. During 2021 approximately 20.7 and 3.5 million tonnes of polystyrene were produced in the world and in Europe respectively [1].

In contrast to most addition polymers [17]–[19], polystyrene (PS) shows a different behavior during pyrolysis by giving styrene monomers as major product and with high selectivity. The other products include BTEX (benzene, toluene, ethylbenzene, xylene). The liquid product has always been attractive due to its properties and its potential use as chemical feedstock or fuel. The advantage of the liquid issued from the pyrolysis of PS consists on the narrow distribution of molar masses which make it more valuable than the liquid issued from the pyrolysis of other polyolefins such as polypropylene [20]. The main influencing factors of PS pyrolysis were widely studied and investigated by several researchers such as temperature, heating rate, pressure, residence time, type of reactor, catalyst and the type of feedstock used. Summarized results are available in the review of I. M. Maafa (2021) [17] and the articles of Y. Liu et al [18], D.S. Achilias et al [19], W. Kaminsky [21], K. Murata et al [22] and A. Zayoud et al [23].

The pyrolysis process of PS and its production of liquid and gaseous products relies mainly on the reaction conditions such as temperature, reaction time, reactor type (for instance, fluidized bed reactors and conical spouted bed reactors), the presence of catalysts, etc. All researchers cited above confirmed that at low temperatures (350-500°C), products mainly consist of liquid compounds (monoaromatics) ; and at higher temperatures (> 500°C), gas and coke/char yields are higher.

Nonetheless, there is very little information in the literature on the influence and importance of the use of reflux on the control of the composition of pyrolysis oil and, unfortunately, no

quantitative analysis of the liquid and gaseous products has been provided. As mentioned in our previous work [20], only Dobó et al. [40] investigated the influence of reflux temperature in a range of 150–300 °C toward the yield of liquid oil during the pyrolysis of a typical mixture of plastics (PP, LDPE, HDPE and PS). Unfortunately, no quantitative analysis of the liquid and gaseous products was available. Wajima et al. [41] studied the production of oil from HDPE by thermal pyrolysis at 450 °C using a reflux condenser with a temperature range from 150 °C to 200 °C. Only the oil produced was analyzed semi-quantitatively by GC-MS.

In this article, the work focused on pyrolysis of virgin polystyrene (PS) in a semi-batch reactor in an inert environment. The pyrolysis method in this study can recycle waste polystyrene products without cleaning process, but directly obtain high-value styrene monomers.

The principal focus of this research is to investigate the role of the reflux and its operating temperature on the efficiency and properties of the liquid and gas produced during the pyrolysis of PS. The reflux principle refers to the same principle of a classic and conventional distillation. It consists then of a separation of 2 different phases, a gas mixture and a condensed liquid by removing the heat continuously. When the boiling temperature of the gas mixture is reached and becomes above than the reflux zone temperature, the gas condenses and the liquid flows down the walls of the reflux zone until reaching the bottom of the reactor to undergo a second cracking, while the light compounds with a boiling temperature lower than the reflux zone temperature remain in a gas phase and escape the reactor to condense in the liquid traps.

It is expected that the use of the reflux could promote the formation of lighter products by reducing waxes (or oligomers) [20], [24], [25]. More specifically, it is intended to identify the conditions that allow to enhance the styrene and BTEX yields.

## **2. MATERIALS AND METHODS**

## **2.1. Origin and characteristics of the materials**

PS was provided by Sigma-Aldrich in a pellets form (2 mm). Its melting point is 240°C and its average molecular weight is 192,000 g/mol. The use of PS without additives provided a better understanding of the pyrolysis process. Glass beads in the form of pellets (6 mm) were used as packing elements in the reflux zone. The solvent used for GC analysis and the internal standard were dichloromethane (DCM) [26] and 1-decanol respectively; both were purchased from Sigma Aldrich. Nitrogen was purchased by Messer and was used as inert gas during the pyrolysis experiments; its purity was above 99.995 %.

## **2.2. Analytical characterization of PS**

Briefly, the ultimate analysis was done by using a CHNS analyzer (Elementar vario cube CHNSO), the proximate analysis by ASTM D3173-75. Thermogravimetric analysis (TGA) was achieved using a Mettler Toledo Star<sup>e</sup> instrument. The experimental conditions of the three analytical methods were similar to our work for polypropylene (PP). More details are provided in our previous research study [20].

## **2.3. Experimental apparatus and procedure**

### **2.3.1. Pyrolysis pilot system**

The oil obtained from PS was produced via pyrolysis performed in the laboratory. The system consists of a glass semi-batch reactor (height  $30 \pm 0.2$  cm, internal diameter  $5 \pm 0.2$  cm) with a total volume of 2355 cm<sup>3</sup>. Regarding the volume of the reflux zone, it was around 1805.5 cm<sup>3</sup> (400 cm<sup>3</sup> of filling elements and 1405.5 cm<sup>3</sup> of effective volume) and the volume of the feedstock zone was around 549.5 cm<sup>3</sup>

The reactor was supplied by N<sub>2</sub> as inert gas and was equipped with different thermocouples. An absolute pressure sensor was used to prevent an increase in pressure that could lead to a reactor explosion.

In all the experiments, 20 g of PS were placed in the bottom of the reactor before the experiment started. After this step, the apparatus was purged for 20 min with nitrogen having a flow rate of 100 mL/min to ensure that any O<sub>2</sub> present was removed. Then, the system was warmed from ambient temperature to the required target temperature at the lower part of the reactor (setpoint temperature: 500°C). The flow of N<sub>2</sub> sweep gas was 100 mL/min during all the experiments. The off-gas zone was heated to a temperature higher than the top of the reflux to prevent the solidification of waxes that could clog this area at lower temperatures. Glass beads were used as filling elements to increase the contact area between the liquid and gas phases and thereby improve the exchange between the phases in the reflux zone. The temperatures were controlled by using K type thermocouples. Nine thermocouples (regulation and measurement) were used to control and monitor the pyrolysis pilot during all the experiments; T<sub>0</sub> for the sample temperature; T<sub>1</sub> for temperature of the low reflux position; T<sub>2</sub> for temperature of the middle reflux position; T<sub>3</sub> for temperature of the high reflux position; T<sub>4</sub> for gas exit temperature and T<sub>5</sub> for external wall temperature of the reactor. Moreover, three regulation thermocouples were used, T<sub>r1</sub> to regulate the temperature of the feedstock zone (pyrolysis regulation temperature), T<sub>r2</sub> to regulate the temperature of the reflux zone and T<sub>r3</sub> to regulate the temperature of the exit gas zone.

Transverse temperature gradient ( $\Delta T = T_5 - T_2$ ) was measured and it was less than 20 °C after temperature stabilization.

The sample was maintained at the desired temperature until the reaction was completed. The duration of the reaction was noted when there was no longer any flow of liquid oil through the liquid collectors. It was approximately 3.5 hours. The gaseous products flowed through the reflux zone, which was kept at a lower temperature than the reactor [20]. Lighter gas compounds escaped the reflux column and entered three liquid collectors (the first at ambient temperature, the second at 0°C by using ice and the third at -40°C by using liquid N<sub>2</sub> and propanol). The use of a third collector with a small volume (25 ml) of propanol was necessary to condense all highly volatile hydrocarbons compounds and especially BTEX in

order to ensure that they are all condensed and collected; the non-condensable gases that were not trapped and not condensed in none of the three collectors, remain gaseous and get collected in a gas bag before being analyzed by an off-line  $\mu$ -GC.

The scheme is shown in Fig.1 and more details are available in [20].

After the reaction was completed, the liquid products that were trapped in the liquid collectors were weighed. The liquid products were then dissolved in DCM and analyzed by GC-MS/FID (section 2.4.2). As soon as the reactor was cooled to room temperature, the char was collected and weighed.

The product yields were divided into three categories: permanent gas (non-condensable gas), char residue which remained in the bottom of the reactor and liquid oil consisting of hydrocarbons from six to twenty-five carbons that depends on the use of the reflux.

The mass yields calculations are presented in equations (1), (2) and (3) as following:

$$\text{Mass yield of liquid oil (\%Y}_L) = \frac{M_1 * 100}{M_{PS}} \quad (1)$$

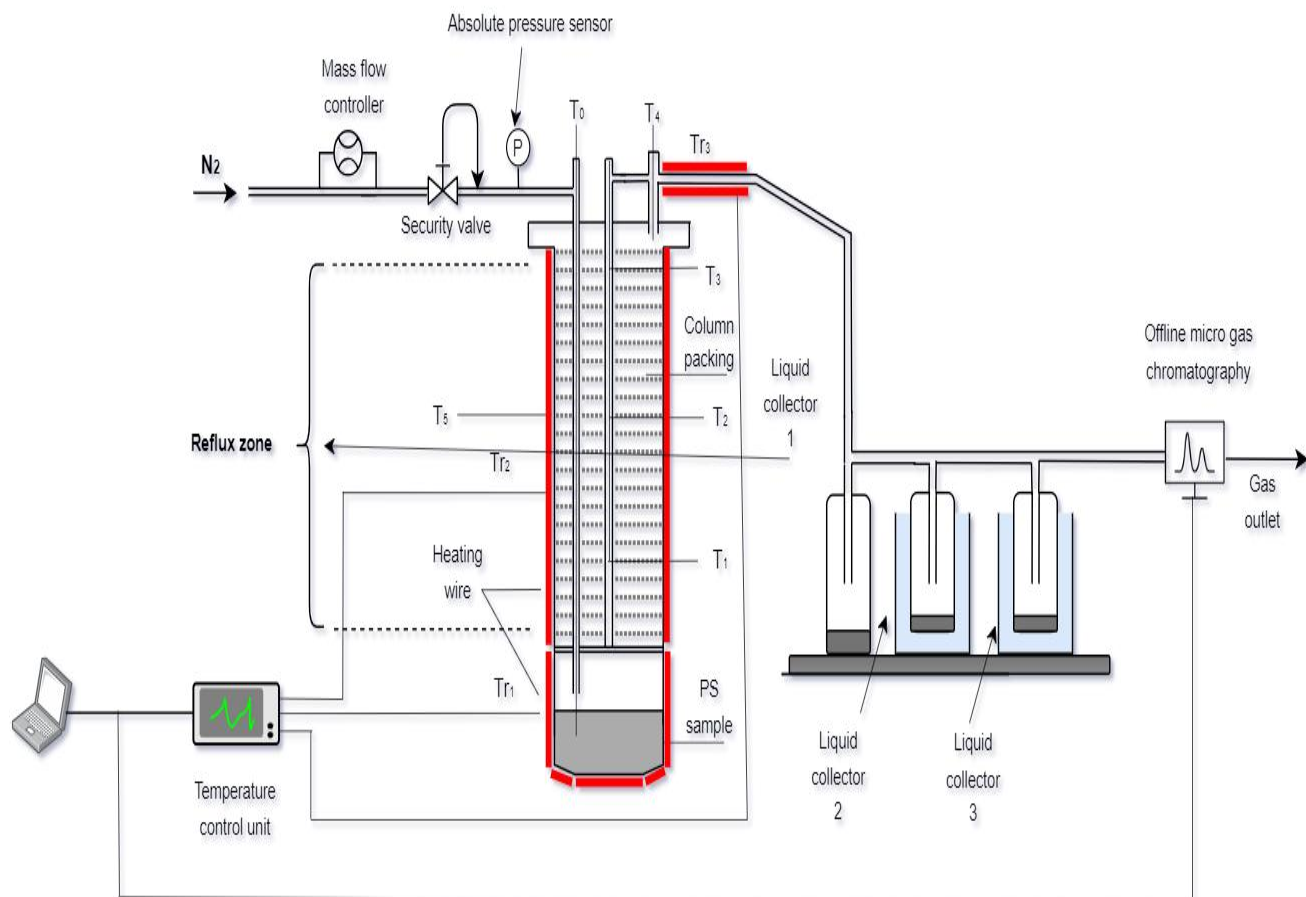
$$\text{Mass yield of char in the bottom of the reactor (\%Y}_{char}) = \frac{M_2 * 100}{M_{PS}} \quad (2)$$

$$\text{Mass yield of non-condensable permanent gas (\%Y}_G) = 100 - Y_L - Y_{char} \quad (3)$$

Where:  $M_{PS}$ : initial mass of PS (20g);  $M_1$ : Mass of all the liquid oil in the collectors;  $M_2$ : Mass of the char remaining in the bottom of the reactor.

It should be noted that the yield of non-condensable gas was precisely determined from the mass balance due to the fact that the  $\mu$ -GC did not quantitatively detect the hydrocarbons that comprise four carbons (too poor sensitivity) and the GC-MS/FID could not detect the hydrocarbons with five and six carbons. Indeed, hydrocarbons with five and six carbons were condensed in the collectors and diluted in a solvent. Due to the solvent lead time/delay in the GC-MS/FID, they were hindered and could not be quantified.





**Fig. 1.** Scheme of the reflux pyrolysis system of PS.

### 2.3.2. Experimental conditions

Each experiment (Table 1) was performed three times and the result presented in this work is the mean with standard deviation. Experiment 4, also called the "no-reflux experiment," was performed without filling elements and the reflux zone was heated to the same regulation temperature as the feedstock zone.

It should be noted that the longitudinal temperature in the reflux zone was stabilised at the desired reflux temperature and the reflux temperature was similar in the low (T<sub>1</sub>), middle (T<sub>2</sub>) and high (T<sub>3</sub>) reflux positions. Therefore, the regulation temperature of the reflux zone T<sub>r2</sub> is identical to the T<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub> temperatures.

**Table 1.** Parameters of the experiments

Pyrolysis temperatures for each experiment				
Exp Temperature	Feedstock zone		Reflux and exit zones	
	Experimental temperature	Regulation temperature	Temperature of the reflux zone	Temperature of the exit gas zone
Experiment 1	480 °C	500 °C	200°C	250 °C
Experiment 2	480 °C	500 °C	300 °C	350 °C
Experiment 3	480 °C	500 °C	400 °C	450 °C
Experiment 4	480 °C	500 °C	500°C	500°C
Pyrolysis parameters				
Nitrogen flow		100 mL/min		
PS mass		20 g		
Pressure		Atmospheric pressure		

#### 2.4. Analytical methods of pyrolysis products

A GC-MS/FID type Agilent 7890A coupled to an MS Agilent 5975C TAD (Triple-Axis Detector) Series GC/MSD (Mass Selective Detector) system and a Flame Ionization Detector (FID) was used to identify and quantify the compounds in the liquid products. The solution was injected with a split ratio of 50 into an Agilent HP-5MS (diphenyl 5%, dimethylpolysiloxane 95%, non-polar, 30 m × 250 µm × 0.25 µm) column [25]. The column was connected to the FID and the MS, in order to identify and quantify the products in the same analysis. The GC oven temperature was stabilised at 50 °C for 5 min, then increased with a 5 °C/min ramp to 320 °C and held at this temperature for 10 min. Quantitative results were obtained from GC-FID. An external calibration curve was established for nonane and hexadecane, and the quantification of the compounds was estimated by internal calibration, as in [20]. The internal standard used was 1-decanol because it cannot be produced by PS pyrolysis and comes out in the middle of the chromatogram and can therefore be easily distinguished.

A  $\mu$ -GC type Agilent 3000A was used to analyze and quantify the composition of the non-condensed gaseous compounds. Three modules (A, B and C) and three TCD (Thermal Conductivity Detector) were coupled to the  $\mu$ -GC, thus, three streams of gases can be analyzed simultaneously. For module A (Molsieve 5A (MS5A)), argon was used as the carrier gas, and measures  $N_2$ ,  $H_2$ ,  $CH_4$  and  $CO$ . For module B (PoraPLOT U), helium was used as the carrier gas to measure  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_2$ . For module C (Alumina), helium was also used as the carrier gas to measure hydrocarbons with three and four carbons such as propylene, propadiene, methylacetylene, butane, butadiene and butene and its isomers. Shortly, the experimental conditions of the  $\mu$ GC were similar to our work for polypropylene (PP) [20]. Different previous research studies provided more details for this section [20], [27]–[29].

### 3. RESULTS AND DISCUSSION

#### 3.1. TGA, proximate and ultimate analysis results

In similarity with the TGA results obtained by N. Nishizaki et al [30] and J.P. Siregar et al [31] for his HIPS (High Impact Polystyrene) sample, the weight loss confirmed that there is only one-step degradation which means that there is one major degradation reaction. The weight loss of the PS began at  $350^\circ\text{C}$  and was achieved around  $484^\circ\text{C}$  when the heating rate was  $20^\circ\text{C}/\text{min}$ . From these measurements, it was possible to estimate the required pyrolysis regulation temperature, i.e., about  $500^\circ\text{C}$ , in order to reach  $480^\circ\text{C}$  in the reactor.

The thermogravimetric (TGA) proximate and ultimate analysis of this study are similar to the previous literature results [30]–[33].

Proximate analysis confirmed that the volatile matter matched to 100%, as the PS samples did not contain ash. The low amount of sulfur in the PS samples may be due to slight contamination during manufacturing, although the purchased PS was virgin and contained no impurities and additives [34]. C, H, N, O and S amounts of PS are given in Table 2.

**Table 2.** Proximate and elemental analysis of PS compared to other research studies

Proximate analysis (wt%)	<b>Our work</b>	<b>D.Oh et a l[32]</b>	<b>F. Abnisa et al [33]</b>
<b>Moisture</b>	0	-	0.25
<b>Volatile matter</b>	100	99.9	99.63
<b>Fixed carbon</b>	0	0.1	0.12
<b>Ash</b>	0	-	0
Ultimate analysis (wt%)			
<b>C</b>	91.98	92.8	91.34
<b>H</b>	7.16	7.2	7.8
<b>N</b>	0	-	0.34
<b>S</b>	0.07	-	0
<b>O</b>	0	-	0.52

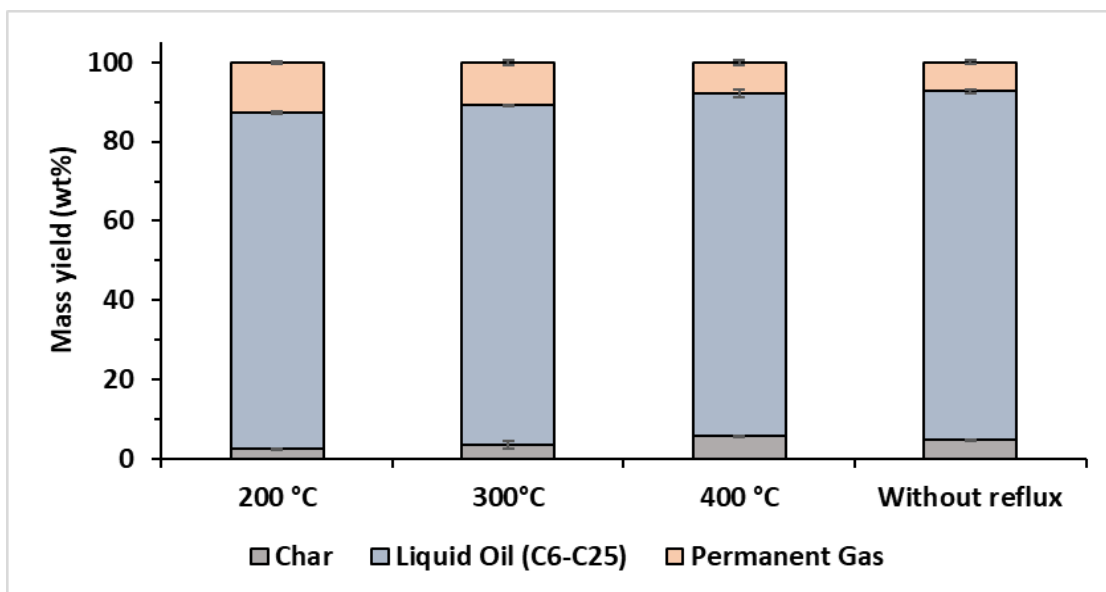
## 3.2. Characterization of pyrolysis products

### 3.2.1. Product distribution analysis

The product yields of PS pyrolysis are presented in Fig.2. The remaining char in the bottom of the reactor was inferior than 1 g (inferior than 5 % of the initial mass of PS). The liquid products were rcollected from the three condensers. The liquid products produced in the first condensers with reflux were liquid, slightly yellow and transparent in comparison to the liquid oil obtained without reflux which was liquid (non viscous in comparison with the liquid oil obtained from the PP pyrolysis [20]) and dark brown. The texture and the color of the collected liquid oil in the first condenser at different reflux temperatures are presented in Fig.3; as the liquid colour becomes darker, the liquid contains more polyaromatics, and the cracking of PS to styrene becomes less advanced.

Regarding the other collectors, nothing was collected in the second collectors and the volume of propanol of the third collector was constant at the end of all the experiments which means that nothing was collected as well.

For most experiments, the overall mass yield of liquid products was more than 84 wt.%, and the formation of char was insignificant compared to the initial mass of the polymer put in the reactor.



**Fig.2.** Reflux temperature effect on product yields issued from PS pyrolysis at different temperatures of reflux (200-300-400 °C) and without reflux.



**Fig.3.** Texture of the collected liquid oil at different setpoint temperatures of reflux.

- (a) Liquid oil sample when the reflux was not used.
- (b) Liquid oil sample for a reflux temperature of 400°C
- (c) Liquid oil sample for a reflux temperature of 300°C
- (d) Liquid oil sample for a reflux temperature of 200°C

The liquid oil yield is slightly modified by the reflux temperature; it decreased from  $88 \pm 0.4$  wt% without reflux to  $86.5 \pm 0.8$  wt%,  $85.7 \pm 0.2$  wt% and  $84.8 \pm 0.4$  wt % respectively at 400 °C, 300 °C and 200 °C. The yield of gas was deduced and precisely determined from the mass balance to complete it. Its yield was between  $7.8 \pm 0.8$  wt% and  $12.7 \pm 0.3$  wt% when the reflux was used but it dropped to  $7.3 \pm 0.4$  wt% when the reflux was no longer used. The char yield increased when the reflux temperature increased : from  $2.5 \pm 0.2$  wt% at 200 °C to

$3.6 \pm 0.8$  wt% at 300 °C and  $5.7 \pm 0.1$  wt% at 400 °C. When the reflux was no longer used, the char yield was  $4.7 \pm 0.1$  wt%.

A recent investigation of PP pyrolysis [20] showed that the molecular distribution of the gaseous and liquid products from the PP pyrolysis is continuous, ranging from low molecular weight to high molecular weight products. In the case of the PS pyrolysis, the products distribution was quite different, with only a few major components in the liquid products. PS was cracked during the pyrolysis into styrene, non-condensable gases and other light aromatics. The low quantity of non-condensable gas confirmed that no significant secondary cracking reactions occurred on the primary pyrolysis products. As a result, PS pyrolysis products were mainly formed during primary reactions. However, compared to our previous PP pyrolysis [20], the char content produced in the PS pyrolysis was much higher (6%) and consisted of black chips accumulated on the bottom of the pyrolysis zone.

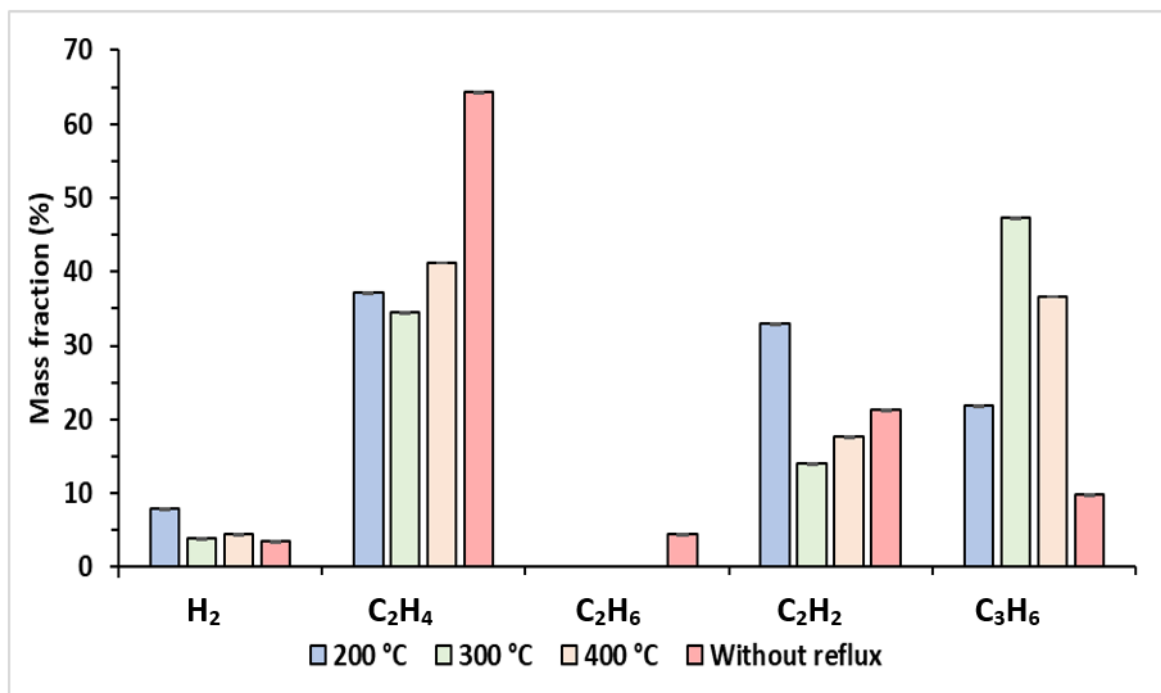
It should be precised again that the analysis of liquid products and non-condensable gas do not provide and detect the hydrocarbons with four, five and six carbons since the sensitivity of  $\mu$ -GC towards  $C_4$  is poor and the  $C_5$  and  $C_6$  are hindered by the solvent delay in GC-MS/FID.

### **3.2.2. Analysis of the non-condensable gas products**

The quantity of non-condensable gas from the PS pyrolysis was much less than that of the PP pyrolysis. The total non-condensable gas from pyrolysis of 20 g of PP was between 10.5 wt.% and 25.8 wt.% of the total products [20]. However, for the same weight of material (20g) in the PS pyrolysis, 7.3 to 12.5 wt.% gas was collected of the total products. Theses gas production differences between the different types of polymers are due to the different primary cracking process and the structure of the polymer chain.

Fig.4. presents the results from the  $\mu$ -GC analysis of PS pyrolysis non-condensable gas. The results were calculated relatively to all the detected gases as follows:

$$\text{Mass fraction } i (\%) = \frac{\text{mass detected } (i)}{\sum_{i=1}^n \text{mass detected } (i)}$$



**Fig.4.** Mass fraction of gas compounds issued from PS pyrolysis at various temperatures of reflux (200-300-400 °C) and without reflux.

The results show that there were three major components with corresponding fraction greater than 5% when the reflux was used. The highest mass fraction of ethylene (C<sub>2</sub>H<sub>4</sub>) was 41.1 ± 0.01 wt% at a reflux temperature of 400°C. Regarding propene (C<sub>3</sub>H<sub>6</sub>) its highest mass fraction was 47.4 ± 0.01 wt% at a reflux temperature of 300°C and for acetylene (C<sub>2</sub>H<sub>2</sub>), it was 33.1 ± 0.001 wt% at a reflux temperature of 200°C. Comparably to when the reflux was not used, the mass fraction of ethylene (C<sub>2</sub>H<sub>4</sub>) was 64.4 ± 0.002 wt%, around the double when the reflux was 300°C. Concerning H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>, they did not have such mass fractions and interest as ethylene, propene and acetylene.

The mass fraction of hydrogen gas was higher than in the PP pyrolysis investigation [20], probably during char formation. The overall low proportion of the non-condensable gas and the gas component concentration could be attributed to the operation temperature and the structure of the PS, yielding a lot of styrene. Regarding methane (CH<sub>4</sub>), it was not detected at all in all the experiments.

Comparably to other researcher works [17], [18], [23], [35]–[37], this work provides a quantitative analysis of all the gas components detected during the pyrolysis of PS with and without reflux.

### 3.2.3. Analysis of the liquid products

During the PS pyrolysis using reflux, the liquid product was found to be clear brown oils on the contrary to the liquid oil obtained without reflux, which was dark brown. It is interesting to note also that the liquid oil appearance changed with the reflux temperature.

The main liquid components obtained by pyrolysis and identified by GC–MS/FID, are presented in Table 3. The results were calculated relatively to all the detected components. It was calculated as follows:

$$\text{Mass fraction } i \text{ (\%)} = \frac{\text{mass detected } (i)}{\sum_{i=1}^n \text{mass detected } (i)}$$

For information and precision purpose, 93.3% of the injected oil in the GC-MS/FID was detected and quantified, which is very good.

The total list of all the liquid compounds identified and quantified in the liquid oils with and without reflux by the GC-MS/FID are provided in the table S1 in the Supporting Information for Publication.

The names of the compounds correspond to the tentative assignments provided by the MS database and have been compared with bibliographic data and chemical analytical standards.



The oil products consisted mainly of aromatics compounds. As shown in Fig.5, hydrocarbons with 7, 8, 9, 14, 15 and 16 carbons were the main species present in the liquid oil when the reflux was used. The highest production of C<sub>8</sub> occurred at a reflux temperature of 200°C with 81.9 ± 0.6 wt%; then, the mass yield decreased at 300°C to 80.2 ± 0.2 wt%; followed by another decrease at 400 °C with 78.1 ± 0.3 wt%. The mass fraction of toluene which represents the only C<sub>7</sub> exhibited a huge decrease from 13.5 ± 0.3 wt% at 200 °C to 3.1 ± 0.004 wt% at 300 °C, then it slightly increased to 3.9 ± 0.03 wt% at 400°C. Since the intervals coincide, it can be presumed that the variation of toluene was steady between 300°C and 400°C. The mass fraction of C<sub>14</sub> to C<sub>16</sub> showed a slight variation from 200 °C to 400°C, it decreased from 2.4 ± 0.01 wt% at 200°C to 1.6 ± 0.01 wt% at 300°C then it drastically increased to 12.8 ± 0.1 wt% at 400 °C. The mass fraction of C<sub>9</sub> increased from 2.2 ± 0.03 wt% at 200°C to 4.1 ± 0.01 wt% at 300°C then to 4.4 ± 0.03 wt% at 400°C.

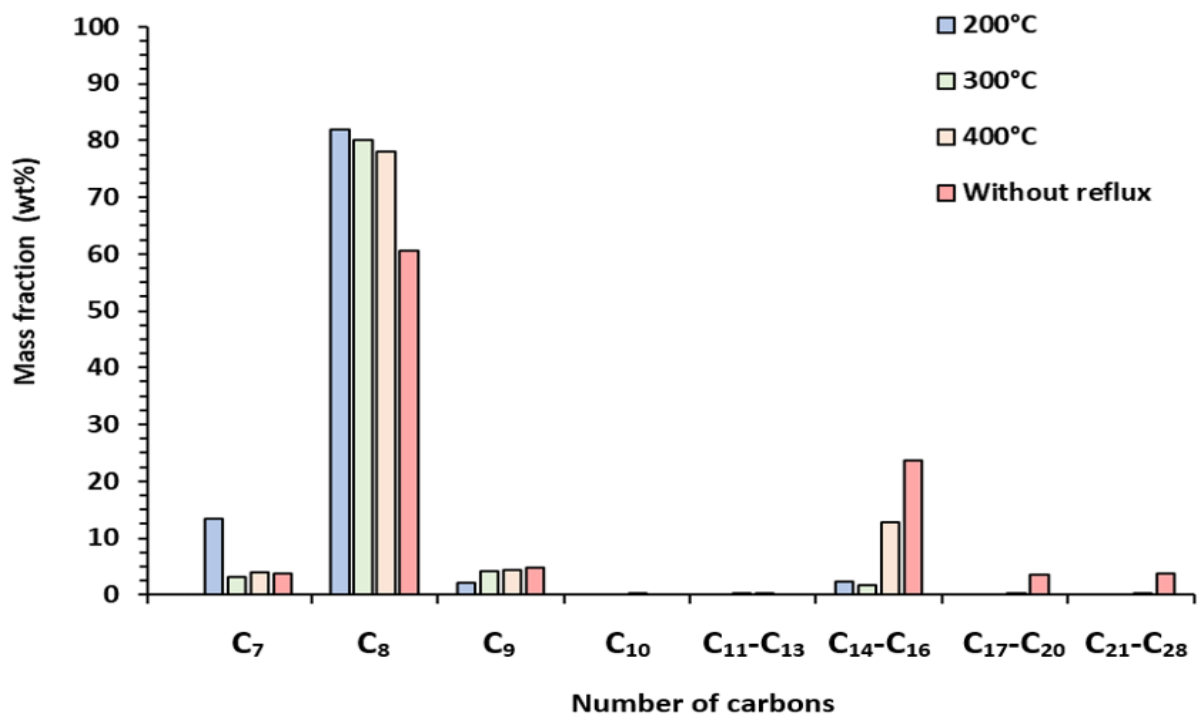
Ethylbenzene and the other compounds exhibited a negligible variation in the entire temperature range of reflux. Concerning xylene, it was detected in all the experiment.

When the reflux was not used, the mass fraction of C<sub>8</sub> considerably decreased to 60.5 ± 0.02 wt% and the mass fraction of hydrocarbons with 14 to 16 carbons increased to reach 23.6 ± 0.04 wt% which represents around the double of the mass fraction of C<sub>14</sub>-C<sub>16</sub> at a reflux temperature of 400°C, a ratio of 10 of the mass fraction at a reflux temperature of 200°C and a ratio of 15 of the mass fraction at a reflux temperature of 300°C.

Table 3 shows that in all the experiments, styrene is the most abundant component. The next most common components found are toluene and α-Methylstyrene. This observation was coherent with the findings of other researchers. In various studies [17], [18], [23], [35]–[37], the mass fraction of styrene in the liquid oil varies from 36% to 79%; whereas, in this study the mass fraction of styrene reached 81.2 ± 0.6 wt% of the liquid oil analyzed when the reflux was used (26.75 g of styrene per 100 g of polystyrene). This difference is probably due to differences in pyrolysis conditions. For instance, styrene mass fractions of 79% and 50.1 % have been obtained at 600°C (a temperature of 120°C higher than in this study) in a fluidized

bed reactor and a CSBR (conical spouted bed reactor) respectively [16], [38]; However, it is more interesting to use the reflux, since a very high yield of styrene can be achieved without having to heat the reactor to over 500°C.

One of the main cracking reactions in the PS pyrolysis is the chain strip cracking where the side functional group (styrene monomer) breaks off from the carbon backbone and forms the principal component in the liquid product. The main reason is that the styrene side groups break off from the carbon backbone of the polystyrene represents the principal reaction in the PS pyrolysis. Therefore, the possibility of obtaining valuable aromatic hydrocarbons, such as the three mentioned above, from plastic waste, makes pyrolysis more attractive than other recycling methods such as incineration and landfilling.



**Fig.5.** Liquid compounds mass fraction issued from PS pyrolysis and related to the initial mass of PS at various temperatures of reflux (200-300-400°C) and without reflux.

**Table 3.** List of the main compounds of PS pyrolysis identified in the liquid oils with and without reflux

Retention time (min)	Compound	Formula	Reflux temperature			Without reflux
			200 °C	300 °C	400 °C	
			Mass fraction related to the analyzed oil (wt.%)			
20.938	1-Decanol	C <sub>10</sub> H <sub>22</sub> O				
4.756	Toluene	C <sub>7</sub> H <sub>8</sub>	13.45	3.12	3.87	3.73
7.671	Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	0.79	0.19	1.64	1.17
8.726	Styrene	C <sub>8</sub> H <sub>8</sub>	<b>81.16</b>	<b>79.97</b>	<b>76.46</b>	<b>59.32</b>
9.89	Benzene, (1-methylethyl)-	C <sub>9</sub> H <sub>12</sub>	0.00	0.00	0.10	0.00
11.89	α-Methylstyrene	C <sub>9</sub> H <sub>10</sub>	2.21	4.06	4.30	4.80

### 3.2.4. Analysis of the char product

At the end of all the pyrolysis experiments, there was some char formation. Van Krevelen and Te Nijenhuis in their book [39] concluded that the tendency to form char in the decomposition of certain polymers depends on the chemical structure of the polymer. That tendency increases when the polymer contains some specific groups which are capable to react with hydrogen atoms of the polymeric structure.

The char produced was at the bottom of the reactor where the pyrolysis reaction took place. The mass yield of char from PS pyrolysis was between  $2.5 \pm 0.2$  and  $5.7 \pm 0.1$  wt%, which is much higher than that from PP pyrolysis (inferior than 0.5%) [20] and similar to others works [17], [18], [23], [36], [37]. The char from PS pyrolysis had also a distinctive appearance from that in the PP pyrolysis. PS pyrolysis char was in a black chips form with metallic reflections and a bright shine on their surfaces. The elements in the char were analyzed with a CHNS analyzer (Elementar vario cube CHNSO). The PS pyrolysis char consisted of only carbon (87.6%), hydrogen (11.09%) and sulfur (0.51%). The PS samples used were partly sulfured, but not the volatiles formed by pyrolysis. The sulfur concentrated then in the char by

increasing from 0.07% to 0.51%, which represents a factor of 7, and consequently the percentage of carbon slightly decreased in comparison to PS.

## 4. CONCLUSION

PS pyrolysis was studied in a semi-batch reactor using a reflux condenser. This work describes in detail the pyrolysis of PS with an emphasis on the importance of the reflux in controlling liquid and gaseous products compositions. This work presents the first quantitative GC-MS/FID analysis combined with  $\mu$ -GC applied to the PS pyrolysis using reflux. The pyrolysis results demonstrated the significant influence of the use of a reflux on the PS decomposition.

In the PS pyrolysis, the side group of polystyrene has very significant effects on the pyrolysis process and the products. The side group, styrene monomer, is the most produced component due to the chain strip cracking which represents the main reaction in the initial reactions. As a result, the mass fraction of styrene is 81.2 wt % of the total liquid oil analyzed when the reflux was at 200 °C and the pyrolysis reactor at 480°C. Compared to results in the literature (600°C), this reaction temperature is much lower, which highlights the interest of the reflux reactor.

The mass yield of non-condensable gases, oils and char was 7.3 to 12.5 wt% wt, 84.8 to 88 wt% and 2.5 to 4.7 wt% respectively. The composition of the gases consisted of H<sub>2</sub> and C<sub>2</sub>-C<sub>3</sub> hydrocarbon gases. The liquid oil contained high fraction of styrene, toluene,  $\alpha$ -Methylstyrene and other aromatics.

Therefore, the importance of the reflux was confirmed and approved in order to maximise the molecules of interest, especially those corresponding to styrene, toluene and ethylbenzene comparably to usual pyrolysis without reflux and at lower temperature, without catalyst.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org>

Table S1. List of the all the liquid compounds identified and quantified in the liquid oils with and without reflux by the GC-MS/FID.

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## Notes

The authors declare no competing financial interest.

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# ABSTRACT GRAPHIC

