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Analysis and control of products obtained from pyrolysis of Polypropylene using a reflux semi-batch reactor and GC-MS/FID and FT-ICR MS

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Abstract

Pyrolysis of plastic waste allows to produce liquid fractions, but their molecular weight distributions are typically very large whereas it would be interesting to focus on light hydrocarbons. In this study, the pyrolysis of polypropylene (PP) was investigated using a semi-batch, vertical glass reactor heated at 480 °C equipped with a reflux condenser. The pyrolysis was performed with and without a reflux condenser. The temperature at the top of this reflux condenser was ranged from 125 °C to 200 °C depending on the heating power at the wall of this condenser. The permanent gas yield (C₁ to C₄) ranged between 20.9 wt% and 25.8 wt% when the reflux was used. The gas contained mainly hydrocarbons with a carbon range from C₁ to C₄ and H₂ in a smaller extent. Their kinetic profiles followed a similar trend, i.e they exhibited a maximum with time.

The GC-MS/FID detected mainly olefinic hydrocarbons (olefins) with less than 28 carbons. The major hydrocarbons obtained were light and heavy naphtha cuts when the reflux was used. The range of light naphtha (C₅-C₇) was between 13.1 and 16.7 wt% and the range of heavy naphtha (C₈-C₁₂) was between 69.1 and 87.2 wt% of the total mass fraction detected. The experiments demonstrated that the presence of the reflux has a significant impact on the liquid and gas yields. It allows to narrow the molecular weight distribution range of the liquid, which was confirmed by FT-ICR MS. As a consequence, the molecules of interest are maximised, especially those corresponding to the naphtha cuts.

Key words: Pyrolysis; Polypropylene; Reflux; Semi-batch reactor; Recovery and waste management; Naphtha cuts.

1. Introduction

Plastics are one of the most widely used materials due to their various advantages and numerous applications in our daily life. Their consumption and production have increased worldwide every year and the waste generated by their production, transport and disposal creates a variety of environmental problems. In 2020, more than 450 million tons of plastics were produced worldwide and it is estimated that this demand will quadruple by 2050. However, the quantities of post-consumer plastics packaging waste sent to recycling did not exceed than 10% of the 9.2 billion tons of plastics that have been put into circulation since the 1950s [1]. The increased demand and production of plastics have led to the accumulation of large amount of waste in the final waste stream due to their low useful life. The incineration which is considered as an energy recovery route (quaternary recycling), is not favourable from an environmental and economic point of view because of the emissions associated with combustion products [2], [3]. Indeed in situations where plastics are incinerated, a net negative contribution of greenhouse gases is unavoidable [4]. Moreover, it should be kept in mind that the incineration of plastics introduces the need for costly pollution control measures, which are highly regulated in Europe by the EU Hazardous Waste Incineration Directive [5]. Indeed the incineration of plastics raises serious environmental and public health concerns [6]. Based on the type and composition of the plastic waste, incineration can lead to the emission of toxic volatile organic compounds (VOCs)[2]. Nevertheless, and from an economic point of view, incineration is still worthwhile and better option than landfill. Exhaust gas cleaning is also very sophisticated; thus, environment polluting species are not that big an issue because emitted exhaust gas from waste incineration plants are often cleaner than ambient air due to the intensive instalment used during the cleaning stages. This leaves the greenhouse gases issue as the main problem.

However, plastic waste constitutes a good source of carbon and its disposal in landfills or incineration constitutes a waste of valuable resources [7]. Mechanical recycling is economically feasible when costly separation steps are not required, that means when the plastic waste are not contaminated and not complex [2], [8]. Moreover, mechanical recycling of virgin plastic material can only be done 2 to 3 times because, after every recycling cycle, the strength of the plastic material is reduced gradually due

to thermal degradation [9]. In comparison to mechanical recycling and among different chemical recycling methods, pyrolysis has a high potential for heterogeneous and contaminated plastic waste material [10]. Pyrolysis is considered one of the most promising technologies for plastic waste feeds which are complicated to be recycled mechanically and are also difficult to depolymerize [2]. Chemical recycling is a positive route for future economy introducing major savings [11]. From an environmental point of view, pyrolysis can potentially reduce greenhouse gas (GHG) emissions [8]. Pyrolysis has an additional economic advantage as it does not require as many feedstock pre-treatment steps as other waste treatment methods. Depending on the choice of the reactor and operating conditions, the product distribution can be targeted towards a given fraction like gas, oils, or waxes. For instance, pyrolysis of polypropylene (PP) can be directed towards waxes at low temperatures, while gases and light oils can be obtained using high temperatures [12]. The liquid has always been attractive due to its properties and its potential use as chemical feed stock or fuel. However, the disadvantage of this liquid issued from the pyrolysis of the PP consist in the wide distribution of molar masses which make it less valuable. The main influencing factors of plastic waste 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 articles of Dogu et al (2021) [2], Kumar Jha et Kannan (2021)[13] and Anuar Sharuddin et al (2016) [14]. Nevertheless, very limited information can be found in the literature about the influence and the importance of using reflux on the pyrolysis oil composition [15]–[18]. Dobó et al [16] investigated the influence of reflux temperature in a range of 150–300 °C toward the yield of liquid oil during the pyrolysis of the typical plastic mix in the European Union in 2018 (mixture of PP, LDPE, HDPE and PS) [19]. They reported that the pyrolysis gas yield increases by lowering the reflux temperature. They also confirmed that although the pyrolysis oil yield is decreased by lowering the reflux temperature, the gasoline yield increases, as the heavy hydrocarbon molecules undergo a second cracking into the reactor for further molecule scissoring. Unfortunately, no quantitative analysis of liquid and the gaseous products were provided. Wajima et al [18] investigated the oil production from HDPE by thermal pyrolysis at 450 °C using a reflux condenser whose temperature varies from 150 °C to 200 °C and only the product oil was analysed semi-quantitatively by using GC/MS. They reported that the yield of oil increased and the residue decreased while the reflux temperature is increased, that means that the components with higher molecular weight can pass through the reflux zone, due to the higher boiling points [18].

In this article, the work focused on pyrolysis of polypropylene (PP), one of the most produced commodity plastics (after polyethylene) [20]. PP is a linear thermoplastic polyolefin partially crystalline and non-polar. Its properties are similar to polyethylene, except that it is slightly harder and more heat resistant. PP is made from the polymerization of propylene monomer, generally by two different: Ziegler-Natta polymerization or Metallocene catalysis polymerization.

The pyrolysis was achieved in a semi-batch reactor in an inert environment with a highlight on the evolution of gas as a function of time and the liquid obtained was analysed by GC-MS/FID and FT-ICR MS.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) offers unprecedented mass resolution and accuracy, allowing the complex composition of petroleum and its cuts fractions to be analysed at a molecular level. Accurate mass measurements define the unique elemental composition and DBEs (double bond equivalent) which facilitates material classification by heteroatom content and the degree of aromaticity [21], [22].

The main objective of this research is to understand the role of the reflux and its operating temperature on the yield and properties of the liquid and gas obtained from PP pyrolysis. The principle of the reflux consists in the separation of the gas mixture, in the reflux zone, by the selective condensation of the liquid, under continuous heat removal. Reflux condensation works as displayed in Fig. 1. A mixed vapor stream is continuously stripped of heavy components in up-flow, and the reflux liquid flow is enriched with these components. The principle of the reflux is similar to the conventional distillation. When the boiling temperature of the gas mixture is higher than the temperature of the reflux zone, the gas condenses and the liquid flows downward along the condensation tube walls of the reactor, while the light compounds whose boiling temperature is lower than the temperature of the reflux zone remain in the vapor phase and escape from the reactor to condense in the liquid traps.

More specifically, this study is intended to identify the conditions that allows obtaining a liquid with high content of naphtha cuts molecules (in this article, light naphtha is defined as molecules that comprise 5 to 7 carbon atoms whereas heavy naphtha molecules comprise 8 to 12 carbon atoms).

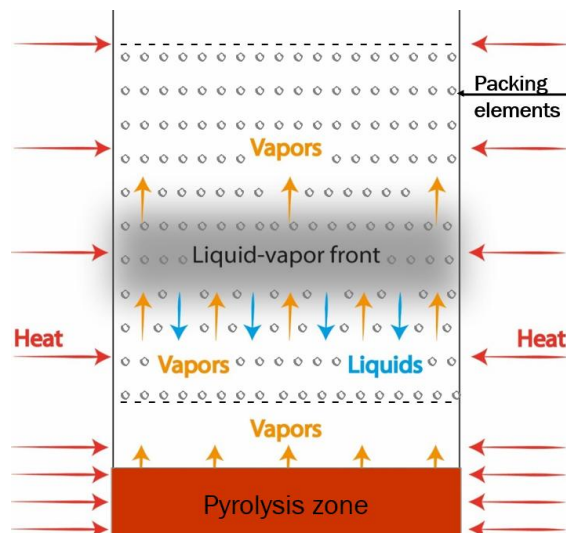


Fig. 1: Principle of the reflux used during the pyrolysis of PP.

2. Experimental

2.1. Materials

PP was provided by Total Petrochemicals (PPH9020) in the form of pellets (2-3 mm) and with the following properties: melting point of 165 °C and a density of 0.905 g/cm³. The use of virgin polymer (with no additives) aimed at better understanding the process of pyrolysis with reflux and then modelling the various phenomena in future works. Chemically neutral packing elements (SiC) were used in the reflux zone and they were purchased from ACM Advanced Ceramics-Materials GmbH in the form of 2 mm pellets. The dichloromethane (DCM) with a purity above 99.8% was used as solvent and was purchased from Fluka. The 1-decanol with a purity above 98% was purchased from Sigma Aldrich and chosen as internal standard. N₂ was provided by Messer, its purity was above 99.995 % and it was used as inert gas during the pyrolysis experiments. The viscosity of the liquid oil products was measured using a rotary rheometer provided by ARES/TA Instruments.

2.2. Thermogravimetric analysis (TGA)

PP pyrolysis was first studied by thermogravimetric analysis (TGA) using a Mettler Toledo Star^e instrument. About 5-6 mg of PP were used in each measurement. These samples were heated in a silica crucible at a constant heating rate between 5 and 15 °C/min operating in a stream of N₂ with a flow rate of 50 ± 0.5 mL/min from 30 ± 2 °C to 550 ± 4 °C.

2.3. Proximate and ultimate analysis

The proximate analysis was done by ASTM D3173-75 and the ultimate analysis was done by using a CHNS analyzer (Elementar vario cube CHNSO). The sample, which was about 1 mg, was placed in a tin crucible and then subjected to flash oxidation in the furnace. The gases produced are fed into the column by a helium stream, separated by GC and analysed by a TCD detector.

2.4. Pyrolysis setup

The pyrolysis experiments were carried out in a glass semi-batch reactor (height 30 ± 0.2 cm, internal diameter 5 ± 0.2 cm). The reactor was equipped with different thermocouples and an inert gas supply. Heat was supplied to the reactor and the reflux column using a heating wire of 2 mm of diameter purchased from Thermocoax SAS. A differential pressure sensor was used to detect flooding in the reflux zone during the pyrolysis process. An absolute pressure sensor and a safety valve were used to avoid an increase of absolute pressure that can lead to an explosion of the reactor.

In the first step, a fixed amount of plastic (20 g) was fed at room temperature at the start of the experiment into the reactor which was purged for 20 min with nitrogen gas having a flow rate of 100 ± 1 mL/min. The inert gas was continuously flowed through the system to eliminate the presence of oxygen. In laboratory conditions, it was preferable to use small quantities of plastics to avoid high needs in effective heating power. As soon as these steps were carried out, the system was then heated from ambient temperature to the desired setpoint temperature at the bottom part of the reactor (setpoint temperature of the heating wire: 500 °C). The flow of N_2 sweep gas was 100 ± 1 mL/min. For reproducibility reasons, three measurements for each reflux setpoint temperature were performed. The exit gas zone was heated at a higher temperature than the upper part of the reflux to avoid the solidification of waxes which could clog this zone at lower temperatures. S_iC pellets of 2 mm diameter were used as packing/filling elements to increase the contact surface between the liquid phase and the gas phase, thus improving the exchanges between the phases in the reflux zone. The temperatures were monitored by using K type thermocouples with an uncertainty of ± 2.5 °C for a range of temperature between, -40 °C and 333 °C and an uncertainty of $\pm 0.0075*|T|$ (according to the standards of class 2 - NF EN 60584-2 : 1993 or IEC 584.2 :1982). The main thermocouple T_0 was used to measure the temperature of the PP sample (that becomes liquid over 165 °C), three thermocouples (T_1 - T_2 - T_3) were also used to control longitudinal reflux temperature at 3 different positions; at the same position than T_2 , another thermocouple (T_5) was used to measure the external

wall temperature in order to determine radial temperature gradient and the last one (T_4) was used to control the temperature at the gas outlet. Obviously, three thermocouples of regulation in 3 different heating zones ($Tr_1-Tr_2-Tr_3$) were also used and were controlled by external PID controllers. The sample was held at the desired temperature till completion of the reaction. The time at the completion of reaction was noted when there was no more liquid oil flowing into the liquid collectors and there was no more gas detected in the μ -GC. It was approximately 210 minutes. The gas products passed through the reflux zone, which was maintained at a lower temperature than the reactor, which resulted in the heavier (i.e. high boiling point) components of the vapour being condensed and recycled back to the reactor for further cracking. Lighter compounds escaped the reflux column and entered two liquid collectors (the first at ambient temperature and the second at 0 °C by using ice). The schematic is provided in Fig. 2 and more details are provided in the supplementary materials (section A-0).

After completion of reaction, the liquid products that remained in the liquid collectors were weighed. Then, they were dissolved in DCM and analysed by GC-MS/FID (section 2.5.2). The reactor was cooled to ambient temperature and the residue was also collected and weighed. Then, the product yields were divided into three categories: permanent gas for hydrocarbons from one carbon to four carbons (C_1-C_4), heavy oil for hydrocarbons from eight carbons to twenty-eight carbons (C_8-C_{28}) and a third category that depends on the use of the reflux. This category might be light hydrocarbons with five carbons to seven carbons when the reflux was used and super heavy hydrocarbons compounds when the reflux was not used.

The calculations of the product yields were performed in equations (1), (2) and (3) as following:

Where: M_{PP} : initial mass of PP (20g); M_1 : Mass of the C_1-C_4 detected by the μ -GC; M_2 : Mass of the C_8-C_{28} detected by the GC-MS/FID and proportional to the mass weighted of liquid oil in the liquid collectors.

$$\text{Yield of permanent gas (C}_1\text{-C}_4\text{) (\%Y}_P\text{)} = \frac{M_1 \times 100}{M_{PP}} \quad (1)$$

$$\text{Yield of heavy oil (C}_8\text{ - C}_{28}\text{) (\%Y}_H\text{)} = \frac{M_2 \times 100}{M_{PP}} \quad (2)$$

$$\text{Yield of light naphtha (C}_5\text{-C}_7\text{) and/or heavy compounds (\%Y}_{LHC}\text{)} = 100 - Y_P - Y_H \quad (3)$$

It should be noted that the yield of light naphtha (C_5-C_7) and/or heavy compounds ($\%Y_{LHC}$) was determined precisely from the mass balance due to the fact that the μ -GC did not detect quantitatively

the hydrocarbons that comprise more than five carbons and the GC-MS/FID did not detect quantitatively the hydrocarbons with six and seven carbons. The presence of these category will be checked using the FT-ICR MS characterization and it will depend on the use of the reflux condenser.

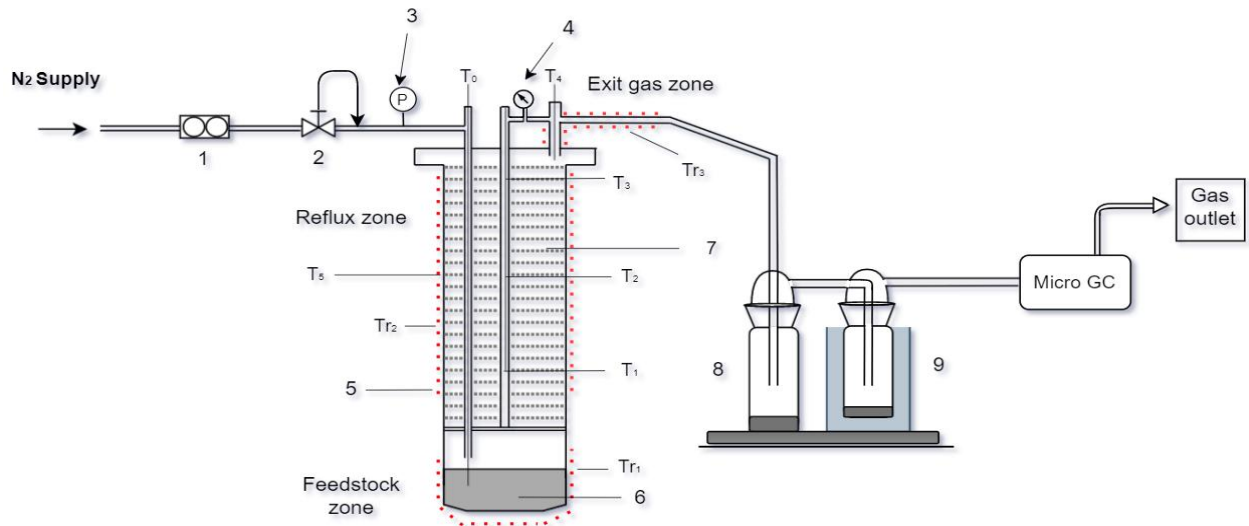


Fig. 2: Representation of the pyrolysis system with a reflux zone.

- (1) Mass flow controller; (2) safety valve; (3) absolute pressure sensor; (4) differential pressure sensor (pressure range from -50 Pa to +50 Pa); (5) heating wire; (6) PP sample; (7) Column packing (S₁C pellets of 2mm diameter); (8) First liquid product collector (at ambient temperature); (9) Second liquid product collector (using ice).

Measurement thermocouples: T_0 to T_5

T_0 : sample temperature; T_1 : temperature of the low reflux position; T_2 : temperature of the middle reflux position; T_3 : temperature of the high reflux position; T_4 : gas exit temperature; T_5 : external wall temperature of the reactor

Regulation thermocouples: T_{r1} to T_{r3}

T_{r1} : regulation temperature of the feedstock zone (pyrolysis regulation temperature)
 T_{r2} : regulation temperature of the reflux zone
 T_{r3} : regulation temperature of the exit gas zone

2.5. Characterization of pyrolysis products

2.5.1. Analysis of gas by micro-GC

The gases from the experiment were analysed using a μ -GC type Agilent 3000A coupled to three modules (A, B and C), thus, three streams of gases can be analysed simultaneously. Module A (Molsieve 5A (MS5A)) uses argon as the carrier gas, which measured N_2 , H_2 , CH_4 and CO . In module B (PoraPLOT U), helium is used as the carrier gas to measure CO_2 , C_2H_4 , C_2H_6 , C_2H_2 . In module C (Alumina), helium is used as the carrier gas to measure propylene, propadiene, methylacetylene, butane, butadiene and butene and its isomers. The parameters of micro-GC are summarized in supplementary material (A-1).

The external calibration used in μ -GC allows to define a molar fraction value for a given area value. The μ -GC is equipped with TCD detectors renowned for their linearity. So, it requires at least 3 calibration points. Three different bottles of mixed hydrocarbon standards provided by Air liquid were used to determine the response coefficients for each component likely to be present in the analysis of non-condensable gases from the pyrolysis process.

The gas yield was calculated thanks to the μ -GC analysis by integrating the temporal evolution profile of each species (as described in more details in supplementary material (A-2))[23]. The experiments were carried out at least three times and the result expressed in this paper is the average with standard deviation. The experiments were also complementary in terms of gas analysis. Indeed, the run time of gas analysis was 3 min, which corresponded to a difference of sample temperature of 25 °C between two consecutive measurements. Moreover, the gas analyses were slightly shifted during each reproducibility run to better define the gas production curves

2.5.2. Analysis of liquid products by GC-MS/FID

Liquid products were analysed using a GC-MS/FID and were dissolved in DCM. Others solvents were tested, but it was only with DCM that the extracted oil was soluble [24]. One μ L of this solution was then analysed with an Agilent 7890A Gas Chromatography system coupled to an Agilent 5975C TAD (Triple-Axis Detector) Series GC/MSD (Mass Selective Detector) system and a Flame Ionization Detector (FID). The solution was injected with a split ratio of 50 into an Agilent HP-5MS (diphenyl 5%, dimethylpolysiloxane 95%, non-polar, 30 m \times 250 μ m \times 0.25 μ m) column [25]. The HP-5MS was connected to the FID and the MS, thus allowing the quantification and the identification of products for the same injection. 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, it is summarized in supplementary material (C-1) and (C-2). The quantification of the compounds was estimated by internal calibration using the method of De Saint Laumer et al.[25]–[27], the details of the method is summarized in supplementary material (C-2). The internal standard used was 1-decanol because it is a linear carbon chain alcohol that cannot be produced by polyolefins and comes out halfway through the GC-MS/FID analysis. Therefore, it could be easily distinguished in the chromatogram.

2.5.3 Analysis of liquid products by FT-ICR MS

Ultra-high-resolution mass measurements of liquid products were performed in positive-ion mode with a 7 T FT-ICR mass spectrometer (Solarix 2XR, Bruker Daltonics, Bremen, Germany). As saturated hydrocarbons are expected from pyrolysis of polypropylene, atmospheric pressure chemical ionization (APCI) was employed as source of ionization. Indeed, this ion source demonstrates its ability to ionise saturated compounds such as n-paraffinic petroleum fractions by hydride abstraction mechanism using a short-chain alkane as a solvent/reagent [28]–[32]. To study pyrolysis products of PP by APCI FT-ICR MS, heptane was selected as solvent/reagent. Before analysis, each sample was centrifugated during 10 min at 13,000 g and only the supernatant was collected and diluted in heptane with a dilution factor of 1000.

APCI and instrument parameters were optimized by the FTMS-Control V2.3.0 (Bruker Daltonics) Software. Mass spectrometer was tuned and externally calibrated using a 50 mg.L⁻¹ mix of C₁₀, C₂₀-C₄₀ - alkanes (in heptane – Sigma Aldrich). Mass spectra were acquired over the 115 – 1000 m/z range with a 4 megaword time-domain in 2XR mode (transient of 1.12 s), and 50 scans were accumulated. One scan resulted from an ion accumulation time of 25 ms. Mass resolving power was around 500,000 at m/z 300. Each diluted sample was nebulized in the vaporizer chamber heated at 370 °C with a flow rate of 15 µL.min⁻¹ and an additionnal nebulizer gas set to 2.0 bar. The MS entrance was swept with a drying gas temperature at 220 °C and a flow rate of 3.5 L.min⁻¹, respectively. The corona needle is set to 4000 nA.

Software DataAnalysis 5.2 (Bruker, Daltonics) was used for internal calibration with [M-H]⁺ of alkanes. Only mass peaks with signal-to-noise ratio greater than 4 were kept in the mass list. Composer

software (Sierra Analytics, Modesto, CA) was used for ion assignment with the following search criteria:

$C_{1-100}H_{1-100}N_{0-2}O_{1-30}S_{0-1}$ -general formula, 0.5 ppm tolerance error, and a double bond equivalent (DBE) ranging from 0 to 40. Neutral DBE represent the number of double bonds and rings in a given neutral molecular formula and can be calculated by the following equation (4) for elemental formulae $C_cH_hN_nO_oS_s$:

$$\text{neutral DBE} = c - \frac{h}{2} + \frac{n}{2} + 1 \quad (4)$$

Pure hydrocarbons (HC) are the main family contributing to the MS signal and both M^{++} and $[M-H]^+$ are considered for HC content comparison between samples. Graphs of neutral double bond equivalent (neutral DBE) versus carbon number (#C) are plotted by in-house software (in JS). It allows displaying a point for each elemental composition with a size and a color depending on its abundance in the mass spectrum.

3. Results and discussion

3.1. Proximate and ultimate analysis results

Proximate analysis confirmed that the volatile matter corresponds to 100%, due to the absence of ash in PP samples. The sulfur in the PP samples may not be due to the fillers but rather to other ingredients that are added to the resin during the manufacturing even if the purchased PP was virgin and with slight impurities and additives [33]. Amounts of C, H, N and S of PP are given in Table 1.

Table 1: Characteristics of PP from proximate and elemental analysis

Proximate analysis (wt%)	
Moisture	0
Volatile matter	100
Fixed carbon	0
Ash	0
Ultimate analysis (wt%)	
C	85.48
H	15.42
N	0
S	0.45
O	0

3.2. Thermogravimetric analysis results

The thermal decomposition of PP has been studied by several authors using pyrolysis. Summarized results and detailed TGA and DTG procedure are available in the articles of Mortezaeikia et al. [34], Majewsky et al. [35] and De Blasio [36]. Mortezaeikia confirmed that the mass loss occurs almost totally in one step and the pyrolysis of PP at different heating rates starts at 327 °C and is almost complete at approximately 587 °C.

The thermogravimetric (TGA) and derivative TG (DTG) of this study are similar to the previous literature results [34]–[36]. They are presented for different heating rates and one final temperature in supplementary material (B-1). The mass loss exhibits a one-step degradation which indicates that there is only one major degradation reaction. These measurements confirm that the heating rate parameter has a slight effect on the final degradation temperature. The mass loss of PP starts around 350 °C and is complete at around 480 °C for a heating rate of 10 °C /min. The degradation temperature at which a mass loss of 50% (T_{50}) is reached is about 450 °C. These measurements allowed estimating the required regulation temperature of the pyrolysis reactor, i.e. around 500 °C.

3.3. Pyrolysis setup results

3.3.1. Parameters of the experiments

Each experiment was carried out at least three times and the result expressed in this study is the average with standard deviation. The experiment 4 which was also called « experiment without reflux » was performed with no packing elements and the reflux zone was heated at the same external temperature than the feedstock zone.

Table 2: Parameters of the experiments

Regulation and measurement temperatures for each experiment				
Temperature Experiment	Measurement T°	Regulation T°		
	Feedstock zone	Feedstock zone	Reflux zone	Exit gas zone
Experiment 1	480 ± 4 °C	500 °C	150 °C	200 °C
Experiment 2	480 ± 4 °C	500 °C	200 °C	250 °C
Experiment 3	480 ± 4 °C	500 °C	250 °C	300 °C
Experiment 4	480 ± 4 °C	500 °C	500 °C	500 °C
Fixed parameters				
Nitrogen flow		100 ±1 mL/min		
PP mass		20 ± 0.001 g		
Pressure		Atmospheric pressure with an uncertainty of 0.5%		

3.3.2. Temperature profiles

The temperature is an important parameter to be controlled during the studies of the thermal behaviour of PP. There is a lack of measurement of the sample temperature during the experiment as well as the thermal profile within the reactor in the literature, especially in pyrolysis with reflux and generally only the setpoint temperatures are given. Table 3 gives the stabilized temperatures of the pyrolysis setup when the reflux setpoint temperature is fixed at 200 °C and the exit gas zone at 250 °C, after 40 minutes of transition stage until reaching a stabilized temperature profile. It can be observed a slight difference between the setpoint and the measured temperatures. Longitudinal temperature gradient was also measured (Fig. 3) and compared with the setpoint temperatures. It can be noticed that when the reflux temperature increased, the gradient of temperature decreased. The temperature in the reflux zone showed a decreasing profile from the bottom to the top and while using the reflux, they condense and flow downward along the condensation tube walls, while the light components remain in the vapor phase.

Transverse temperature gradient ($\Delta T = T_5 - T_2$) was measured for all the experiments and was always less than 40 ± 2 °C after temperature stabilization. Due to the insulation, the gradient remained low and constant throughout the experiments.

At this level, it would be interesting to indicate that the reference temperatures of the experiments are now the T_3 temperatures corresponding to the minimum observed in the reflux zone.

Table 3. Stabilized temperatures during the pyrolysis of PP when the setpoint temperature of reflux was 200 °C

Regulation/ setpoint temperature	T_{r1}	500 °C
	T_{r2}	200 °C
	T_{r3}	250 °C
Measurement temperature	T_0	480 ± 4 °C
	T_1	330 ± 3 °C
	T_2	213 ± 2 °C
	T_3	154 ± 1 °C
	T_4	182 ± 2 °C
	T_5	258 ± 2 °C

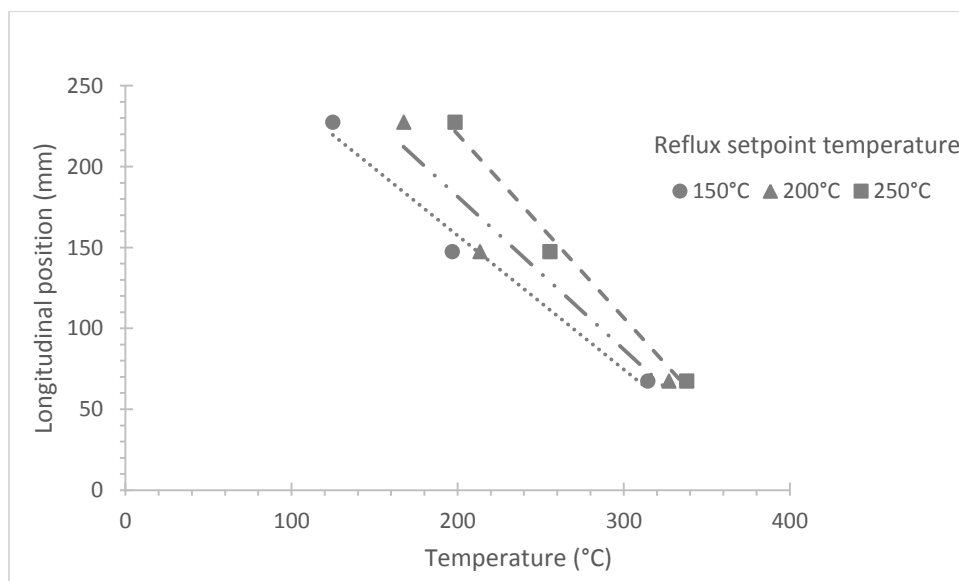


Fig. 3: Longitudinal gradient as a function of thermocouples position at different reflux zone setpoint temperatures (150 °C – 200 °C – 250 °C).

3.4. Characterization of pyrolysis products

The product yields of PP pyrolysis are shown in Fig. 4. The residue remaining in the bottom of the reactor and the liquid residue stuck in the reflux zone were less than 0.25 g (less than 1 % of the initial mass of PP). The liquid products were recovered from the two condensers. The products obtained in the condensers were transparent and slightly yellow in comparison to the liquid oil obtained without reflux which was viscous and close to a gel (Fig D-2 in supplementary material (D)); its dynamic viscosity at 20 °C was around 67 mPa.s when the shearing rate was 100 s⁻¹, while for the liquid oil obtained with reflux regardless of the reflux temperature, the dynamic viscosity was around 0.15 mPa.s when the shearing rate was 1 s⁻¹ (Fig D-1 in supplementary material (D)). The same observation was found by Gao [37].

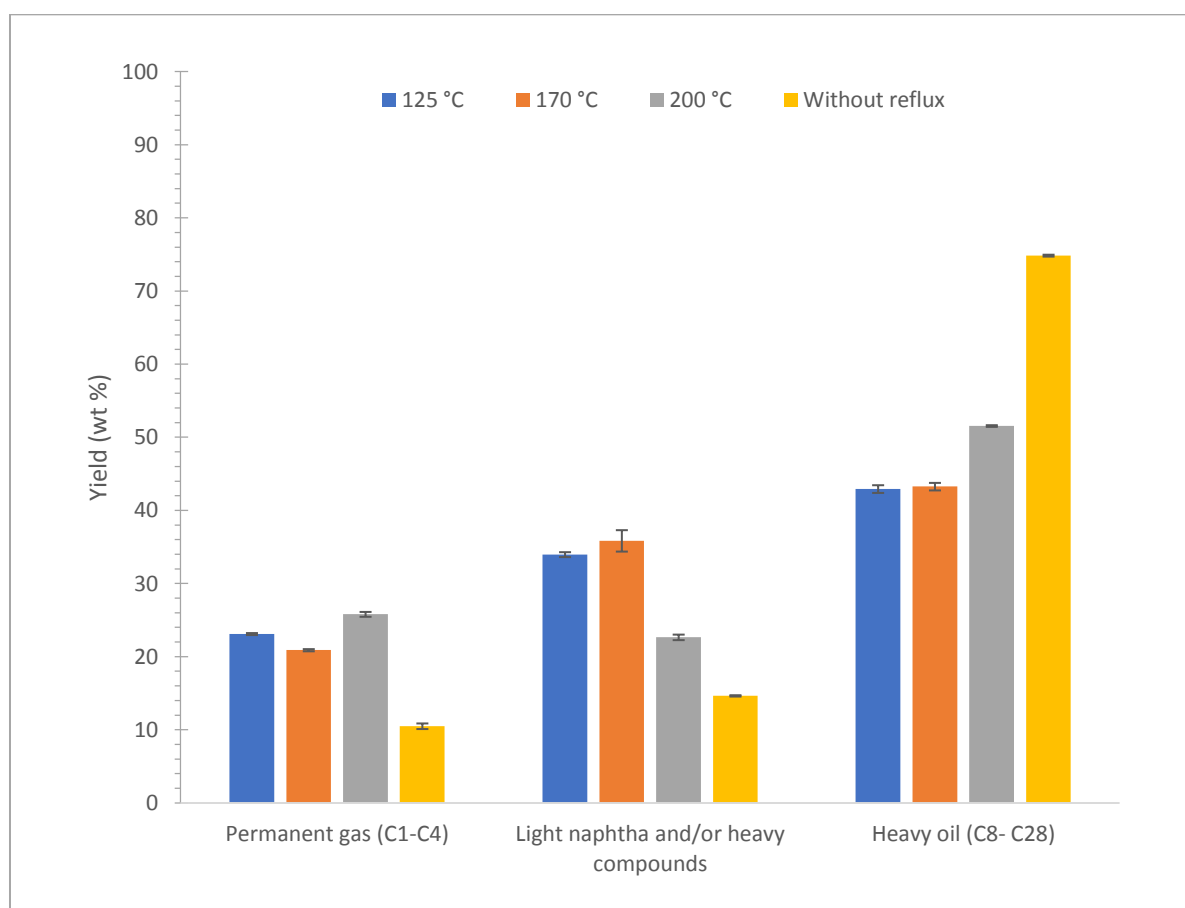


Fig. 4: Effect of the reflux temperature on product yields issued from PP pyrolysis at various temperatures of reflux (125 °C – 170 °C – 200 °C) and without reflux.

The yield of each product was calculated and the effect of the reflux temperature was studied. No significant effect on the permanent gas yield was observed while using the reflux; it could be due to

the small range of temperature measured at the top of the reflux zone (between 125 and 200 °C). However, the permanent gas (C₁-C₄) yields increased from 10.5 wt% without reflux to 23.1 wt% then it decreased to 20.9 wt% then it slightly increased to 25.8 wt% respectively at 125 °C, 170 °C and 200 °C (T₃ reflux temperatures). The yield of the third category (light naphtha (C₅-C₇) and/or heavy compounds) were deducted and determined precisely from the mass balance to complete it. Their yields were between 21.7 wt% and 35.8 wt% when the reflux was used but it dropped to 14.6 wt% when the reflux was no longer used. The heavy oil (C₈- C₂₈) yield increased when the reflux temperature varied between 125 °C and 200 °C: the yields increased slightly from 42.9 wt% at 125°C to 43.3 wt% at 170 °C then it increased to 51.5 wt% at 200 °C. The highest yield of heavy oil (C₈- C₂₈) products was produced without reflux and it was up to 74.9 wt%.

3.4.1. Analysis of volatile species by μ -GC

The gas analysed by μ -GC contained mainly hydrocarbons with one, two, three and four carbon atoms and a small extent of H₂. Propylene was the major compound in all experiments. The temporal evolution profiles of the main gases were plotted in Fig. 5. The time 0 corresponded to the start of the heating. Most gaseous species profiles followed a similar trend, i.e they exhibited a maximum with time. As shown in Fig. 5, the formation of gas started at 20 minutes when the sample temperature was around 470 °C and the maximum of all gas production was observed around 40 to 50 min for a sample temperature around 480 °C which corresponded to the maximal temperature of the degradation of the PP as shown during the TGA analysis (section 3.2).

The mass yields of all species at various temperatures were calculated and summarized in Fig. 6. Propylene and butadiene were the major gaseous species when the reflux is not used. In addition to these gases, butene and propadiene were produced when the reflux was used. The mass yield of the other gaseous compounds was minor and showed negligible variation in the whole reflux temperature range 125–200 °C.

When the reflux was used, the highest production of propylene and butadiene occurred at around 125 °C, they were respectively 7.8 ± 0.1 wt% and 8.1 ± 0.1 wt%. The mass yield of 1,3 butadiene also exhibited a variation from 8.1 ± 0.1 wt% at 125 °C to 5.0 ± 0.1 wt% at 170 °C, then an increase at 200 °C with 8.5 ± 0.6 wt%. Moreover, the mass yield of 1-butene also exhibited a variation from 2.3 ± 0.1 wt% at 125 °C to 4.4 ± 0.6 wt% at 170 °C, then a decrease at 200°C with 3.5 ± 0.3 wt%.

When the reflux was not used, the mass yield of propylene and butadiene were respectively 4.5 ± 0.1 wt% and 4.1 ± 0.1 wt%.

It should be noted that the molar fraction of all the gaseous species were measured relatively to the total gases measured (without N_2) by the μ -GC while for the mass yield of all the gaseous species, they were measured relatively to the initial mass of PP.

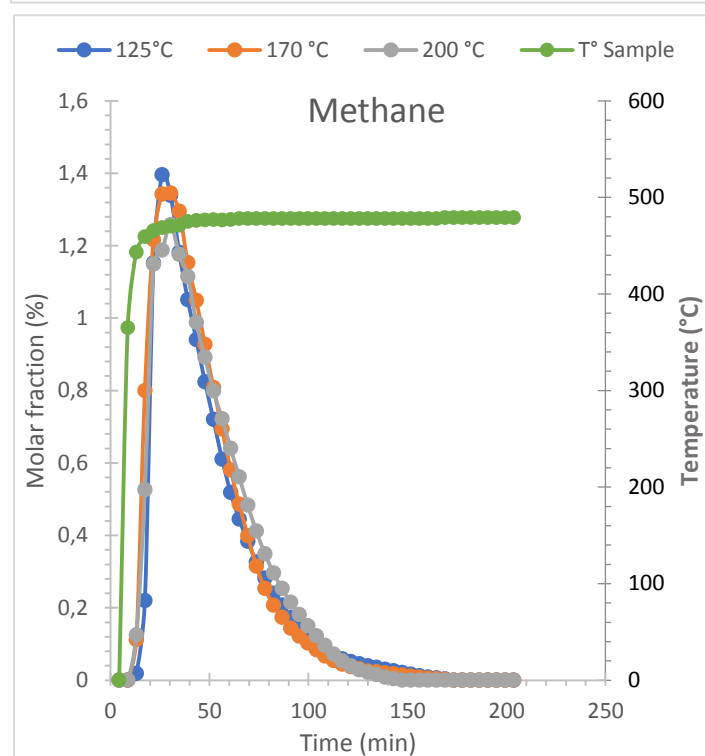
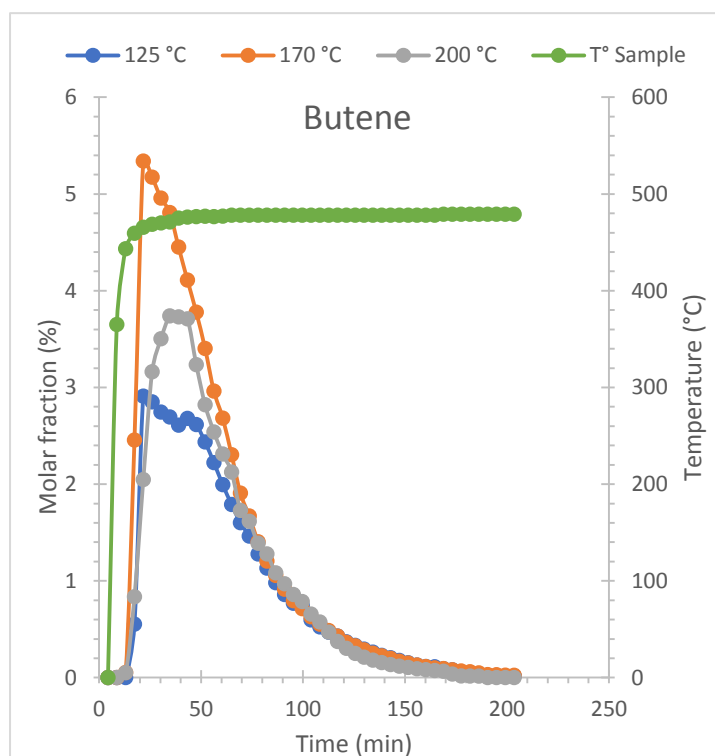
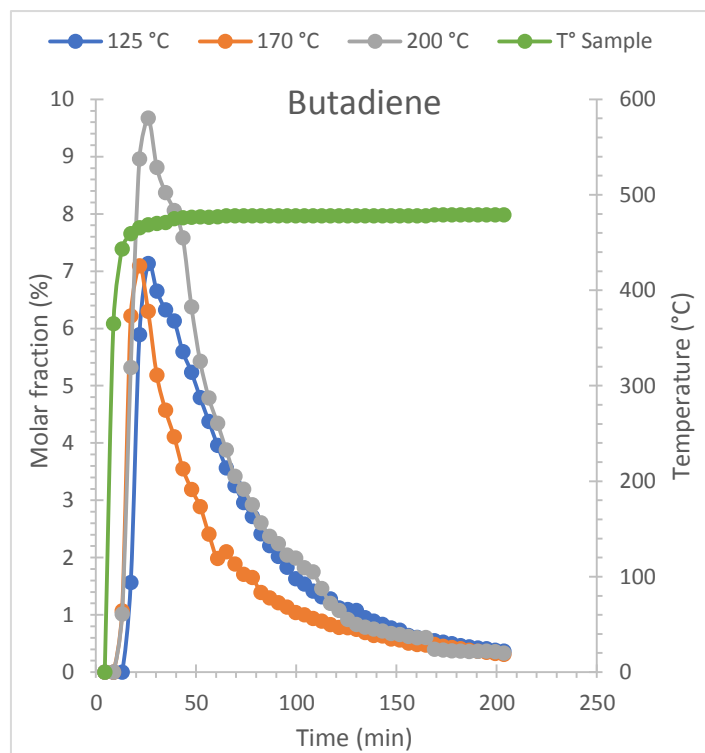
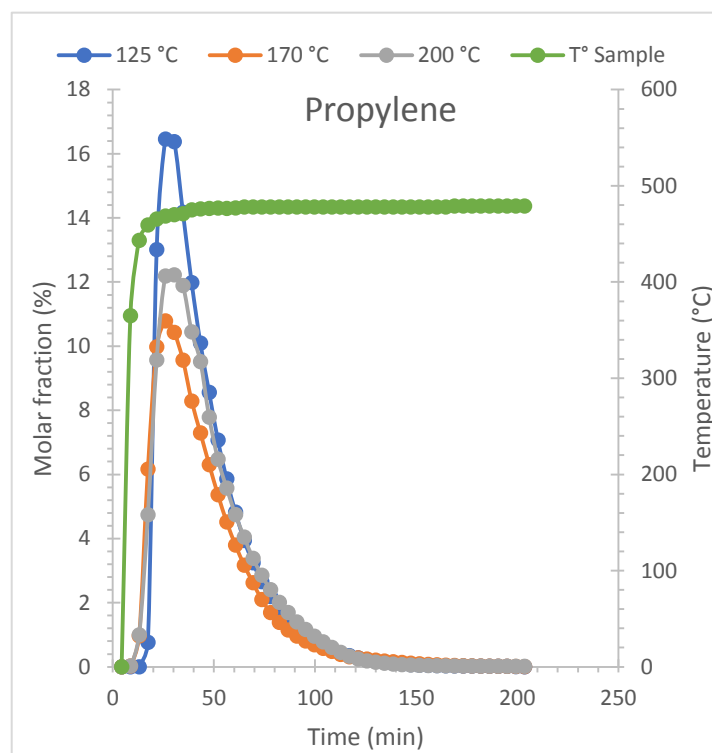


Fig. 5: Temporal evolution of the molar fractions (left Y-axis) of main gases (propylene, butadiene, butene and methane) during PP pyrolysis at various temperatures of reflux (125 °C – 170 °C – 200 °C) combined with the temporal evolution of the measured temperature (T° sample – right Y-axis) of the melting PP in the pyrolysis zone.

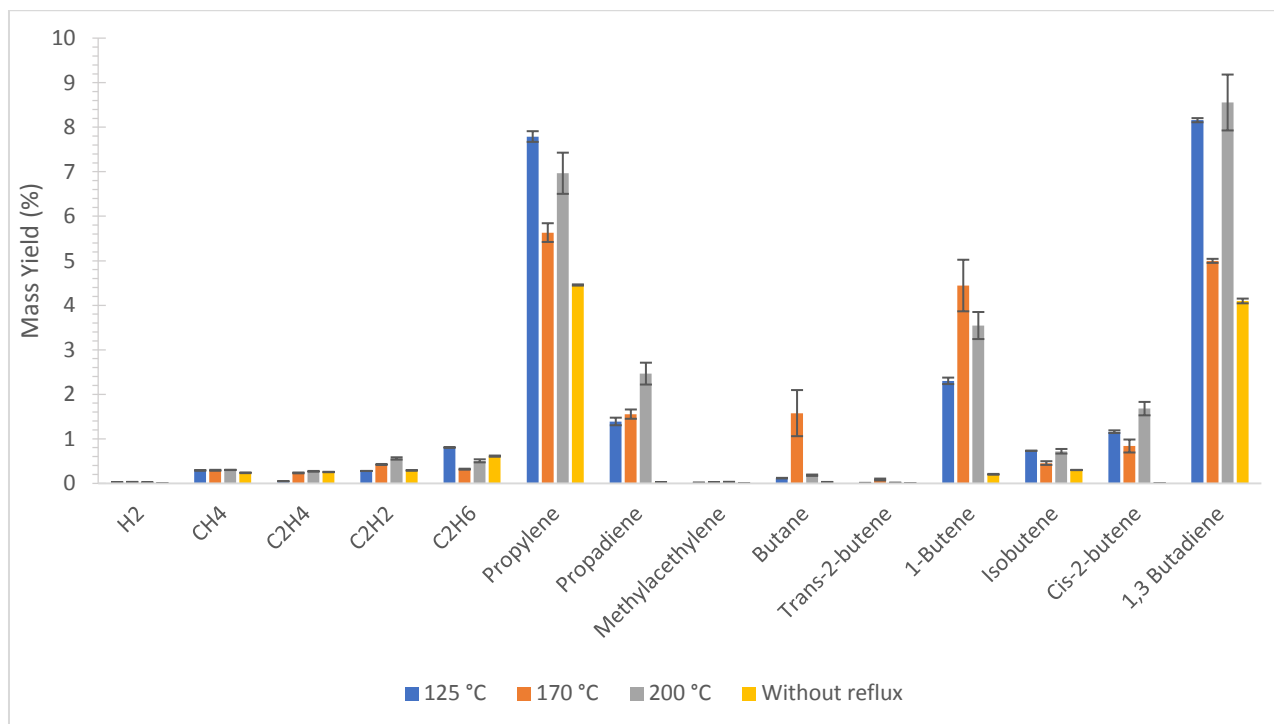


Fig. 6: Mass yield of gas compounds issued from PP pyrolysis at various temperatures of reflux (125 °C – 170 °C – 200 °C) and without reflux.

3.4.2. Analysis of liquid products by GC-MS/FID

The liquid oil products obtained from the pyrolysis of PP were dissolved in dichloromethane and analysed for their chemical compositions. As for the mass fraction, it was calculated relatively to the detected oils. It was calculated using the formula (5) as follows:

$$\text{Mass fraction } i \text{ (\%)} = \frac{\text{mass detected } (i)}{\sum_{i=1}^n \text{mass detected } (i)} \quad (5)$$

It should be noted that the detection rate of GC-MS/FID was between 22 and 64% (i.e only 22 to 64% of the liquid injected in the GC-MS/FID was analyzed, other compounds were identified by FT-ICR MS, see subsection 3.3.3).

Table 4 shows the list of the major compounds identified in the liquid oils obtained with and without using the reflux. All the compounds have one or two unsaturations, except one which has 4 unsaturations.

Table 4. List of the major compounds identified in the liquid oils with and without reflux

Retention time (min)	Compound	Formula	Reflux temperature (T ₃)			Without reflux
			125 °C	170 °C	200 °C	
27.41	1-Decanol	C ₁₀ H ₂₂ O	Mass yield related to the analysed oil (%)			
5.713	2-Pentene, 3-methyl-, (Z)-	C ₆ H ₁₂	2.09	0	0	0
5.758	2-Pentene, 4-methyl-, (Z)-	C ₆ H ₁₂	0	0	2.28	0
5.762	2-Butene, 2,3-dimethyl-	C ₆ H ₁₂		2.83	0	0
5.979	Cyclohexane	C ₆ H ₁₂	0	0	0.58	
6.106	Bicyclo[2.1.0]pentane, 1,4-dimethyl-	C ₇ H ₁₂	0	0	0	0.75
6.118	2-Pentene, 2,4-dimethyl-	C ₇ H ₁₄	0	0	2.06	0
6.221	1-Butene, 2-ethyl-3-methyl-	C ₇ H ₁₄	0	0	0.75	0
6.42	2-Hexene, 3-methyl-, (Z)-	C ₇ H ₁₄	0	0	5.28	0
6.892	2-Pentene, 3,4-dimethyl-, (E)-	C ₇ H ₁₄	0	0	1.92	0
7.118	2-Hexene, 3-methyl-, (Z)-	C ₇ H ₁₄	4.62	0	0	0
7.201	3-Hexene, 3-methyl-, (Z)-	C ₇ H ₁₄		8.68	7.19	0
7.316	1-Butene, 2-ethyl-3-methyl-	C ₇ H ₁₄	1.59	0	0	0
7.355	2-Hexene, 3-methyl-, (Z)-	C ₇ H ₁₄	0	2.66	0	0
7.427	2-Pentene, 2,3-dimethyl-	C ₇ H ₁₄	1.85	0	0	0
7.489	2-Pentene, 2,3-dimethyl-	C ₇ H ₁₄	0	2.90	0	0
7.491	2-Pentene, 4,4-dimethyl-, (E)-	C ₇ H ₁₄	0		2.32	0
8.283	1-Pentene, 3-ethyl-2-methyl-	C ₈ H ₁₆	1.49	0	0	0
8.338	2-Hexene, 2,3-dimethyl-	C ₈ H ₁₆	0	1.91	1.68	0
8.634	2-Pentene, 3-ethyl-2-methyl-	C ₈ H ₁₆	0	0	1.38	0
8.672	1-Heptene, 4-methyl-	C ₈ H ₁₆	0	0	0	0.92
8.836	2-Methyl-2-heptene	C ₈ H ₁₆	2.09	0	0	0
8.868	Heptane, 4-methyl-	C ₈ H ₁₈	0	0	6.34	0
8.877	2-Hexene, 2,5-dimethyl-	C ₈ H ₁₆	0	2.17	0	
8.929	Heptane, 4-methyl-	C ₈ H ₁₈	5.61	0	0	2.03
9.007	Heptane, 4-methyl-	C ₈ H ₁₈	0	6.40	0	
9.215	Cyclohexene, 3,5-dimethyl-	C ₈ H ₁₄	0	0	0	0.68
10.013	Bicyclo[3.1.0]hexane, 1,5-dimethyl-	C ₈ H ₁₄	0	0	0	0.52
10.487	2,2-Dimethyl-3-heptene trans	C ₉ H ₁₈	6.39	0	0	0
10.492	Cyclopentane, 1,1,3,4-	C ₉ H ₁₈	0	0	0	0.74

	tetramethyl-, cis-					
10.895	Heptane, 2,3-dimethyl-	C ₉ H ₂₀	0	0	0	0.22
10.55	Cyclopropane, (2,2-dimethylpropylidene)-	C ₈ H ₁₄	0	0	4.64	0
10.558	2,3-Dimethyl-3-heptene	C ₉ H ₁₈	0	10.47	0	
11.204	1,4-Dimethyl-1-cyclohexene	C ₈ H ₁₄	0	0	0	0.28
11.324	Cyclohexane, 1,3,5-trimethyl-, (1 α ,3 α ,5 α)-	C ₉ H ₁₈	0	0	0	1.83
11.477	2,3-Dimethyl-2-heptene	C ₉ H ₁₈	0	29.81	16.15	0
11.695	2,4-Dimethyl-1-heptene	C ₉ H ₁₈	10.89	7.80	10.92	31.77
12.026	3-Heptene, 4-ethyl-	C ₉ H ₁₈	4.99	0	0	0
12.095	2,4-Heptadiene, 2,4-dimethyl-	C ₉ H ₁₆	0	0	2.89	0
12.276	Cyclohexane, 1,2,3-trimethyl-, (1 α ,2 β ,3 α)-	C ₉ H ₁₈	13.06	0	0	2.42
12.318	Cyclohexane, 1,3,5-trimethyl-	C ₉ H ₁₈	0	10.85	7.85	0
12.776	3-Nonene, (E)-	C ₉ H ₁₈	4.01	0	1.92	0
12.878	Cyclopentane, 2-ethylidene-1,1-dimethyl-	C ₉ H ₁₆	0	0	0	0.74
12.965	Cyclohexane, 1,2,3-trimethyl-	C ₉ H ₁₈	0	0	2.61	0
13.229	Cyclohexene, 3,3,5-trimethyl-	C ₉ H ₁₆	0	0	0	0.39
13.716	3-Octene, 2,2-dimethyl-	C ₁₀ H ₂₀	0	0	0	1.07
13.834	4-Nonene	C ₉ H ₁₈	2.38	1.72	0	0
13.844	3-Heptene, 4-ethyl-	C ₉ H ₁₈		0	1.81	0
13.93	2,3-Dimethyl-3-heptene, (Z)-	C ₉ H ₁₈	5.05	0	3.18	0
14.56	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, [1R-(1 α ,2 α ,5 α)]-	C ₁₀ H ₁₈	0	0	0	0.33
17.866	Benzene, 1,2,4-trimethyl-	C ₉ H ₁₂	1.65	2.18	0	0
17.907	Nonane, 2-methyl-3-methylene-	C ₁₁ H ₂₂	0	0	0	0.25
18.254	Decane, 2,6,7-trimethyl-	C ₁₃ H ₂₈	0	0	0	0.92
18.32	3-Ethyl-3-methylheptane	C ₁₀ H ₂₂	8.5	6.44	2.35	0
18.41	Decane, 4-methyl-	C ₁₁ H ₂₄	0	0	0	1.00
20.909	5-Ethyl-1-nonene	C ₁₁ H ₂₂	0	0	0	4.36
20.942	1-Tetradecene	C ₁₄ H ₂₈	0		0.69	
21.063	1-Decene, 2,4-dimethyl-	C ₁₂ H ₂₄	0	0	0	3.59
21.105	1-Tridecene	C ₁₃ H ₂₆	0	0	1.03	0
28.504	1-Nonadecene	C ₁₉ H ₃₈	0	0	0	6.79
28.525	3-Eicosene, (E)-	C ₂₀ H ₄₀	0	3.17	5.7	0
28.761	1-Heptadecene	C ₁₇ H ₃₄	0	0	0	3.77
29.031	9-Eicosene, (E)-	C ₂₀ H ₄₀	0	0	0	5.73
29.856	E-7-Octadecene	C ₁₈ H ₃₆	0	0	0	0.33
30.677	7-Octadecyne, 2-methyl-	C ₁₉ H ₃₆	0	0	0	1.10
31.192	2,4,6-Tris(cyclohexyl)hept-1-ene	C ₂₅ H ₄₄	0	0	0	0.81
32.79	4-Methyldocosane	C ₂₃ H ₄₈	0	0	0.45	0
33.052	Tetradecane, 2,6,10-trimethyl-	C ₁₇ H ₃₆	0	0	1.02	0
33.291	5-Methyl-Z-5-docosene	C ₂₃ H ₄₆	0	0	0.27	0
34.805	2-Methyl-Z-4-tetradecene	C ₁₅ H ₃₀	0	0	0.65	0
35.071	5-Eicosene, (E)-	C ₂₀ H ₄₀	0	0	0	1.12

35.282	3-Eicosene, (E)-	C ₂₀ H ₄₀	0	0	0	0.61
35.549	1-Docosene	C ₂₂ H ₄₄	0	0	0	3.35
35.837	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	C ₂₀ H ₄₀	0	0	0	0.58
36.764	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-	C ₂₅ H ₄₈	0	0	0.69	0
37.463	2,4,6-Tris(cyclohexyl)hept-1-ene	C ₂₅ H ₄₄	0	0	0	0.56
40.373	Cyclopentane, (4-octylododecyl)-	C ₂₅ H ₅₀	0	0	0.34	0
40.389	1-Docosene	C ₂₂ H ₄₄	0	0	0	2.24
41.064	Cyclopentane, (4-octylododecyl)-	C ₂₅ H ₅₀	0	0	0	2.80
41.574	3-Heptadecene, (Z)-	C ₁₇ H ₃₄	0	0	0	2.03
41.83	Cyclohexane, 1,1'-(2-tridecyl-1,3-propanediyl)bis-	C ₂₈ H ₅₄	0	0	0.13	0
42.174	Cyclopentane, 1,1'-[3-(2-cyclopentylethyl)-1,5-pentanediy]bis-	C ₂₂ H ₄₀	0	0	0.17	0
42.829	Cyclopentane, 1,1'-[3-(2-cyclopentylethyl)-1,5-pentanediy]bis-	C ₂₂ H ₄₀	0	0	0	0.62
45.995	Cyclohexane, 1,2,3,4,5,6-hexaethyl-	C ₁₈ H ₃₆	0	0	0	0.82
47.12	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-	C ₂₅ H ₄₈	0	0	0	7.93
51.85	Cyclohexane, 1,1'-(2-tridecyl-1,3-propanediyl)bis-	C ₂₈ H ₅₄	0	0	0	4.01

The oil products consisted of alkanes, alkenes, alkynes and cycloalkanes compounds. As shown in Fig. 7, the major compounds included a range of hydrocarbons from C₇ to C₁₀ when the reflux was used. It appeared that C₇, C₈ and C₉ were the major species present in the liquid oil when the reflux was used. The highest production of C₉ occurred at 125 °C with 71.2 ± 2.2 wt%; then, the mass fraction decreased at 170 °C to 60.5 ± 1.9 wt% followed by another decrease at 200 °C with 46.8 ± 1.9 wt%. The mass fraction of C₈ exhibited a variation from 125 °C to 200 °C, it increased from 9.3 ± 1.5 wt% at 125 °C to 11.0 ± 0.8 wt% at 170 °C then to 14.9 ± 1.6 wt% at 200 °C. Since the intervals overlap, it could be assumed that the variation was constant. The mass fraction of C₇ showed no variation from 125 °C to 170 °C, but it increased when the reflux temperature was increased to 200 °C with 16.3 ± 0.5 wt%. The mass fraction of the other compounds showed a negligible variation in the whole temperature range 125 °C–200 °C.

When the reflux was not used, the mass fraction of C₉ brutally decreased to 38.8 ± 0.9 wt% and hydrocarbons with more than 17 carbons were the major species present in the liquid oil. The mass fraction of C₁₇ - C₂₀ and C₂₁ - C₂₈ were respectively around 23.0 ± 0.8 wt% and 22.5 ± 1.9 wt%.

The major hydrocarbons obtained were heavy naphtha cuts (C_7 - C_{10}) when the reflux was used. The range of heavy naphtha was between 69.1 and 87.2 wt% of the total mass fraction detected by the GC-MS/FID. When the reflux was not used, the oil products were chiefly composed by 54.1 wt% of heavy naphtha and 45.5 wt% of heavy compounds (C_{17+}). This liquid product with C_{17+} could be objected to further process to extract some valuable components for industry, and also could be cracked to produce lighter fuel fractions [38].

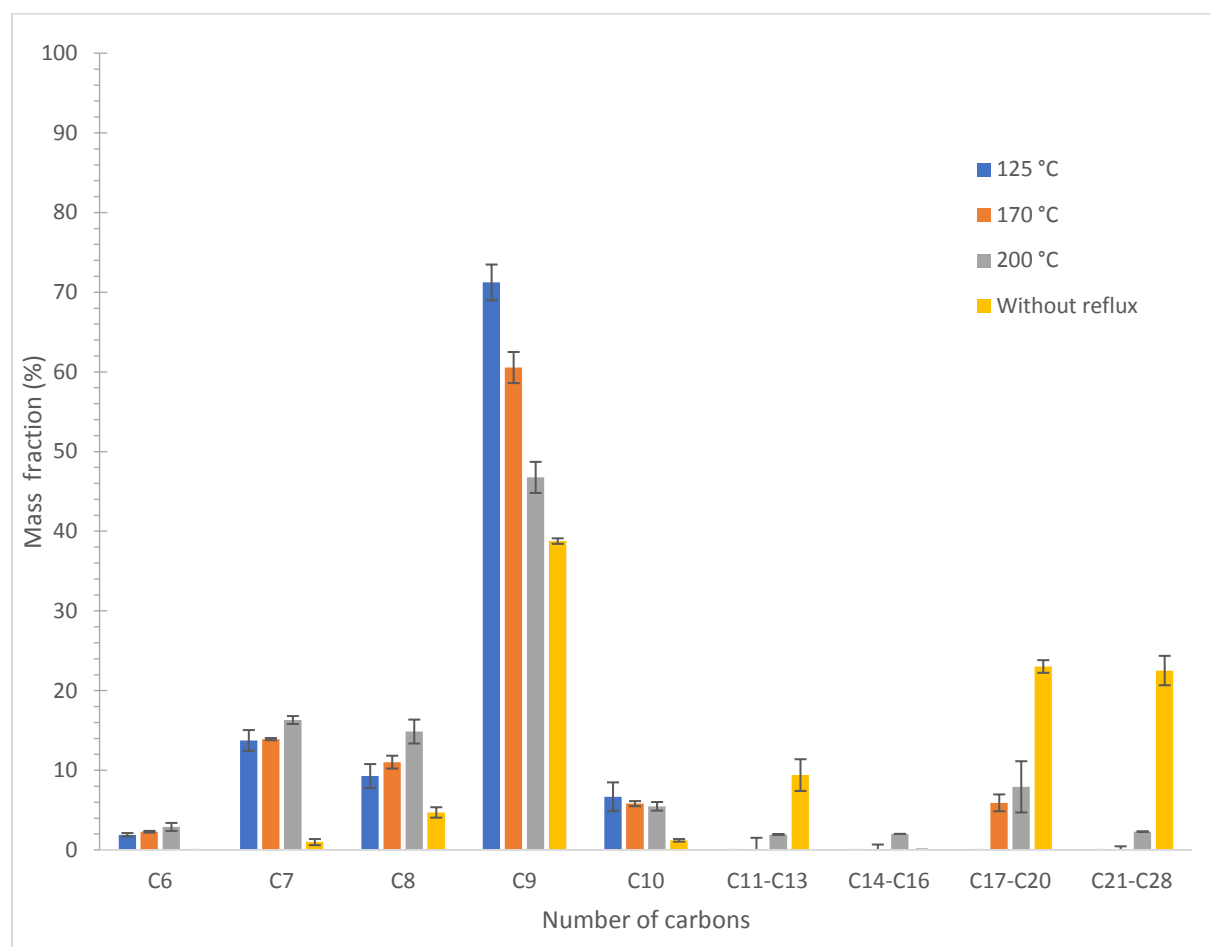


Fig. 7: Mass fraction of liquid compounds issued from PP pyrolysis at various temperatures of reflux (125 °C – 170 °C – 200 °C) and without reflux.

The use of reflux leads directly to lighter fractions like naphtha that is often used in steam cracker to produce light olefins (ethylene, propylene...). The heavy components while using the reflux condense and flow downward along the packing material, while the light components remain in the vapor phase. With increasing the temperature of reflux zone, the components with higher molecular weight can pass through the reflux zone despite their higher boiling points. In fact, under the conditions explored, the

reflux temperature does not have that much influence on the distribution of the products, which was unexpected.

Moreover, the heavy compounds (C_{28+}) are not seen in the GC-MS/FID analysis. The same applies to hydrocarbons with 5, 6 and 7 carbons (light naphtha). They are not detected qualitatively. Both are counted in the remaining fraction of the mass balance as yield of light naphtha and/or heavy oil. To overcome this ambiguity and since this category of products is estimated by mass balance, we use the FT-ICR MS as a characterisation technic to identify the exact composition of this category, depending on the use of the reflux or not. The analysis of the liquid products by the FT-ICR MS characterization is described in the following section.

3.4.3. Analysis of liquid products by FT-ICR MS

The pyrolysis oils were analysed via FT-ICR MS using APCI (Atmospheric Pressure Chemical Ionization) as ionization source in positive ion mode (+). APCI (+) allow to ionize less polar species such as hydrocarbons, especially saturated hydrocarbons. Moreover, APCI (+) offers higher reproducibility than electrospray (ESI), due to the lower selectivity of the APCI towards ionization compounds, which can significantly affect the ionization process and subsequently biases the pyrolysis oil analysis by ESI [25], [39]–[41].

FT-ICR MS does not only provide a detailed characterisation of the chemical composition, it also helps to complement the GC-MS/FID by giving access to bigger oil components. This is crucial for evaluating the reflux efficiency to control product composition.

The DBE reflects the “unsaturation degree” of molecules. It is higher for unsaturated molecules with a lower H/C ratio. The neutral DBE versus carbon number of HC detected in liquid oil issued from reflux at 125 °C and without reflux are evaluated and plotted in Fig. 8. The dot size and colour are relative to the MS abundance of each compound. First of all, it is clear that much less diversity of HC when reflux was activated. The main differences observed between these two conditions is the extent of the carbon chain for low unsaturated species. With reflux at 125 °C, the main components range from C_9 to C_{20} while without reflux, the products range from C_9 to more than C_{50} . At intermediate temperatures, the reflux is already efficient in producing less spread carbon chain compounds but with higher carbon content range than at 125 °C. A slight wider DBE distribution is exposed for liquid oil without reflux (ranging 0–13 and carbon atoms up to 65) while the liquid oil issued from reflux at 125 °C has DBEs

from 0 to 11 and a carbon range between 7 and 35 (mostly lower than 20). For liquid oil issued from reflux at 125 °C, compounds with DBE of 1,2,3 and 4 are more abundant, being in majority the unsaturated hydrocarbons than tend to be the naphtha cuts with a carbon range number between 7 and 20. For liquid oil without reflux, the compounds with a DBE of 2 are more abundant followed by compounds with DBE=3 then with compounds with DBE=1 and 0 with a lower abundance. It corresponds to a mix of alicyclic hydrocarbons and heavy compounds (alkanes, alkenes...). With the use of the reflux, the DBE increased, which indicates that the cracking of PP was accelerated by the secondary reactions that promoted the creation of unsaturated compounds. For the other reflux temperatures (170 °C and 200 °C), the plots of their DBE versus carbon number is presented in the supplementary material (section E).

It is important to notice the effect of the reflux on the distribution of species. As confirmed above, much wider range of species is highlighted by FT-ICR MS, from C₉ to C₃₀ in liquid products with reflux, whereas species up to C₇₀ without reflux.

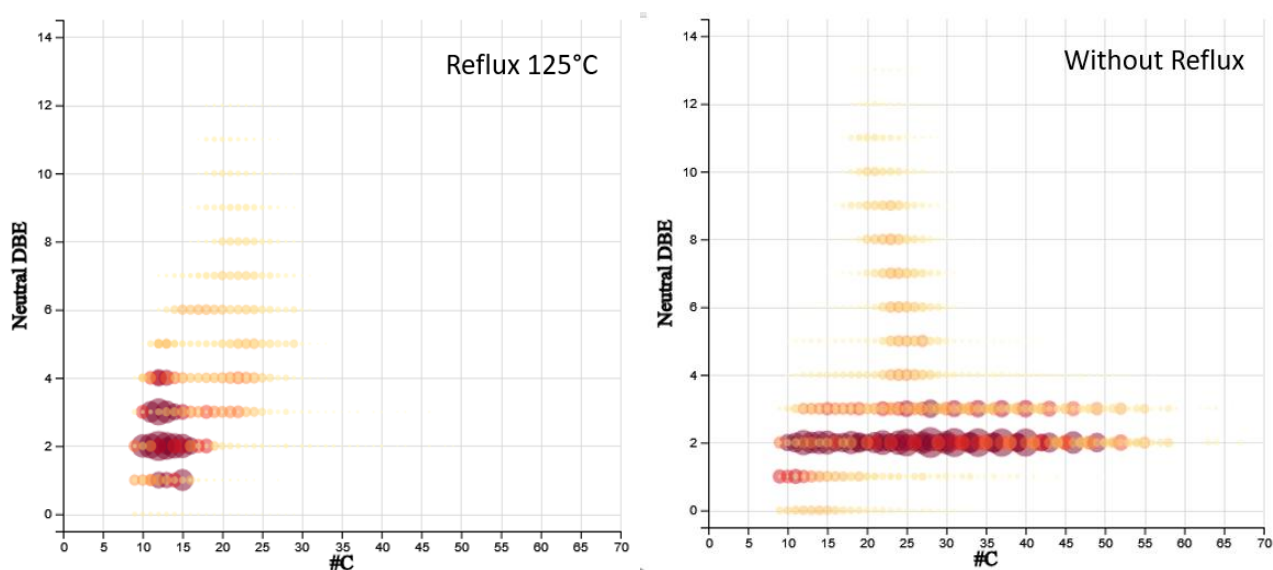


Fig. 8: Plots of double bond equivalents versus carbon number for pyrolysis liquid oil samples, shown as a function of a reflux temperature (125 °C) and without reflux.

FT-ICR MS demonstrated and confirmed that when the reflux was the fraction that we called light naphtha and/or heavy compounds was mostly light naphtha, whereas without reflux, it was mostly heavy compounds. Therefore, we can confirm that with reflux, the range of light naphtha was between

13.1 and 16.7 wt% Hence, the use of reflux has allowed to narrow the molecular weight distribution of hydrocarbons and the molecules of interest (naphtha cuts : light and heavy naphtha) were maximised.

4. Conclusion

The pyrolysis of PP was investigated in a vertical glass and tubular batch reactor using a reflux condenser. This study provides details about the pyrolysis of a virgin plastic (PP) where the importance of the reflux to control products compositions is the main focus as well as the online gas profiles and quantitative analysis of liquid products. To the best of our knowledge, this article presents the first quantitative GC-MS/FID analysis combined with very high resolution mass spectrometry analysis (FT-ICR MS) and an online monitoring of gas emission (μ -GC) applied to the pyrolysis of polypropylene using reflux. These two analytical methods (GC-MS/FID and FT-ICR MS) are very complementary and are needed to assess and confirm the presence in majority of the light hydrocarbons species when the reflux is used. The focus on online monitoring of gas emission lies on helping researchers in the construction of a comprehensive kinetic model of PP pyrolysis with reflux in future works. The pyrolysis results showed that the use of a reflux condenser influenced strongly the PP decomposition. Propylene is the main gas detected in all experiments, followed by butadiene. The characterization of liquid products achieved by GC-MS/FID showed that the major compound produced was C_9 with a mass fraction of 71.2 wt% at 125 °C of reflux temperature. The characterization of liquid products by FT-ICR MS confirmed the importance of the use of a reflux to control products composition by showing that the hydrocarbons compounds issued from the pyrolysis without reflux can reach 65 carbons unlike the hydrocarbon compounds issued from the pyrolysis with reflux that do not exceed 35 carbons, even if the temperature range between 125 °C and 200 °C did not have that much influence on the distribution of the products.

Therefore, it could be shown that the molecular weight distribution of hydrocarbons could be narrowed when the reflux was used and we could produce hydrocarbons with a narrow distribution of light

molecular weight (MW) compounds which are more highly valuable. Consequently, the molecules of interest were maximised, especially those corresponding to the naphtha cuts.

5. Acknowledgement

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