Kinetic Modeling of Plastics Pyrolysis

Joana Raquel Antunes Paulino

Instituto Superior Técnico

Setembro 2020

Abstract

The pyrolysis reaction of high-density polyethylene has been extensively studied and although the final products formed are known, the reaction mechanism is not fully known yet. The purpose of this work is to determine which reaction mechanism is most likely to occur when thermal degradation of HDPE occurs. With this purpose seven reaction models were proposed and the mass balance and heat flow equations that best suit the system under study were presented. The experimental data were obtained through tests with pure HDPE under dynamic heating conditions up to 600ºC and under a nitrogen atmosphere, thus allowing to obtain the respective TG and DSC curves. The results show that the preferred mechanism is the M5 model. In this model, the polymer degrades into volatiles, liquids and waxes and there are two secondary reactions in which the wax is degraded into volatiles and liquids. It is also possible to verify that there are two more models that are likely to occur, model M3 and M4.

Keywords: High density polyethylene, Pyrolysis, Chemical recycling, Kinetic model, Thermogravimetric analysis, Differential scanning calorimetry

1 Introduction

Over the past 20 years there has been a significant increase in plastic consumption and production. In 2018, 359 million tons of plastics were produced worldwide, which represents an increase of 3% in relation to 2017. The main source of monomers used in plastic production are fossil fuels and therefore the life cycle of plastics increases a series of environmental issues, one of which is plastic waste management. [1–5]

Today, there are three possible processes for plastic waste management: recycling, incineration with energy recovery and landfill disposals. Recycling is the only process in which there is a waste transformation, which may be chemical or mechanical. Mechanical recycling consists in a series of physical processes in order to obtain grains from the initial polymer. Chemical recycling consists in several chemical processes in which there are polymers degradation and the final products are more varied, ranging from monomers to simpler polymer chains. In 2018, 29.1 million tons of used plastics were collected, from which, only 33% were recycled. [1–3,6]

Pyrolysis is a process used in chemical recycling and consists in a chemical and thermal degradation that happens at high temperatures and preferably under an inert atmosphere. The main products of pyrolysis are gases, liquids, waxes and carbonaceous solids similar to coal. These products can be directly applied to fuels, petrochemicals products or used as monomers. The main advantage of pyrolysis is the possibility to recycle mixtures of plastics simultaneously, without a previous separation stage by type of plastic.[2,3,6,7]

2 Materials and Methods[8]

This section was based on the previous work presented by Coelho *et al.*[8]

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

2.1.1 Materials and Sample preparation

The polymer used was pure high density polyethylene (M_w ~ 290.000) offered by Borealis.

All TG/DSC experiments were caried out in a TA Instruments SDT 2960 simultaneous DSC–TGA apparatus. The pure HDPE sample, with 11–12 mg, was placed in an alumina TG at room temperature.

2.1.2 Degradation runs

The runs were performed under a nitrogen atmosphere with a continuous flow rate of 80 mL/min and a 10 ºC/min temperature increase rate from room temperature up to 600ºC. The temperature was maintained for 10 min after the run.

3 Proposal of reaction models

3.1 Reaction models

Several authors have already proposed reaction schemes for the thermal degradation of high density polyethylene, from which the final products are gases, liquids, waxes and carbonaceous solids.

In order to adapt the models described in the literature, the following assumptions were taken into account: the final products that at the run temperature are in the gas phase are removed by the nitrogen flow; the reactions that may exist in the gas phase are not considered in the calculation of the heat flow since they are no longer in the system; no differentiation will be made between gaseous and aromatic products, which will be grouped into volatile products; at the end of the run no residues were obtained, so all reactions that originate carbonaceous solids will not be considered.

The models proposed for HDPE degradation are shown in figure 1.

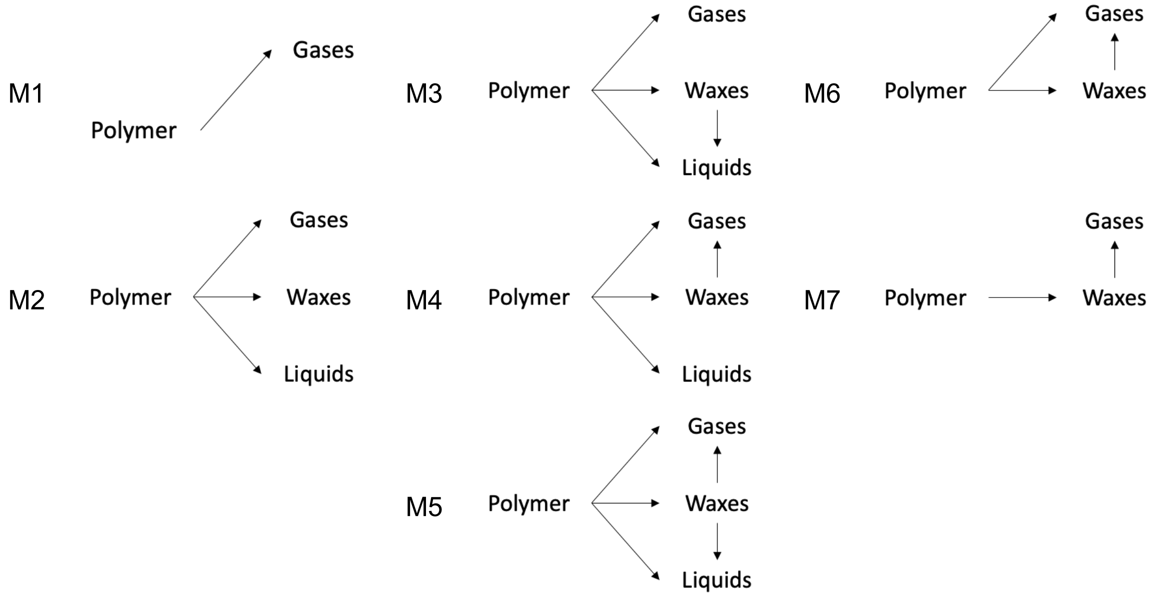


Figure 1 - Models proposed for the HDPE degradation reaction

3.2 *Kinetic equations*

To estimate the kinetic parameters, such as activation energy and reaction rate constant, a first approach is to consider that the kinetics of the degradation reaction is similar to the kinetics of a 1st order reaction(n = 1), shown in equation 1. [9,10]

$$-\frac{dm}{dt} = k \cdot m^n \quad (1)$$

Where k is the reaction rate is constant, m is the sample mass and n is the order number of the reaction.

The temperature dependency from the reaction rate constant can be described by the Arrhenius equation, presented in equation 2. [3,9]

$$k = k_0 e^{E_a/_{RT}} = k_{ref} e^{-\left(E_a/_R\right)\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \quad (2)$$

Where T_{ref} is a reference temperature chosen within the range of the experimental values (350ºC was chosen for this work), E_a is the activation energy of reaction and k_{ref} is the kinetic constant at the temperature reference.

According to this approach the mass variation during the HDPE degradation reaction is given by equation 3.

$$-\frac{dm}{dt} = k_{ref} e^{-\left(E_a/_R\right)\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \cdot m \quad (3)$$

3.3 *Enthalpic equations*

From the DSC curve obtained through the experimental data, it is possible to estimate the reaction enthalpy and the heating capacity for high density polyethylene..[11–13]

There are two contributions to the heat that must be considered: the reaction enthalpy corresponding to the depolymerization reaction (equation 4), and the heat required to heat the sample (equation 5).[8,11,14]

$$HF1 = \Delta H_r \cdot \frac{dm}{dt} \quad (4)$$

$$HF2 = -m \cdot C_p \cdot \frac{dT}{dt} \quad (5)$$

Where m is the sample mass, ΔH_r is the reaction enthalpy and C_p is the heat capacity of the sample.

However, it is possible to consider that the enthalpy of polymerization of a monomer in the gas phase to form an amorphous solid is equivalent to the enthalpy of depolymerization of an amorphous solid to form monomers in the gas phase. [9,15]

According to this approach the heat flow during the degradation reaction is given by equation 6.

$$HF = -k \cdot m \cdot \Delta H_{dep} - m \cdot C_p \cdot \frac{dT}{dt} \quad (6)$$

3.3.1 Optimization

Equations 3 and 6 were solved numerically using the Euler method, and the parameters $E_a, k_{ref}, \Delta H_{desp}$ and C_p were estimated by a least-squares procedure, using the sum of the squares of the residues on mass variation and heat flow equation as the objective function (FO) to be minimized. The optimization procedure was carried out using the Excel "Solver" tool (©Microsoft Corp.).

The objective function for the system is given by equation 7.

$$FO = \sum_{all\ points} \left[HF_{exp} - HF_{teo}\right]^2 + \sum_{all\ points} \left[BM_{exp} - BM_{teo}\right]^2 \quad (7)$$

4 Results and discussion

4.1 Experimental results

Figure 2 shows the TG and DSC curves obtained in the runs performed.*[8]*

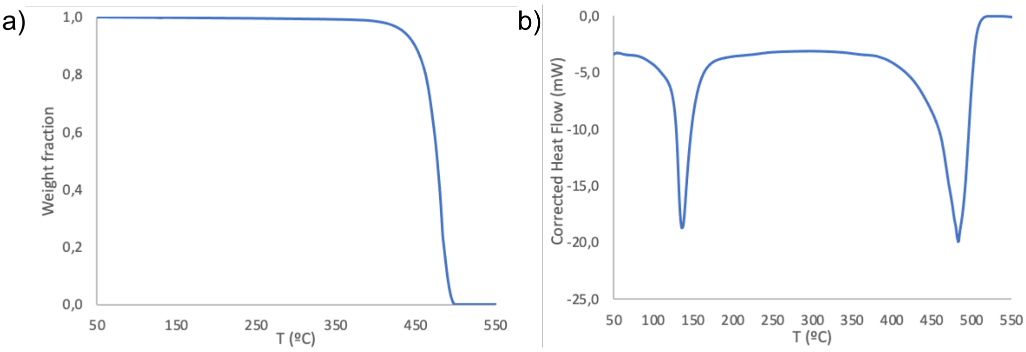


Figure 2 - a) TG Curve and b) DSC curve from the experimental data.

Based on the TG curve it is possible to verify HDPE degradation occurs in one step, since there is only a sharp mass drop.

On the DSC curve it is possible to verify that there are 2 endothermic peaks. The first peak occurs at a temperature of ~140ºC and corresponds to the melting temperature of the polymer. The second peak occurs at a temperature of ~485ºC and corresponds to the temperature at which the rate of the degradation reaction is maximum (T_{max}). It is also possible to verify that there is a region in the curve before the peak of the reaction, between 375ºC-440ºC, in which there is a 2nd order transition, not causing a loss of mass. [8,16]

4.2 Models proposed

The models were built starting from the simplest and increasing the degree of complexity. Table 1 shows the values of the objective function for each of the models.

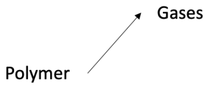
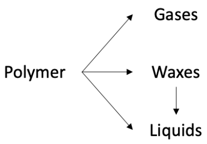
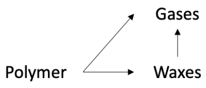
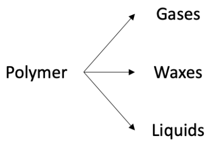
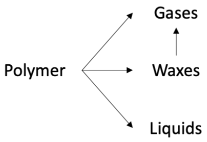
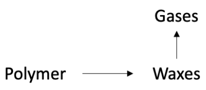
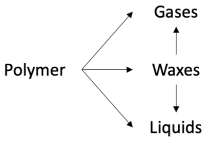
The simplest model is the M1, since it considers that the degradation of HDPE only produces volatiles as final product and although the fit to the TG curve was good, the fit of the DSC curve was not satisfactory. For this reason, liquids and waxes were added to the M2 model as final products. Like the M1, the M2 model has a good fit to the TG curve, but it does not have a satisfactory fit to the DSC curve.

The next step in the construction of the models was the introduction of a secondary degradation reaction of the formed wax. In models M3 and M4, the degradation of the wax causes, respectively, liquids and volatiles and in the model M5 the degradation of the wax causes both liquids and volatiles. For these three models a quite satisfactory fit to the TG and DSC curves was obtained.

Then, in the M6 model, the reaction that originates liquids from the HDPE degradation was removed and, similarly to the M3, M4 and M5 models, it was found that the TG and DSC fits were quite satisfactory.

Finally, in the M7 model the reaction that originates volatiles from the HDPE degradation was removed, leaving only wax as the final product and this was degraded into volatiles. Comparing with the M6 model, it was found that the adjustment to the DSC curve was equally good, but the adjustment to the TG curve worsened, this means that the reactions of formation of volatile products are necessary to achieve a good adjustment both in the DSC curve as in the TG curve.

Table 1- Comparison of FO values for the various models

Model	FO	Model	FO	Model	FO
M1 	390,9	M3 	7,9	M6 	8,0
M2 	364,9	M4 	7,8	M7 	17,7
		M5 	7,3		

4.2.1 Chosen model

From the proposed models, it is possible to verify that the model that best describes the HDPE pyrolysis reaction is the M5 model. The adjustments to the TG and DSC curves for this model are shown in figure 3. The characteristic temperatures of the TG curve are shown in table 2. In parallel, in table 3 are presented the kinetic constants and in table 4 are presented the enthalpic constants estimated for this model.

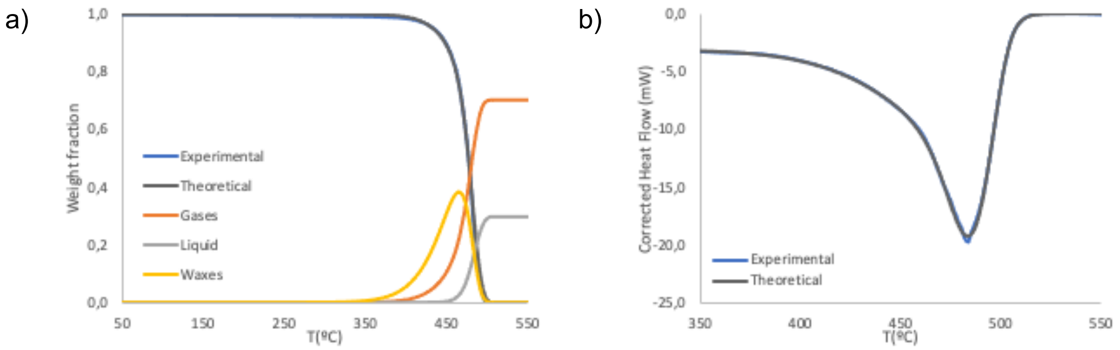


Figure 3 – Adjustment of the TG curve (a) and DSC curve (b) between the experimental and theoretical values for the M5 model

Table 2 – Characteristic temperatures of the TG curve for the M5 model

$T_{5\%}$ (ºC)	**T_{max} (ºC)**	**$T_{95\%}$ (ºC)**
434,0	483,4	494,7

Table 3 – Estimated kinetic constants for the M5 model, for $T_{ref} = 350\ °C$

Reaction	**E_a (kJ/mol)**	**k_{ref} (s^{-1})**
Polymer → Gases	197,97	$5{,}16\times10^{-6}$
Polymer → Wax	149,77	$4{,}69\times10^{-5}$
Polymer → Liquid	824,26	$1{,}84\times10^{-15}$
Wax → Gases	418,45	$9{,}79\times10^{-9}$
Wax → Liquid	488,61	$5{,}13\times10^{-10}$

Table 4 – Enthalpic constants estimated for the M5 model

ΔH_{dep} Polymer (J/g)	**ΔH_{dep} Wax (J/g)**	**C_p Polymer (J/K.g)**	**C_p Wax (J/K.g)**
251,9	318,1	1,85	1,86

For this model, the characteristic temperatures are in conformity with the values described in the literature. [17–21] On the one hand, the estimated values of ΔH_{dep} and C_p are not in accordance with the values presented by other authors. [22–25]

5 Conclusions and Future Perspectives

From the proposed models, it is possible to verify that the model that best describes the HDPE pyrolysis reaction is M5 model, since it presents the lowest value of the objective function. In this model, the polymer degrades into volatiles, liquids and waxes, and there are two secondary reactions in which there is a degradation of wax into volatiles and liquids. It is also possible to verify that there are two more models likely to occur, being the models M3 and M4, since they also present low values for the objective function.

In order to continue the work developed in this paper, the following topics are suggested for future work: characterize the volatiles obtained, in order to calculate the volatile and liquid yield; change the reaction conditions: vary the heating speed, vary the N2 flow rate, use an H2 atmosphere; repeat the test for samples of HDPE residues.

6 References

1. Aguado, J. & Serrano, D. P. *Feedstock Recycling of Plastic Wastes*. (RSC, 1999). doi:10.1007/978-3-319-19485-1
2. Geyer, R., Jambeck, J. R. & Law, K. L. Production , use , and fate of all plastics ever made. 25–29 (2017).
3. Scheirs, J. & Kaminsky, W. *Feedstock recycling and pyrolysis of waste plastics*. (John Wiley & Sons, 2006). doi:10.1016/s1351-4180(06)71853-0
4. PlasticsEurope. Plastics – the Facts 2018. *Plastics – the Facts 2018* 38 (2018). Available at: https://www.plasticseurope.org/en/resources/publications/619-plastics-facts-2018. (Accessed: 29th August 2020)
5. PlasticsEurope. Plastics – the Facts 2019. *PlasticsEurope* (2019). Available at: https://www.plasticseurope.org/en/resources/publications/1804-plastics-facts-2019. (Accessed: 29th August 2020)
6. Perugini, F., Mastellone, M. L. & Arena, U. A life cycle assessment of mechanical and feedstock recycling options for management of plastic packaging wastes. *Environ. Prog.* **24**, 137–154 (2005).
7. Singh, R. K., Ruj, B., Sadhukhan, A. K. & Gupta, P. Thermal degradation of waste plastics under non-sweeping atmosphere : Part 1 : Effect of temperature , product optimization , and degradation mechanism. *J. Environ. Manage.* **239**, 395–406 (2019).
8. Coelho, A. *et al.* Catalytic degradation of low and high density polyethylenes using ethylene polymerization catalysts: Kinetic studies using simultaneous TG/DSC analysis. *Appl. Catal. A Gen.* **374**, 170–179 (2010).
9. Csukás, B. *et al.* Simplified dynamic simulation model of plastic waste pyrolysis in laboratory and pilot scale tubular reactor. *Fuel Process. Technol.* **106**, 186–200 (2013).
10. Murata, K., Hirano, Y. & Sakata, Y. Basic study on a continuous flow reactor for thermal degradation of polymers. *J. Anal. Appl. Pyrolysis* **65**, 71–90 (2002).
11. O'NEILL, M. J. Measurement of Specific Heat Functions by Differential Scanning Calorimetry I _. *Anal. Chem.* **38**, 1331–1336 (1966).
12. Kodre, K., Attarde, S., Yendhe, P., Patil, R. & Barge, V. Differential Scanning Calorimetry: A Review. *J. Pharm. Anal.* **3**, 11–22 (2014).
13. Esposito, M., Sayer, C., Henrique, P. & Arau, H. De. In-Line Monitoring of Emulsion Polymerization Reactions Combining Heat Flow and Heat Balance Calorimetry. *Macromol. React. Eng* **4**, 682–690 (2010).
14. Korber, F., Hauschild, K., Winter, M. & Fink, G. Reaction Calorimetric Investigation of the Propylene Slurry Phase Polymerization with a Silica-Supported Metallocene / MAO Catalyst. 3323–3328 (2001).
15. Kishore, K. & Prasad, G. Thermo-chemical interpretation of polymer degradation. **130**, 125–130 (1980).
16. Caneverolo, S. V. *Técnicas de Caracterização de Polímeros*. (Artliber Editora Ltda, 2017).

17. Singh, R. K., Ruj, B., Sadhukhan, A. K. & Gupta, P. A TG-FTIR investigation on the co-pyrolysis of the waste HDPE , PP , PS and PET under high heating conditions. *J. Energy Inst.* **93**, 1020–1035 (2020).
18. Kunwar, B., Moser, B. R., Chandrasekaran, S. R., Rajagopalan, N. & Sharma, B. K. Catalytic and thermal depolymerization of low value post-consumer high density polyethylene plastic *. *Energy* **111**, 884–892 (2016).
19. Wu, J. *et al.* TG / FTIR analysis on co-pyrolysis behavior of PE , PVC and PS. *Waste Manag.* **34**, 676–682 (2014).
20. Peterson, J. D., Vyazovkin, S. & Wight, C. A. Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene , Polyethylene and Poly (propylene). 775–784 (2001).
21. Cuadri, A. A. The effect of thermal and thermo-oxidative degradation conditions on rheological , chemical and thermal properties of HDPE. *Polym. Degrad. Stab.* **141**, 11–18 (2017).
22. Gaur, U. & Wunderlich, B. Heat capacity and other thermodynamic properties of linear macromolecules . II . Polyethylene. *J. Phys. Chem. Ref. Data* **10**, 119–152 (1981).
23. MARK, J. E. *POLYMER DATA HANDBOOK*. (Oxford University Press, Inc., 1999).
24. Jessup, R. S. The Heat and Free Energy of Polymerization of Ethylene. *J. Chem. Phys* **16**, 661–664 (1948).
25. Ivin, K. J. & Dainton, F. S. Changes of entropy and heat content during polymerization. *Nature,* **162**, 331–348 (1948).