

Feedstock Recycling of Plastic Waste

Abstract

The thermal pyrolysis of polystyrene (PS) and acrylonitrile-butadiene-styrene (ABS) from waste of electrical and electronic equipment (WEEE) was investigated by thermogravimetric analysis coupled with differential scanning calorimetry (TG/DSC). The experiments were performed under dynamic and isothermal conditions in inert atmosphere. Virgin PS with two different molecular weight distributions were studied and compared to waste PS. The thermal degradation of the waste plastics under air was studied as well.

The TG results showed that the decomposition of waste PS occurs at higher temperatures than that of virgin PS. Waste polystyrene showed two degradation peaks, while virgin PS presented only one. Waste ABS decomposes in two degradation peaks as well. The TG results were used to study the kinetics of the decomposition of virgin PS and of waste plastic. The degradation of virgin PS is well described by a one component degradation model. The degradation of waste PS and ABS is well described by a two pseudo-component degradation model.

The pyrolysis of PS in a bench-scale reactor was also studied and compared with virgin polystyrene. The products were analysed using gas chromatography. In terms of liquid yield, both PS samples produce in majority hydrocarbons in the range of C₇ to C₉, which may be used as feedstock for the chemical industry. C₈ hydrocarbons are produced in higher quantity and are mostly constitute by styrene. These results show the possibility of the introduction of waste PS in a Circular Economy approach.

Keywords: Circular Economy, Thermal Pyrolysis, WEEE plastic, Polystyrene, Acrylonitrile-butadiene-styrene, Kinetic model

1. Introduction

The waste of electrical and electronic equipment (WEEE) is currently considered to be one of the fastest growing waste streams in Europe.^[1] The quantity of WEEE amounts to 9.5 million tonnes per year, of which 1.2 million tonnes are plastic materials. Polystyrene (PS) and Acrylonitrile-butadiene-styrene (ABS) are plastics present in WEEE.^[2] The challenge of recycling WEEE plastics lies on the complicated recycling process due to the existence of diverse plastic materials and additives.^[2] Pyrolysis is a promising route for plastic waste treatment because it permits to treat mixed and unwashed plastic waste and to convert it into valuable feedstock for the chemical industry.^[4]

The thermal degradation can be studied using the TG/DSC analysis. One single degradation peak has been observed for virgin ^[5] and for waste PS ^[6]. Experiments have been performed in laboratory scale reactors. Achilias *et al.* obtained for the pyrolysis of virgin polystyrene at 510 °C in a fixed bed reactor 91.8% liquid product, 2.5 % gas and 5.7 % char.^[7] The pyrolysis of waste polystyrene has also been studied and liquid yields between 65.71 % and 95.79 % have been obtained.^[8,9] Zhang *et al.* and Lee *et al.* reported styrene, dimer, α -methylstyrene, toluene, ethylbenzene as main liquid products.^[10,11] The gaseous products of waste PS decomposition are found to be pentane, 2-methyl-1-pentene, 1-pentene, 1-heptene, hexane, benzene, toluene,

octane, styrene and ethylbenzene. [8] Various authors observed a single degradation peak for virgin ABS. [12,13] The degradation of ABS found in WEEE containing brominated compounds as flame retardants and antimony trioxide as a synergist showed two degradation peaks. [14]

Diverse authors have studied the kinetics of the degradation mechanism of polystyrene and ABS using different models. The reported activation energies for virgin PS vary between 190 and 262 kJ/mol under dynamic conditions. [5,9,15,16] Kiran *et al.* reported an activation energy of 269 kJ/mol for waste PS.[17] For waste ABS, the reported activation energies for virgin ABS vary between 121.6 and 332 kJ/mol under dynamic conditions [9,16,18].

Thus, the objective of the present work is to study the thermal degradation of WEEE PS and ABS by using a TG/DSC analysis and to perform the thermal pyrolysis of waste PS in a bench-scale reactor and compare with virgin polystyrene. A kinetic model capable of representing the degradation mechanism of the WEEE plastic is also studied.

2. Materials and Methods

2.1 Materials

The WEEE ABS and PS used in this study derived from a food blender and a television's outer casing, respectively. It was collected in Portugal by *Ambigroup Reciclagem, Seixal*. The collected equipment was manually dismantled; chipped on a guillotine to fit the *Retsch 2000* mill feed; in the mill, the plastics were fragmented to a caliber of less than 8 mm and thereafter the two plastics were classified by dry screening in the particle sizes <2 mm and 4-5.6 mm. Two virgin PS samples with different molecular weight (MW) were purchased from *Sigma-Aldrich*, with MW~192 000 - designated as PS1 - and with MW ~350 000, Mn ~170 000 and density of 1.04 g/mL at 25 °C - designated as PS2. The proximate analysis of the samples is shown in Tab. 1.

Table 1 - Proximate analysis of the samples.

Sample	Volatile material (wt%)	Fixed Carbon (wt%)	Ash (wt%)
Waste ABS	96.47	3.48	0.05
Waste PS	95.18	4.34	0.48
PS1	99.83	*	*
PS2	99.04	*	*

*The remaining quantity of residue was very low (less than 1 %) and the combustion was not performed.

2.1 Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses

2.1.1 Sample preparation

The TG/DSC experiments were conducted in a Perkin-Elmer STA 6000 simultaneous thermal analyser. Around 20.3 ± 1.8 mg of samples were prepared using an analytical balance and placed in an alumina TG crucible. Waste plastic samples with grain size <2 mm was used. Regarding the virgin polystyrene samples 33.4 mg of PS1 and 27.7 mg of PS2 was used.

2.1.2 Degradation runs

Experiments at dynamic and isothermal conditions were performed under nitrogen (continuous flow rate of 20 mL/min). For the dynamic conditions, the temperature range was of 40 °C to 900 °C with heating rates of 5 to 200 °C/min. The experiments were performed at temperatures between

300 and 500 °C with holding time of 1 h. A combustion experiment up 700 °C at 10 °C/min was performed to study the behaviour of the samples under air (20 mL/min flow rate). To analyse the composition of the remaining residue at the end of the pyrolysis experiments and estimate the proximate analysis, additional combustions experiments were performed, with the same conditions. For each experiment baseline experiments were conducted without samples.

2.3 Reactor

The pyrolysis experiments were carried out using a bench-scale reactor in semi-batch operation at atmospheric pressure (Fig. 2.1). The reactor works as a reactive distillation system. The reactor, a Schlenk-type glass vessel of around 0.1 L was placed in a furnace. For all the experiments approximately 10 g of samples were placed in the reactor. The granulometry of waste polystyrene was of 4-5.6 mm. The reactor is equipped with a thermocouple to monitor the temperature inside the reactor. The reactor was insulated with glass wool and aluminium foil. The liquid collector is connected with reactor. A condenser promotes the condensation of the liquid products. The coolant feeding to the condenser was controlled by a thermostat at 20 °C to control the exit of the products in the gaseous phase. The products that are gases at atmospheric temperature exit by the top of the condenser and are collected in a gas collector. The reactor system was initially flushed with nitrogen to inertize the system during 10 min. The samples were heated at 10 °C/min to different set point temperatures (400, 450 and 500 °C) with a holding time of 1 h. All the products generated from the pyrolysis (solid, liquid and gas phase) were collected and analysed.

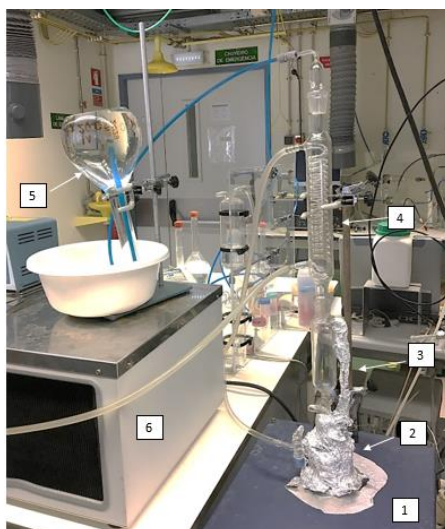


Figure 2.1 - Experimental pyrolysis reactor. 1 – Furnace, 2 -Reactor, 3 – Liquid collector, 4 – Condenser, 5– Flask of gas collection, 6– Thermostatic Bath.

2.4 Product Analysis

The chromatograph used to analyse the gaseous products was *Shimadzu GC-9A* gas chromatograph, working at 2 bar. It is equipped with a 50 -meter capillary column PLOT (KCl/Al₂Cl₃), a flame ionization detector where the outlet gas was analysed, and a split/splitless injector (with a splitting ratio of 100/1) was used. The gas chromatograph (GC) was coupled to a Shimadzu C-R3A integrator that was used to analyse the chromatographic signal and to integrate

the peak. The gases introduced in FID ignite under a flow rate of hydrogen and air of the 0.6 kg/cm² and 0.5 kg/cm², respectively.

For the liquid phase, the chromatograph used was a *Perkin-Elmer 680* gas chromatograph equipped with a flame ionization detector (FID) and an SFE BP1 capillary column 30 m long x 0.25 mm width. The injector and detector were kept at 250 °C, and nitrogen was used as carrier gas. The flow rates used in the detector were 45 cm³/min of hydrogen and 450 cm³/min of air, measured at atmospheric pressure and room temperature.

The solid products were analysed using the TG/DSC. The samples were heated in an inert atmosphere up to 700 °C at 10 °C/min and maintained during 10 min at that temperature.

3. Results and discussion

3.1 DSC and TG analysis

3.1.1 Virgin PS vs Waste PS

Fig. 3.1 presents the TG/DSC results for the degradation of waste and virgin PS at a heating rate of 10 °C/min. Waste PS starts to degrade at lower temperatures than virgin PS (Fig. 3.1 and Tab. 3.1) which is likely related with the presence of additives.^[19] The DSC curve (Fig. 3.1b) shows one endothermic peak for both virgin plastics in the temperature range of 370 °C and 450 °C. The DSC curve for waste PS shows two endothermic peaks between 350 °C and 500 °C. The DTG curve (Fig. 3.1c) confirms that a maximum weight loss occurs at the same temperature range, indicating that the peak is related with the plastic degradation. The first maximum degradation temperature (T_{max}) of waste PS is lower than of virgin PS and this first peak is likely the degradation of additives.^[19] The second T_{max} is close to the maximum degradation temperature of virgin PS, indicating that this second peak is likely the degradation of polystyrene itself.^[20]

The molecular weight of the polymers seems to not have a significant impact on the degradation of the polymer (Tab. 3.1), which has been observed by Marcilla and Beltrán as well.^[15]

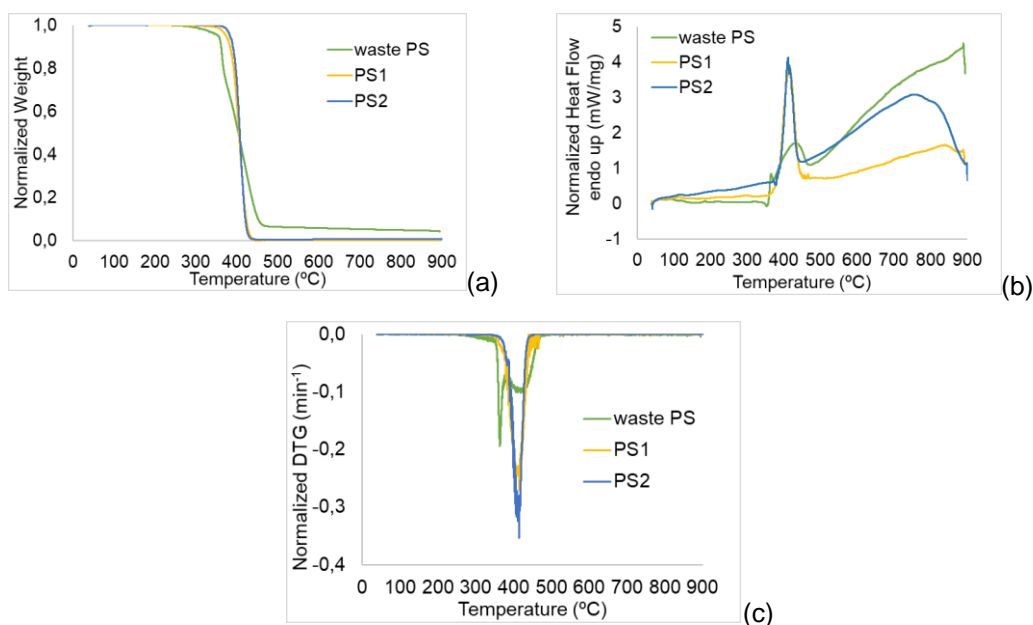


Figure 3.1 - TG(a), DSC (b) and DTG (c) curve for the thermal degradation of waste PS, PS1 and PS2.

Table 3.1 - TG results for virgin (PS1, PS2) and waste PS.

Plastic	Initial Mass (mg)	Tonset (°C)	Tmax1 (°C)	Tmax2 (°C)	Heat transferred (J/g)	Residue (%)
Waste PS	19.73	355.19	364.73	417.78	449.17	4.22
PS1	33.54	386.34	417.71	-	677.54	0.17
PS2	27.78	388.72	414.88	-	535.26	0.96

3.1.2 Dynamic conditions

The effect of the heating rate on the thermal decomposition of waste PS and ABS was study and the TG/DSC curves are shown in Fig. 3.2. For both plastics that as the heating rate increases, the onset and the maximum degradation temperature shift to higher temperatures.

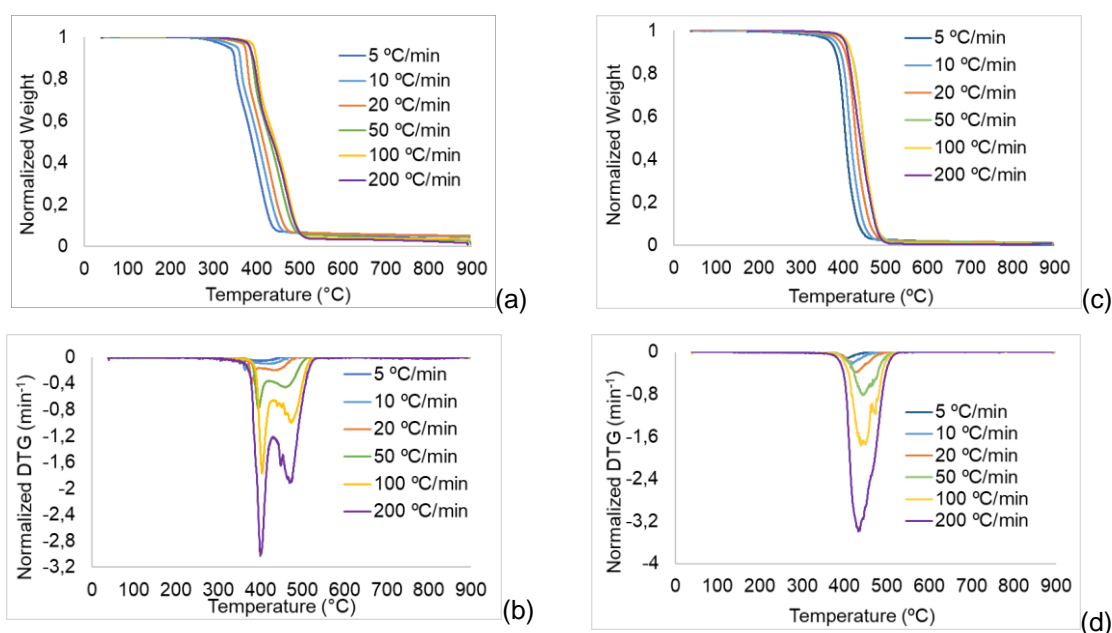


Figure 3.2 – TG (a) and DTG (b) curves for PS degradation and – TG (c) and DTG (d) curves for ABS degradation at dynamic conditions.

3.1.3 Isothermal conditions

Isothermal experiments were performed at different temperatures between 300 and 500 °C. The TG/DSC results are present in Fig. 3.3. As the temperature increases, the conversion increases. The conversion at 500 °C for waste PS reaches 96.0 % and for waste ABS 98.5 %.

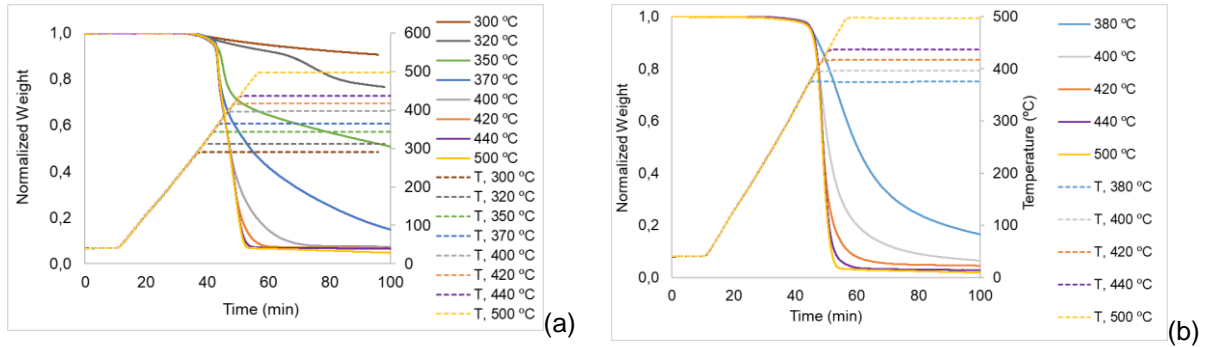


Figure 3.3 – TG(a) curves for PS and TG(b) curves for ABS degradation.

3.1.4 Combustion experiment

The degradation of waste polystyrene and ABS under air was analysed. The TG/DSC results are present in Fig. 3.4. The degradation under air presents a different behaviour from 450 °C on, comparing to the degradation in nitrogen (Fig. 3.4a and c). Part of the residue degrades under air, which results in an extra degradation peak in the DTG curve (Fig. 3.4b and d).

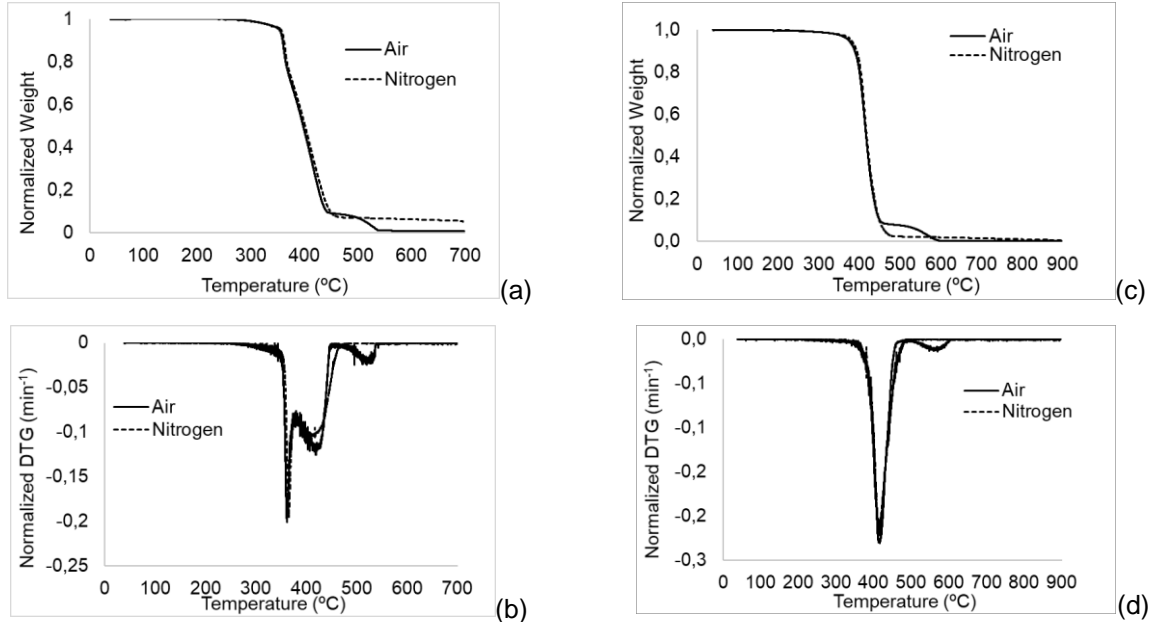


Figure 3.4 – TG (a), and DTG(b) curves for PS and TG (c) and DTG (d) curves for ABS degradation under air and N₂ conditions.

3.2 Kinetic Model

Mechanistic kinetic models were built and analysed for PS and ABS decomposition. The kinetic model was based on the reaction rate equation (Eq. 3.1) and the Arrhenius Law. A kinetic reference constant was applied (Eq. 3.2). Two assumptions were made: a first order kinetics and a reference temperature of 400 °C.

$$\frac{dW}{dt} = -k(T)W^n \quad (3.1) \quad k(T) = k_{ref} e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} \quad (3.2)$$

To calculate the fractioned weight, the Euler method was used. All the models were fitted to the TG curve. The model parameters were estimated by a least-squares procedure, using the sum of

the squares of the residues on the fractioned weight as the objective function to be minimized. The optimization procedure was carried out using the Solver tool from Microsoft® Office Excel. To estimate the standard deviation of the estimated variables the bootstrapping tool was applied by performing 10 sample replacements for each model.

3.3.1 Polystyrene and ABS

A one-component decomposition describes the degradation of both virgin PS (Fig. 3.5). The obtained activation energies, present in Tab. 3.2, show that the molecular weight has some influence on the kinetics.

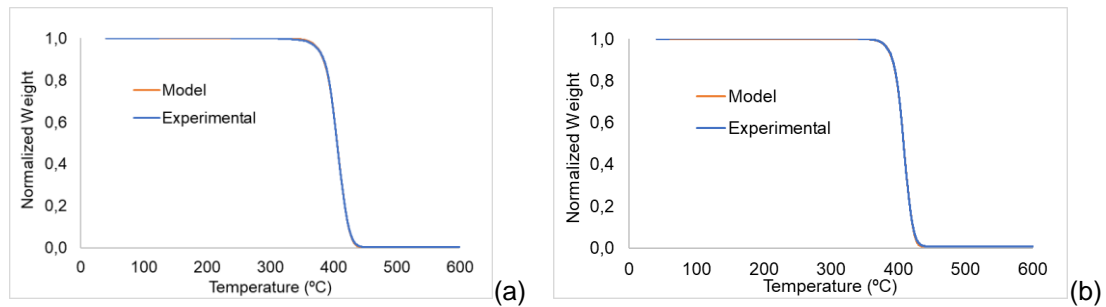


Figure 3.5 - Model vs experimental data for virgin PS. (a) - PS1; (b) - PS2.

The TG curve of waste PS and ABS showed two decomposition peaks and therefore, a two pseudo-component decomposition model was considered. Both pseudo-components are independent from each other and decompose in parallel. To approach the TG curve at the end, a fixed quantity of residue is considered. The model was fitted to different heating rates and isothermals in order to ensure that a single set of kinetic parameters (Tab. 3.2) describes the experimental data. The model describes the ensemble of data (Fig. 3.6).

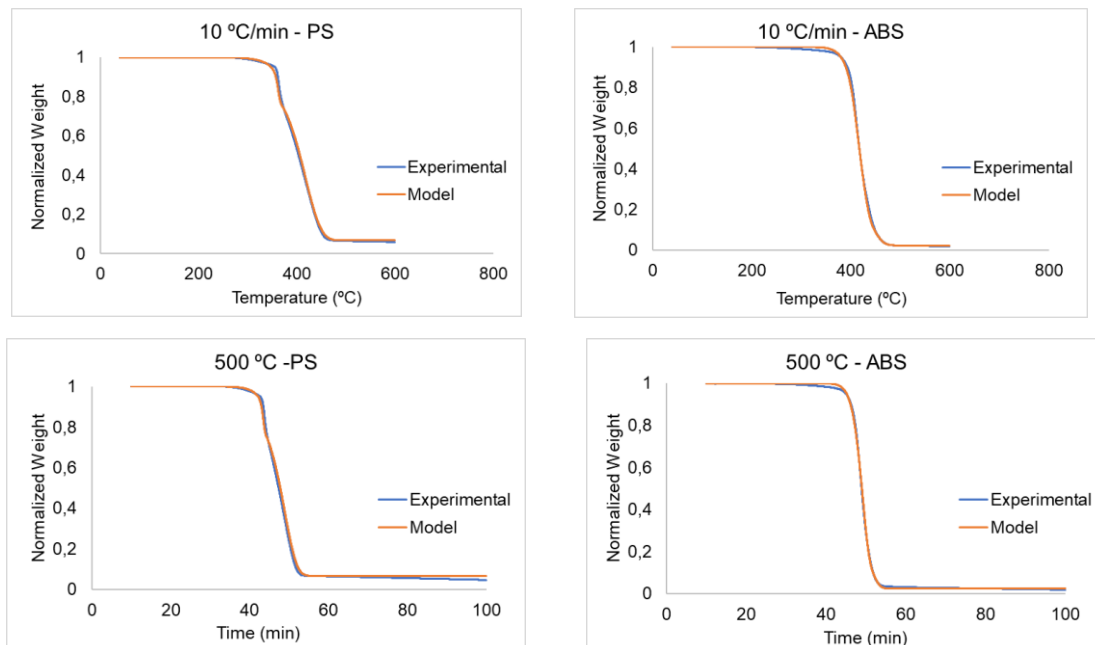


Figure 3.6 - Model vs experimental data for waste PS and ABS at different conditions.

Table 3.2 - Kinetic parameters.

Polymer/Kinetic parameters	PS1	PS2	Waste PS	Waste ABS
$k_{ref,1}$ (s ⁻¹)	$5.02 \times 10^{-3} \pm 2.57 \times 10^{-7}$	$4.59 \times 10^{-3} \pm 8.76 \times 10^{-7}$	283.95 ± 13.55	$3.19 \times 10^{-3} \pm 9.10 \times 10^{-5}$
$E_{a,1}$ (kJ/mol)	282.09 ± 0.05	375.01 ± 0.10	814.73 ± 1.96	255.43 ± 3.26
$k_{ref,2}$ (s ⁻¹)	-	-	$2.96 \times 10^{-3} \pm 2.90 \times 10^{-5}$	$1.11 \times 10^{-3} \pm 5.45 \times 10^{-5}$
$E_{a,2}$ (kJ/mol)	-	-	128.14 ± 0.75	193.34 ± 4.52

3.3 Bench-scale reactor

3.2.1 Yields

The product distributions of virgin and waste PS are present in Tab. 3.3. The results show that with the temperature, the liquid yield increases, the solid yield decreases, and the gas yield is approximately constant. At 500 °C, waste PS produces 59 % liquid and 3 % gas. The TG results (see Chapter 3.1.3) have shown a higher conversion (96 % at 500 °C). The lower conversion obtained in the reactor may be due to inside reflux. The inside temperature of the reactor is always lower than the set point, due to heat losses, endothermicity of the reaction and inside reflux. The temperature profile also shows that the average internal temperature of the reactor for waste PS is always lower than of virgin PS, and this may be due to the presence of additives that influence the kinetics and thus the reaction. In fact, virgin PS produces more liquid than waste PS (Tab. 3.3).

Table 3.3 - Product distribution of the thermal pyrolysis of virgin and waste PS at different temperatures. L=liquid, S=solid, G=gas.

	Virgin PS			Waste PS		
	L (%)	S (%)	G (%)	L (%)	S (%)	G (%)
400 °C	31	67	1	21	73	6
450 °C	72	26	2	33	61	6
500 °C	86	12	3	59	39	3

3.2.2 Product composition

The gaseous products of waste PS are in the range of C₂ and C₆. For virgin PS the quantity of gas produced was very low making it impossible to analyse. The composition of the liquid derived from the pyrolysis of virgin and waste PS is shown in Fig. 3.7. Virgin PS produces in majority C₈ hydrocarbons, which might comprehend in higher quantity styrene, followed by ethylbenzene. C₇ and C₉ hydrocarbons products are also obtained, which are in majority toluene and possibly α-methylstyrene, respectively. These results are concordant with literature [10]. Waste PS produces also in majority C₈ hydrocarbons. The results show that styrene is possibly the main compound and ethylbenzene is no longer produced. Thus, the pyrolysis of waste PS produces high-value hydrocarbons that may be used as feedstock.

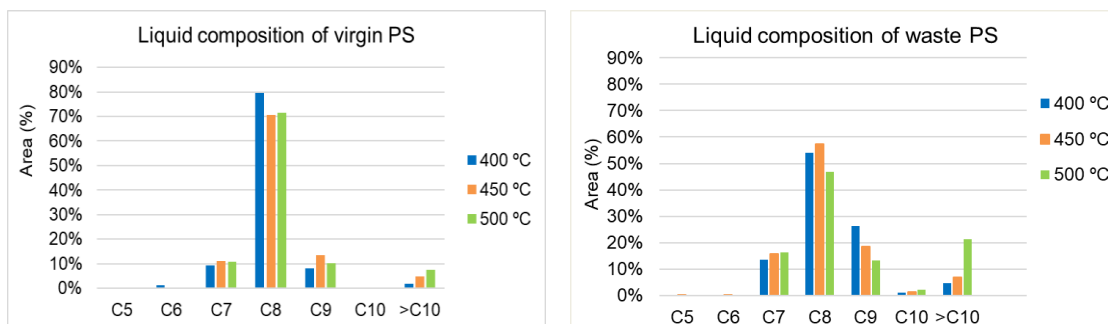


Figure 3.7 - Liquid composition.

The DTG curve of the solid obtained by the thermal pyrolysis at 400 °C of virgin and waste PS shows a degradation peak that might correspond to unreacted polymer, indicating that at set point this temperature the reaction is likely incomplete ^[8] (Fig. 3.8).

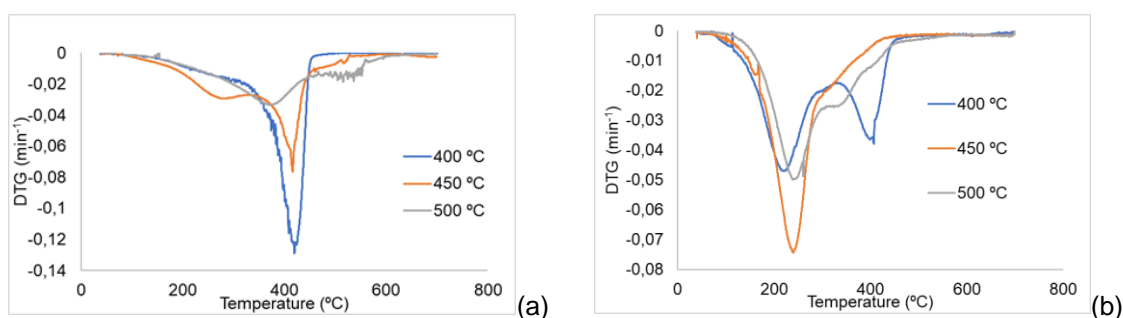


Figure 3.8 - DTG curve of the solid of virgin (a) and waste PS (b) pyrolysis at the different set point temperatures.

4. Conclusions and Future Perspectives

The main conclusions are that the degradation of virgin PS occurs with one degradation and of waste PS occurs with two, where the first peak may be related with the presence of additives. The degradation of waste ABS shows a defined degradation peak followed by a “shoulder”. An increase of the heating rates shifts both the onset and maximum degradation temperature to higher temperatures. The degradation of virgin PS is well described by a one-component degradation model. A two pseudo-component degradation model with a presence of a fixed quantity of residue describes the decomposition of waste PS and of ABS for different heating rates and isothermals. The pyrolysis of waste PS yields 60 % liquid. Both waste and virgin PS yield in majority hydrocarbons in the range of C₆ to C₉. C₈ hydrocarbons are produced in higher quantity, which might correspond mainly styrene monomers in the case of waste PS. Thus, waste PS may be used in feedstock recycling as it generates the monomers that can be used to produce new polystyrene, promoting a circular economy approach.

The future perspectives are: improve the kinetic models by introducing heat and mass transfer phenomena; confirmation of the pyrolysis products by use of patterns in GC or by use of mass spectrometry; co-pyrolysis of PS and ABS with different ratios and/or with another WEEE plastics; study of the pyrolysis of ABS in the reactor; optimization of the conditions of the bench-scale reactor; large – scale reactor; study of the economic feasibility of the process and reactor modelling.

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