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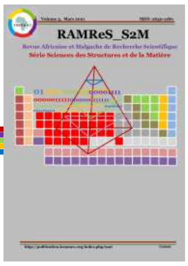

Kinetic study of Pyrolysis of Low Density Polyethylene using Thermogravimetric Analysis: Dynamic study

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***Abstract*:**

Presently, waste management is a problem for large African cities. The solid waste produced by the populations contains a lot of plastic waste. This plastic waste is unfortunately not biodegradable. Pyrolysis seems to be a promising way for their valorization. The control of the thermal kinetics is necessary to optimize the pyrolysis reaction of polyethylene (PE). It is indeed useful in the optimal design and operation of pyrolysis reactors.

The objective of this study is to analyze the kinetics of the pyrolysis of Low Density Polyethylene (LDPE) in dynamic regime. Thermogravimetric analysis (TGA) was used under argon atmosphere at different heating rates 5, 10, 20, 30, 40 and 50 °C min^{-1}. This work aims to analyze the use of simple kinetic models to describe the thermal behavior of the material, taking into account the complex mechanism of the reaction. Due to the complexity of this mechanism, the reaction order of the LDPE pyrolysis was determined. Freidman's method was used to obtain the kinetic parameters from non-isothermal experiments and compare them with values obtained by other authors.

The LDPE degradation temperatures with which the maximum mass losses (Tp) are associated are approximately 470, 490, 500, 505, 510 and 516 °C for heating rates of 5, 10, 20, 30, 40 and 50 °C min^{-1}, respectively. The best results from this study are obtained for reaction orders *n* varying with the heating rate.

***Keywords*:** Thermogravimetric analysis; Reaction kinetic; Activation energy; Reaction order; LPDE.

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1. Introduction

Currently, waste management is a priority problem mainly for large African cities. The demographic growth of cities inevitably leads to the production of more and more important waste. Moreover, the use of plastic bags is a real problem. These non-biodegradable bags accumulate everywhere in the cities, especially in the outskirts. Water is packaged in LDPE bags that serve as a cheaper packaging material. This situation is a real problem for these cities. The recycling of this plastic waste has attracted a lot of interest as an alternative method for its disposal and management over the last decades. Recycling of these wastes can be done mainly in two ways: mechanical reprocessing of plastic waste and thermal or catalytic degradation into gaseous and liquid products. These gaseous or liquid products can then be used as fuels or chemicals in industry. Pyrolysis is an interesting technique for the valorization of these products [1]. Valuable products can be made from waste plastics using pyrolysis technology. According to Wilson [2], the pyrolysis process is assumed to take place from 325 °C up to a maximum temperature of 850 °C. Ademiluyi and Adebayo [3] evaluated the combustible gases produced by pyrolysis of water bags at low and high temperatures. Gonzalez et al. [4] performed catalytic pyrolysis of polyethylene in a fluidized bed reactor and obtained products ranging from C2 to C9. Nema and Ganeshphrasad [5] studied plasma pyrolysis of medical waste. However, there are many serious issues that need to be resolved. Indeed, there is a need for industrial-scale recovery, minimization of production costs, and optimization of higher value products for a wide range of plastic mixtures [6]. On the other hand, the lack of kinetic data hinders the optimal design of the pyrolysis process and the design of a commercial pyrolysis reactor. Therefore, it is important to analyze the kinetics of the thermal degradation of plastic waste for obtaining apparent kinetic parameters. These parameters are very useful for the design and optimal operation of pyrolysis reactors.

Thermogravimetric (TG) analysis is an excellent way to study the kinetics of pyrolysis. Many studies on the pyrolysis of plastic waste have been conducted, and various reaction kinetic models are available to estimate the parameters, including the integral method [7-10]. Kumar and Sing [1] on the one hand and Kayacan and Dogan [6] on the other hand, also studied the dynamic kinetics of pyrolysis of High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE), respectively with Friedman's model [11]. Similarly, Alvarenga [12] compared the kinetic parameters of polyethylene (PE), paperboard and paperboard packaging by three methods: the Kissinger method, the Kissinger-Akahira-Surnose (K-A-S) method and the Starink method [13-15].

Most authors described the thermal decomposition by exponential models and performed experiments in isothermal and/or dynamic regimes. Regardless of the geographical position, heating rate, sample size, etc., the reaction order varies between 0 and 1, while the kinetic parameters show a larger variation. These differences have been associated with different causes such as the existence of temperature profiles within the sample, the temperature difference between the system and the sample, the influence of the heating rate on the reactions taking place during decomposition, and the existence of a complex reaction mechanism [16-18, 10]. Other suggested causes of discrepancy are the mathematical method used in the calculation and the existence of parallel, consecutive or complex reaction mechanisms in general [16, 19].

As indicated above, the reaction mechanism may be the cause of the disparity in results. A radical chain mechanism is the most generally accepted reaction model [20, 16, 21-30]. The mechanism proposed by Bockhorn et al. [16] is a simplified version. The resulting rate law is a function of the amount of polymer to the 0.5 and 1.5 power [16]. The observed reaction order depends on the relative conversion of the hydrogen transfer reactions.

Often, kinetic studies of plastic pyrolysis have been developed under the assumption that the reaction can be described by a first order reaction model. This is also the case for many other authors [31, 32, 10]. Recent studies [33-36] have challenged the first-order assumption and reported a reaction order of 0.5.

The objective of this study is to estimate the reaction model of LDPE pyrolysis as well as the Arrhenius parameters from dynamic kinetics data. The aim is to compare these results with those obtained by other authors and to verify if it is possible to explain the mass loss of polyethylene by a simple rate law, knowing that it is a complex mechanism.

2. Materials and methods

2.1. Raw material

The Low Density Polyethylene (LDPE) used in this work is the plastic bag black color found in abundance in household waste city of Abomey-Calavi in Benin. The plastic waste was cut into small pieces (approx. 1 mm^2) and used in the pyrolysis reaction (Fig. 1).

Fig. 1. Raw LDPE used in this study.

2.2. Raw material analysis

Before thermogravimetric analysis, LDPE was analyzed to determine the main properties affecting thermal conversion. The proximate analyses of the studied sample were determined. The properties including volatile matter, ash, and moisture content were tested in accordance with French standards (NF EN 14774, NF EN 1510, 14775, NF EN 15148 and NF EN 14918). The moisture content was determined by successive weighing of a sample placed in an oven at 103 °C until achieving constant mass. The proximate analyses were performed on the TG apparatus described in the following section.

2.3. Thermogravimetric Analysis

The experimental work was carried out on a computerized thermobalance (NETZSCH STA 449 F3 Jupiter) using a high speed furnace which allows a heating rate faster than 500 °C min^{-1}. The thermobalance configuration gives a sensitivity of ±0.4 µg. In order to establish an inert atmosphere during all experiments, a controlled argon flow (carrier gas) (fixed at 200 mL min^{-1}, 273 K, 1 atm) sweeps the measurement cell that is purged for 20 min before starting the heating program. During experiments, the argon flow is set to 20 mL min^{-1}. The initial dry mass of samples is about 30 - 50 mg.

Kinetic studies with TG instruments are typically conducted under isothermal conditions or non-isothermal conditions. Some experimental difficulties can exist with isothermal experiments: a significant part of the reaction may occur during the setting of the experimental temperature at the beginning of the experiment; for instance, see [37] for more precision about this subject. One advantage of the isothermal conditions is the homogeneous sample temperature after the isothermal reaction temperature has been reached, whereas in non-isothermal mode, a temperature gradient in the sample can occur due to the resistance of heat conduction in the sample and the resistance of outer heat transfer [38]. A way for compensating for this effect is to use low heating rates. Isothermal and non-isothermal methods have been widely used in the literature but papers comparing the results obtained with the two methods are rare [39]. Furthermore, it is not easy to compare the scientific studies published for a given product; the experimental conditions (equipment, technologies, operating conditions, sample conditioning, etc.) are often different and not always well known. Moreover, the models, the data treatments and the computational methods are almost never the same [37].

Waste LDPE sample was taken and heated from room temperature to a final temperature of 900 ºC and a residence time of 30 minutes at 900 ºC. TG was performed in Argon atmosphere at the heating rates of 5, 10, 20, 30, 40 and 50 ºC min^{-1} under 20 mL min^{-1} gas flow rate. Derivative Thermogravimetric (DTG) mass loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of waste LDPE takes place. This mass is high enough that even small temperature gradients are observed in the particles. However, this effect is limited due to the position of the thermocouple close to the center of the sample. As it has been stated in previous works on pyrolysis of lignocellulosic and polymeric materials [40-43], dynamic experiments carried out with constant heating rates present some advantages over isothermal experiments. One of these advantages is the possibility of obtaining results in a larger temperature range and more representative of industrials process.

Furthermore, these experiments allow the study of the influence of the heating rate *β* on the thermal decomposition process. Taking this into account, experiments at different *β* between 5 and 50 °C min^{-1} have been carried out.

2.4. Dynamic kinetic model

The first step consists in choosing the kinetic model: the mathematical model describing the time evolution of the different mass fractions during the thermal degradation process. The complexity of the chosen model depends on the desired objectives. The thermal degradation of heterogeneous and complex materials, such as waste or biomass, cannot be expressed in detail. Simplified reaction schemes with pseudo-components are generally used. At this stage, a key question is to decide whether heat and mass transfer processes have to be taken into account. A large majority of the works assumes the regime of kinetic control : all influences of internal and external mass and thermal transfer are neglected and the sample is assumed to follow the programmed temperature of the thermobalance perfectly and to have a uniform temperature [38]. However, sources of error related to the temperature undoubtedly exist: the placement and the accuracy of the thermocouple, the thermal lag between the sensor and the sample, and the effect of heats of reaction [44]. Some authors have demonstrated the influence of experimental conditions [45, 46].

2.4.1. Kinetic Model

The approach adopted by many researchers in kinetic analysis of TG data for solid fuel pyrolysis is to assume first order reaction for devolatilization [12, 6, 1, 47]. So the *n* order reaction of simple step of waste Polyethylene pyrolysis with respect to the amount of undecomposed material states that,

$$\mathbf{k : A\ (Plastic) \rightarrow\ B\ (Char) +\ C\ (Volatile)}$$

The conversion rate is defined by:

$$x = (m_0 - m_t)/(m_0 - m_\infty) \tag{1}$$

The kinetics equations in dynamic study are:

$$\frac{dx}{dt} = k(T)f(x) \tag{2}$$

$$k = K_0\, e^{\left(-\frac{E_a}{RT}\right)} \tag{3}$$

$$f(x) = (1 - x)^n \tag{4}$$

Where m_t is the sample mass at the time t, m_0 and m_∞ are the initial and final mass of the sample during the reaction, k is the Arrhenius constant; K_o is the pre-exponential factor, E_a is the activation energy, R is the Universal gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), and f is the conversion function.

$$\frac{dx}{f(x)} = \frac{K_0}{\beta} e^{\frac{-E_a}{RT}} dT \tag{5}$$

$$\beta = \frac{dT}{dt} \tag{6}$$

The integration of Eq. (5) gives:

$$g(x) = \int_{x_0}^{x} \frac{dx}{f(x)} = \frac{K_0}{\beta} \int_{T_0}^{T} e^{\frac{-E_a}{RT}} dT \tag{7}$$

For first order reaction, *n* =1, we have:

$$\ln(-\ln(1 - x)) = \ln\left[\left(\frac{K_0 RT^2}{\beta E_a}\right)\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \tag{8}$$

Since it may be shown that for most values of Ea and for the temperature range of the pyrolysis, the following expression is essentially constant: $\ln\left[\left(\frac{K_0RT^2}{aE_a}\right)\left(1-\frac{2RT}{E_a}\right)\right]$, the curve $\ln(-\ln(1-x))$ versus $\left(\frac{1}{T}\right)$ gives a straight line which may be obtained when the process is assumed as a first order reaction [11]. From the slope, $-E_a/R$, the activation energy E_a can be determined.

On the other hand, we can write the evolution of m_t as function of t (Eq. (9)).

$$\frac{dm_t}{dt} = -k(m_t - m_\infty)^n \tag{9}$$

For simple kinetic reaction model, *n* =1 and Eq. (9) becomes:

$$\frac{dm_t}{dt} = -k(m_t - m_\infty) \tag{10}$$

The integration of Eq. (10) gives:

$$\frac{m_t}{m_0} = \left(1 - \frac{m_\infty}{m_0}\right)e^{-kt} + \frac{m_\infty}{m_0} \tag{11}$$

2.4.2. Calculated Error

In this work, only the variations of the total mass of solid and of the cell temperature can be recorded in the course of time. Because a pure kinetic model is used, no mass or thermal transfer is taken into account. The solid sample is assumed homogeneous in temperature and composition. The initial mass of the sample, the flow rate and the properties of the gas have no influence with such a model. In conclusion, the only input available to improve the experimental conditions is the programmed profile of the cell temperature. For better analysis of the results, a calculation error in each case of kinetic was done. $\mathbf{Erf}$ is the instantaneous error on the results of DTG because it is the most sensitive parameter. The total error for each isotherm is $\mathbf{Erf(T)}$ (Eq. (12)).

$$\mathbf{Erf(T)} = \sum_{t=0}^{\infty}\left[\mathbf{DTG_{Experimental}} - \mathbf{DTG_{model}}\right]^2 \tag{12}$$

3. Results and discussion

3.1. Waste LDPE analysis

The proximate analysis of waste material LDPE was performed. The results are shown in table 1. These values are similar with those found in the literature.

Table 1
Proximate Analysis of waste LDPE.

Parameters	Volatile Matter (%)	Fixed Carbon (%)	Ash Content (%)	Moisture Content (%)
Present study (LDPE)	97.72	0.71	1.57	1
Kumar and Singh (HDPE) [48]	100	0	0	0
Wall et al. (PE) [49]	99.98	0.02	0	0
Parka et al. (LDPE) [50]	99.7	0	0	0.3
Aboulkas et al. [51] (LDPE)	99.6	0	0.4	0
(HDPE)	99.4	0	0.6	0
Encinar and Gonzalez (PE) [52]	99.7	0.1	0.2	0
Wu et al. (PE) [53]	99.98	0.02	0	0

3.2. DTG Analysis

Fig. 2 shows the Termogravimetric (TG or loss of mass) and Derivative Thermogravimetric (DTG) curves of LDPE at five heating rates of 5, 10, 20, 30, 40 and 50 °C min^{-1}. The LDPE decomposes thermally within relatively narrow temperature regions between 400 and 600 °C, reflecting a high sensitivity of the decomposition rate with respect to temperature as it has already been established in some work [6, 35, 1] for HDPE and LDPE. Indeed, the initial temperature at which the degradation started and final temperature at which the degradation is complete for waste LDPE were 409 and 489 °C, 440 and 510 °C, 460 and 540 °C, 465 and 560°C, 470 and 570°C, 480 and 590°C at the heating rates of 5, 10, 20, 30, 40 and 50 °C min^{-1}, respectively.

Differential Thermogravimetric (DTG) curves for LDPE at 5, 10, 20, 30, 40 and 50 °C min^{-1} heating rates contain only one peak, this indicates that there is only one degradation step in Fig. 2. Also, when the heating rate increases, the DTG peak and the Tp (The degradation temperature for LDPE at DTG peak) of the plastic also increase at 5, 10, 20, 30, 40 and 50 °C min^{-1} heating rates.

Fig. 3 shows the T_p curve as a function of heating rate. DTG curves at different heating rates were shifted to higher temperature due to the heat transfer enlarging with increasing heating rate. Similar effect of various heating rates on DTG curves for HDPE pyrolysis has been obtained by Aboulkas et al. [54] and, Kumar and Singh [1]. It is also the case for more authors who studied the thermal degradation of polyethylene [55, 56, 52, 35, 50].

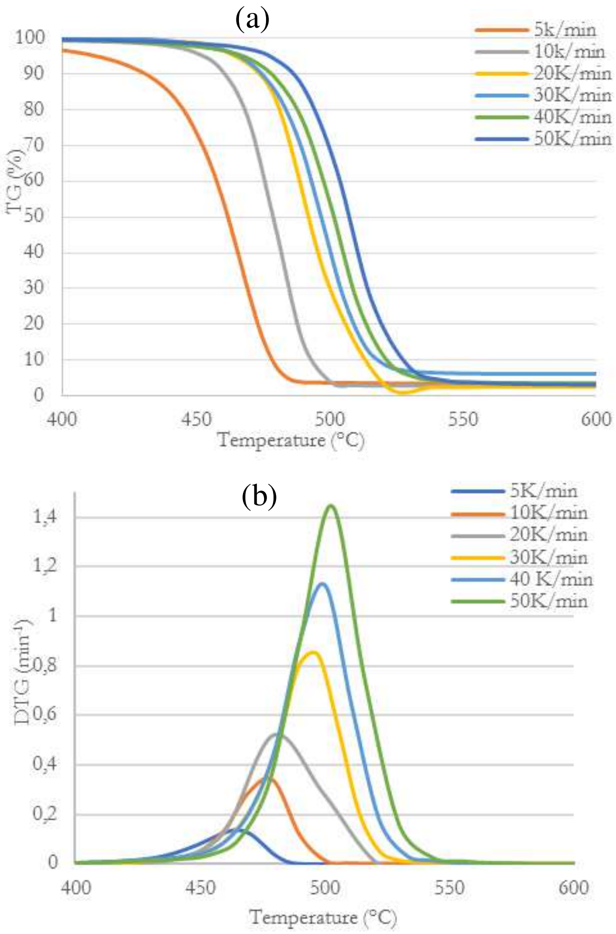

Fig. 2. (a) TG and (b) DTG plots of LDPE at different heating rate.

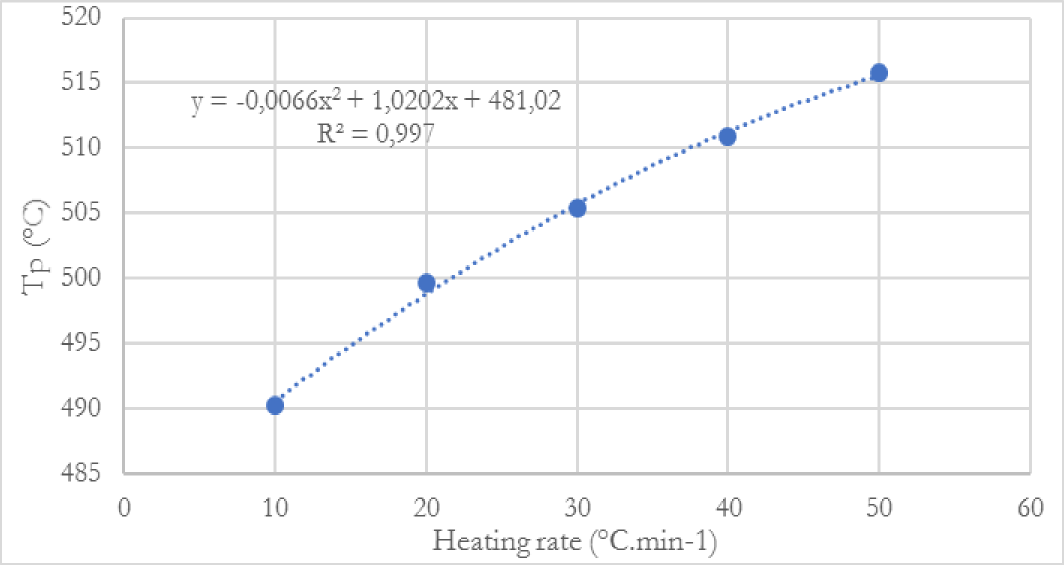

Fig. 3. T_p plot of LDPE as function of heating rate.

3.3. Kinetics model

The following results were found by two methods. On the one hand (method 1), the values of K_{0Exp} and E_{aExp} were determined by Eq. (8) and the curve $\mathbf{ln(-ln(1-x))}$ versus $\left(\frac{1}{T}\right)$. On other hand (method 2) the values of k_{0opt} and E_{aopt} were determined. Indeed, the values of K_{0Exp} and E_{aExp} were used to find the constants of Arrhenius k_i and $d(m_t/m_0)/dt$ (DTG) with the Eq. (10) and Eq. (11) for reaction order n and 1 respectively. The values of K_{0Exp} and E_{aExp} were optimized for determining the $K_{0\ opt}$ and E_{aopt} (K_o and E_a in Table 2) by reducing the error function $\mathbf{Erf(T)}$ obtained by Eq. (12).

3.3.1. Simple step with reaction order n = 1

Table 2 and Fig. 4 show the results of simple step kinetic of LDPE with reaction order $n = 1$. The values of K_o and E_a obtained with the first method are lower than the optimized values found by method 2. Comparing both methods, it is clear that the method 2 used in this paper is better than method 1. Indeed, method 2 is most direct and gives more acceptable results since this method optimizes the first. On the other hand, the method 2 allows to study the kinetic with variable reaction order *n*.

Table 2
Results of simple step kinetic study with reaction order $n = 1$.

β /°C min^{-1}	ln[-ln(1-x)]	R^2	K_0 (min^{-1})	Ea (kJ mol^{-1})	$\mathbf{Erf(T)}$
5	$y = -26439x + 35.53$	0.961	$3.66.10^{21}$	332.75	0.008
10	$y = -48459x + 63.93$	0.991	$6.58.10^{29}$	454.87	0.019
20	$y = -47353x + 61.30$	0.996	$2.95.10^{28}$	439.95	0.129
30	$y = -45008x + 58.00$	0.998	$1.73.10^{25}$	391.00	0.212
40	$y = -32788x + 41.64$	0.962	$6.75.10^{24}$	385.78	0.061
50	$y = -32788x + 41.64$	0.962	$3.91.10^{24}$	382.25	0.060

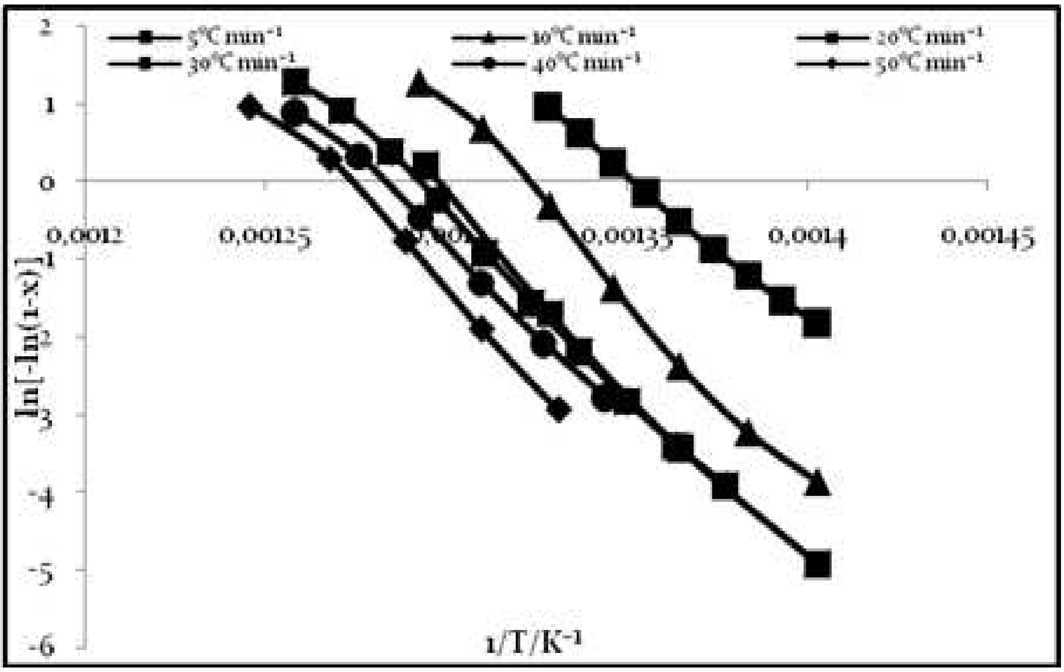

Fig. 4. Curves of ln[-ln(1-x)] versus (1/T) for different values of β.

3.3.2. Simple step with reaction order n

In table 3, we have the values of reaction order *n*, the E_a and K_o obtained by method 2 with different heating rate β. The reaction order varies between 0.8 and 1.5. Similar results were obtained by Bockhorn et al. [57] who found reaction order between 0.8 and 1.4 for the kinetic study of polyethylene. In fact, the reaction order observed depends on the relative conversion of the reactions of inter and intramolecular hydrogen transference. At high temperatures, the intermolecular hydrogen transference is favored, and the reaction order tends to 1.5. Nevertheless, although the reaction order varies, the apparent activation energy remains almost constant. This can be explained that the random scission occurred is the limiting step in the degradation [57, 56]. In the present work, the reaction order reaches the value of 1.50 from heating rate $\beta = 50$ °C min^{-1}. Thus, high temperatures and conversions are favored when the heating rate value is important.

Fig. 5 shows comparatives curves between the Experimental DTG, model DTG obtained by method 1 and optimized DTG obtained by method 2 for each case of reaction order: first and various orders. It is very clear that the case of various reaction orders is the best. In fact the DTG curves in case of various reaction orders are more closed with experimental conditions than curves from first reaction order. Indeed, the best error function (minimum) obtained from various reaction order confirm this observation.

Table 4 summarizes the results of the present study and those found in literature for dynamic kinetic of polyethylene. This table shows that usually the E_a values found with Friedman method are more important than those found with others methods (KAS: Kissinger-Akahira-Sunose method; FWO:

Flynn–Wall–Ozawa method). The works of many authors show that when the heating rate β increases, the activation energy value E_a also increases [1, 6] whereas the present study does not confirm really this result. On the other hand, the E_a values of the present kinetic study vary between 313 and 510 kJ mol^{-1}. These values are more important than those found by other authors. The reason for the wide discrepancy in the measured values of activation energy (apart from the characteristics of the sample) could be attributed to a defective heat transfer and a complex mechanism of decomposition (random scission mechanism) due to diverse operating conditions in the literature [57]. Indeed, it was not possible in the present study to find a stretch of values able to predict the loss mass versus temperature whoever the heating rate value. This can be explained also by the excessive simplification of the kinetic model.

Table 3
Reaction order *n*, Ea and Ko values obtained by method 2.

Heating rate β (°C min^{-1})	Reaction order *n*	E_a (kJ mol^{-1})	K_o (min^{-1})	$\boldsymbol{Erf(T)}$
5	0.84	313.46	$4.45.10^{21}$	0.004
10	1.20	510.00	$2.00.10^{35}$	0.013
20	1.26	481.00	$7.77.10^{32}$	0.115
30	1.40	450.30	$7.27.10^{30}$	0.192
40	1.13	364.00	$6.75.10^{24}$	0.074
50	1.51	452.00	$7.28.10^{30}$	0.0129

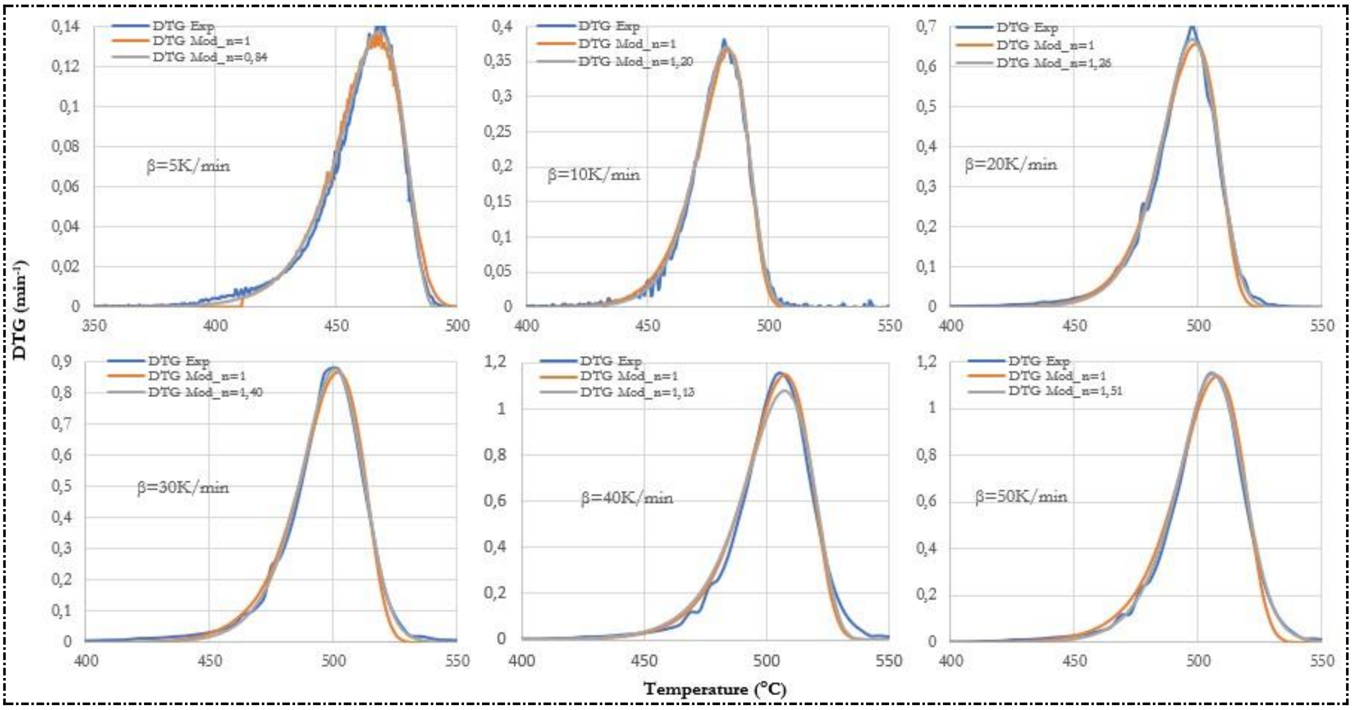

Fig. 5. DTG plots obtained by both methods with heating rates.

Table 4
Comparison of results with literature.

Author	Material	β (°C min^{-1})	Method	Order *n*	E_a (kJ mol^{-1})	K_0 (min^{-1})
Present study	LDPE	5	Friedman	0.84	313.46	$4.45.10^{21}$
		10		1.12	510	2.10^{35}
		20		1.26	481	$7.77.10^{32}$
		30		1.40	450.3	$7.27.10^{30}$
		40		1.13	364	$6.75.10^{24}$
		50		1.51	452	$7.28.10^{30}$
Kumar and Singh [1]	HDPE	10	Friedman	1	207.43	$1.37.10^{11}$
		20			268.22	$5.21.10^{13}$
		40			473.05	$1.68.10^{30}$
Kayacan and Dogan [6]	LDPE	5	Friedman	1	278.74	$2.02.10^{19}$
		10			285.21	$4.42.10^{19}$
		20			271.09	$4.53.10^{18}$
		50			333.43	$6.52.10^{21}$
	HDPE	5	Friedman	1	420.86	$2.05.10^{29}$
		10			464.73	$1.11.10^{32}$
		20			396.05	$1.77.10^{25}$
		50			493.43	$1.47.10^{32}$
Biswas et al. [55]	HDPE		FWO	1	213	
			KAS		211	
			Friedman		221	
Aboulkas et al. [51]	LDPE		FWO	1	218	
			KAS		215	
	HDPE		Friedman	1	247	

3.4. Reaction mechanism

Analysis of the results obtained by ATG according to the mechanism proposed by various authors [16, 20-30] requires consideration of steps involving volatile products. First, the material (PE polymer) degrades to form primary radicals Rp and Rp'. This degradation generates a relatively small number of long radical chains at low temperatures and a large number of short radical chains at high temperatures. If random scission generates radicals with a chain length of less than 72 carbon atoms, they are volatile at 400 °C [24].

The kinetic equation for mass loss would follow an apparent order of around 1, regardless of the secondary steps the radicals may generate in the gas phase. Radicals with very long chain lengths in the liquid phase can generate a high amount of volatile products from temperatures around 500 °C: ethylene by β-scission G1 and alkane by intermolecular hydrogen transfer G3. However, if the temperature or heating rate is low, the primary radicals react to produce mainly secondary radicals by intramolecular hydrogen transfer. This step and the subsequent β-scission reaction of these secondary radicals and intermolecular hydrogen transfer are propagation steps in the mechanism. Intramolecular transfer is favored in the case of a hydrogen transfer of the order of 1.5 [25, 28].

The β-scission reaction generates either a G2 alkene and a short primary radical (predominant reaction) or a nonvolatile material and a primary radical. Intermolecular hydrogen transfer produces alkanes (G3) and secondary radicals Rs. Comparing these three steps, the β-scission reaction is slower than hydrogen transfer, so it is the rate-limiting step [21, 56]. This process continues by generating volatile products and primary radicals with increasingly shorter chains.

Fig. 6 gives a simplified description of the decomposition mechanism described above; P being the polymer (PE), Rp and Rp' primary radicals and Rs a secondary radical.

Considering the volatile products from LDPE pyrolysis, GC/MS analyses of the condensables at 700 °C provided the results in Fig. 7.

These results show that the condensables from LDPE are mainly aliphatic hydrocarbons with carbon numbers between C8 and C25. These identified compounds are in good agreement with those found by Kumar and Singh [48] in their work on PEhD. Indeed, Kumar and Singh [48] identified alkene and alkane hydrocarbons with C9 to C24 [48].

It is also observed that random splitting generates a statistical distribution of the types of species produced for the same number of carbon. Thus the probability of forming an alkene (C = [C]n- C) is twice as great as the probability of forming an alkane (C - $[C]_n$- C) or a diene (C = $[C]_n$= C) [58]. The double bond of alkenes, which can be located on the left or right side of the molecule, explains this distribution, observed in particular in Fig. 8.

The histogram in Fig. 8 shows the quantities of hydrocarbons (alkenes and alkanes) from the pyrolysis of LDPE from 600 to 900 °C. This figure clearly shows that at each temperature, the amount of alkenes is at least twice that of alkanes. These results confirm the previous assertion of the probability of formation of the identified hydrocarbon types in the condensables from LDPE pyrolysis.

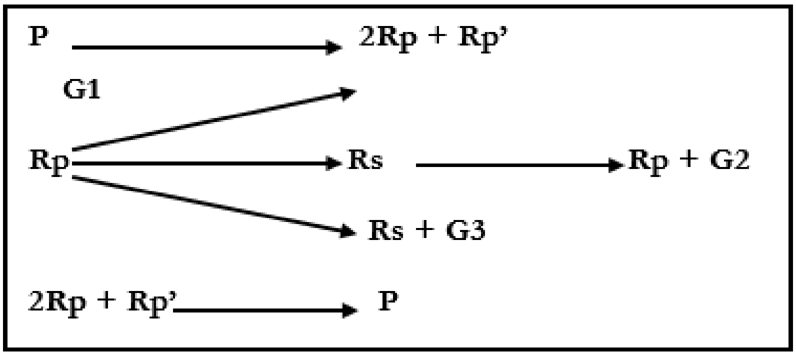

Fig. 6. Decomposition mechanism of LDPE

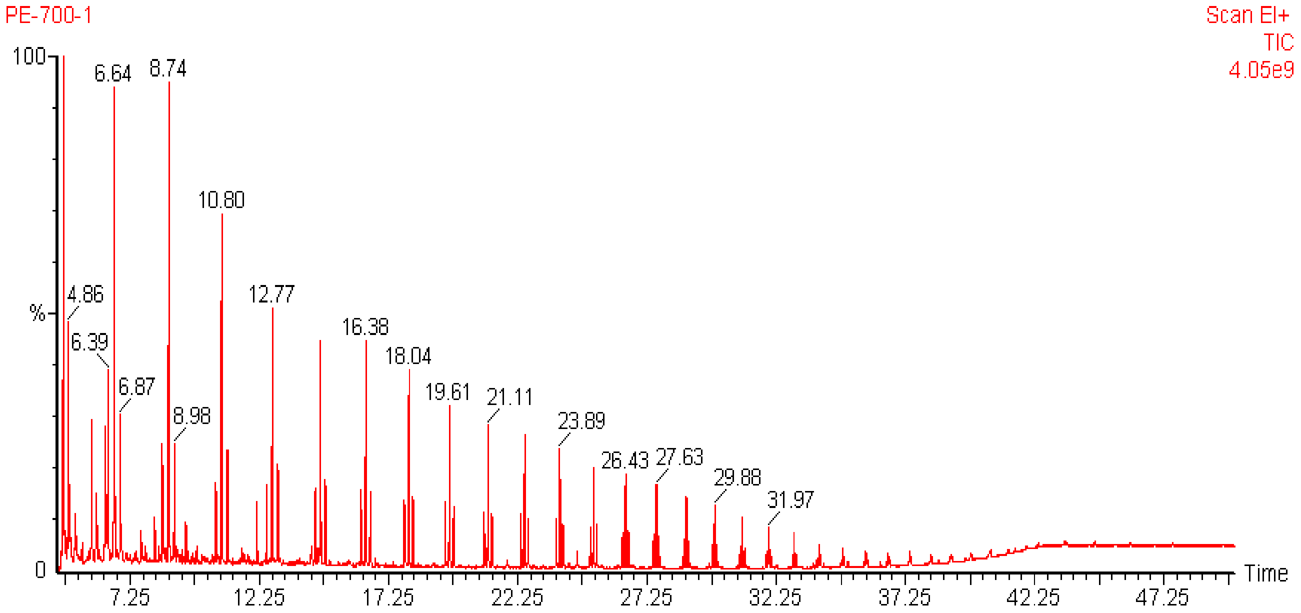

Fig. 7. GC/MS of LDPE at 700 °C.

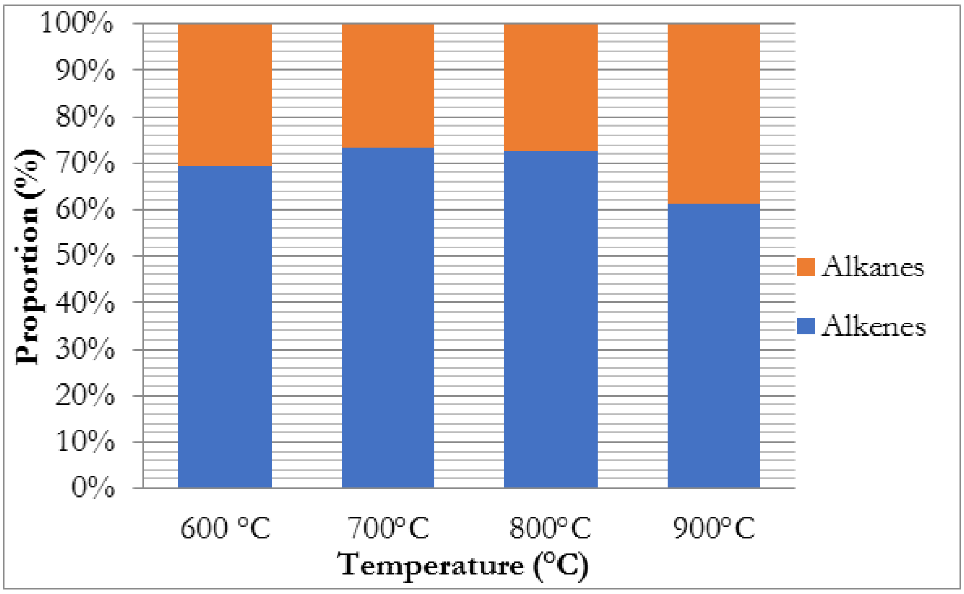

Fig. 8. Quantitative distribution of Hydrocarbons from LDPE.

4. Conclusion

The thermal decomposition and mass loss of low density polyethylene in an inert atmosphere has been studied by thermogravimetric Analysis (TGA). Dynamic experiments using different heating rates have been carried out. Mechanism of decomposition of LDPE is complex and based on Random Scission. Thus, the reaction orders were determined and are variables in function of heating rate and ranges from 0.8 to 1.5. Kinetic parameters provides information to design more effective conversion systems and optimum pyrolysis regimes. The TG experiment showed that the heating rate has an important role on the degradation reaction. When the heating rate increases, the degradation temperature of the LDPE also increases. The degradation temperatures for waste LDPE at which the maximum mass losses (T_p) take place were about 470, 490, 500,505, 510 and 516 °C at the heating rates of 5, 10, 20, 30, 40 and 50 °C.min^{-1}, respectively. The kinetic parameters of waste LDPE pyrolysis were determined with the *n* values. These results were better than those found with first order reaction. In conclusion, these numerical methods get the advantage to be easily scheduled without software or mathematic competences.

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