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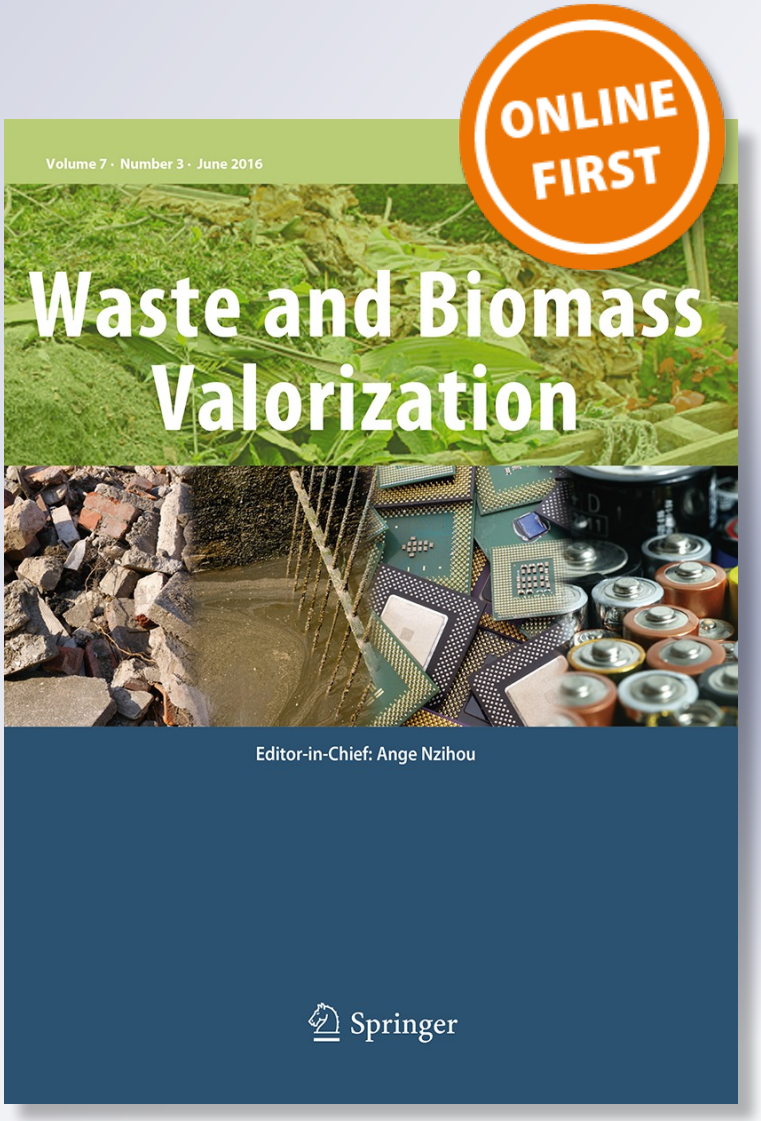
Waste and Biomass Valorization

ISSN 1877-2641

Waste Biomass Valor
DOI 10.1007/s12649-016-9590-5



Springer

Waste Biomass Valor
DOI 10.1007/s12649-016-9590-5

ORIGINAL PAPER

Kinetic Study of Low Density Polyethylene Using Thermogravimetric Analysis, Part 2: Isothermal Study

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Received: 14 May 2015 / Accepted: 18 May 2016

Abstract Thermal behavior of plastic materials can be improved by knowing thermal degradation kinetics for the optimal design and operation of pyrolysis process. In continuity of part 1 of the present study, Thermogravimetric analysis has been used for isothermal kinetic study of waste Low-Density Polyethylene (LDPE) pyrolysis under Argon atmosphere at different temperatures 420, 430, 440, 450, 460 and 470 °C. These isotherms were chosen after determining the range of thermal degradation of LDPE using Thermogravimetric analysis in non-isothermal conditions. This work aims to analyze the applicability of simples kinetic models to the prediction of the thermal behavior of the material, taking into account the complex chain reaction mechanism. Because of this complex reaction mechanism, the reaction order of pyrolysis of LDPE was determined. Freidman method has been used to obtain the activation energy and the frequency factor from isothermal experiments and compare them with the values obtained from non-isothermal experiments obtained in part 1 and with the results obtained by other authors.

Keywords Thermogravimetric analysis · Reaction kinetic · Activation energy · Reaction order · LDPE

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Introduction

Presently, the greatest environmental problem facing developed in countries of West African sub region and especially Benin, is municipal and public waste management. The development of African cities inevitably leads to the accumulation of waste quantities increasingly important and centralized. Moreover, the use of plastic sachet made from PVC (or Low Density Polyethylene: LDPE) is a scourge, these sachets are not biodegradable, they accumulate in all locations of towns and in particular peripheries. Water is packaged in LDPE sachet that serves as a cheapest packaged material. This situation is a real problem for these cities. The recycling of waste plastic bag has attracted much interest as an alternative method for their disposal and management other the last few decades. Waste plastic recycling is mainly divided into two routes: mechanical reprocessing of waste plastic, and thermal or catalytic degradation of waste plastic into gas and liquid products, which can be subsequently be utilized as fuels and valuable chemicals. Pyrolysis is the most attractive technique of chemical feed stock recycling [1]. Valuable product can be produced from waste plastics by using pyrolysis technology. According to Wilson, the pyrolysis process is assumed to take place as from 325 °C and up to a maximum temperature of 850 °C [2]. Ademiluyi and Adebayo [3] evaluated the fuel gases produced by pyrolysis of waste polyethylene waste (pure water sachets) at low and high temperatures. Gonzalez et al. [4] carried out catalytic pyrolysis of polyethylene in spouted bed reactor and obtained products ranging from C_2 to C_9. Nema and Ganeshphrasad [5] studied the plasma pyrolysis of medical waste. However, there are many serious problems to be solved in the near future. The present issues are the necessary scale-up of the industry, minimization of production cost and optimization of higher-valued products

Published online: 01 June 2016

for wide range of plastic mixtures [6]. Especially the lack of kinetic data hampers the optimal design of pyrolysis process and the design of commercial pyrolysis reactor. Therefore, the kinetics of thermal degradation of waste plastic must be analyzed to provide the apparent kinetic parameters that are useful for the optimal design and operation of pyrolysis process. Thermal behavior of plastics can be improved by knowing thermal degradation kinetics.

Thermogravimetric analysis (TG) is an excellent way to study the kinetic of thermal degradation. Many studies on pyrolysis of plastic wastes have been carried out, and also various reaction kinetic models are available to estimate plastic degradation, including 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 pyrolysis kinetics of the HDPE and LDPE respectively with the Friedman [11] model. In the same way, Alvarenga [12] compare the kinetics parameters of PE, cardboard and carton packaging obtained by three methods: the Kissinger's, the Kissinger–Akahira–Surnose (K–A–S)'s and Starink's methods [13–15].

Most authors describe thermal decomposition by a power law equation and perform isothermal and/or dynamic experiments. Depending on the atmosphere, heating rate, sample size, etc. the reaction order has been found to vary between 0 and 1, whereas the kinetic parameters show a more significant variation. These differences have been associated with different causes such as the existence of temperature profiles inside the sample, the thermal gap between system and sample temperatures, the influence of the heating rate on the reactions taking place during the decomposition and the existence of a complex reaction mechanism [10, 16–18]. Other causes of discrepancy suggested are the mathematical method used in the calculation and the existence of parallel, consecutive or complex reaction mechanisms in general [16, 19].

As it is mentioned above, the reaction mechanism considered for the thermal decomposition of polyethylene can be the cause of the disparity of the results. A radical chain mechanism is the more generally accepted reaction model [16, 20–30]. The mechanism suggested by Bockhorn et al. [16] is a simplified version of this. It starts with a random scission to give primary radicals. The propagation is carried out: (1) by scission in β of these radicals, (2) by intramolecular hydrogen transference (backbiting reaction), followed by β-scission, and (3) by intermolecular hydrogen transference (H abstraction reaction). The termination is carried out by a recombination of radicals. The rate law obtained is a function of the polymer amount to the power of 0.5 and 1.5 [16]. The reaction order observed depends on the relative conversion of the reactions of inter and intramolecular hydrogen transference.

At high temperatures and conversions, 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 taking into account that random scission is the limiting step in the degradation. Often, kinetic studies on the pyrolysis of plastic have been developed on the assumption that the reaction can be described by a first-order reaction model. This is also the case of many others authors [10, 31, 32]. Recent studies [33–36] disputed the first-order assumption and reported a reaction order of 0.5.

It is so clear that it has many differences between isotherm and dynamic kinetics. It is necessary to supply a simple kinetic mechanism for cover both isotherm and dynamic conditions.

The objective of this second part of this study was to estimate the reaction model of the LDPE pyrolysis along with the Arrhenius parameters from isothermal kinetic data. It is intended to compare these results with those obtained by other authors in the one hand and those obtained in part 1 in the other hand and to verify if it is possible to explain the mass loss of polyethylene by means of a simple rate law, while knowing fully well that it is a complex mechanism. To minimize decomposition during the course of temperature rise to the isothermal temperature, we have established a consistent program of temperature rise.

Materials and Methods

Raw Material

The Low Density Polyethylene (LDPE) used in this work is the raw material of the plastic bag black color found in abundance in household waste of the city of Abomey-Calavi in Benin that we just picked up. LDPE quantity become more and more important in household solid waste. It is not biodegradable and causes many waste management problems in Benin. Thus, in objective to study of valorization methods of household waste in Benin, it was suggested to treat LDPE, which have high calorific value, by thermochemical ways. The raw material used is black LDPE bag waste that serves as a cheapest packaged material in Abomey-Calavi city.

Because the reactor used for pyrolysis process allows smalls sample mass and volume, raw LDPE was cut into small pieces (approx. 1–2 cm^2) and used in the pyrolysis reaction. Indeed, we use the pair of scissors and measurement instruments (ruler) in order to get small pieces of 1 cm^2.

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. It allows us to use small sample mass (10–50 mg) which is needed to ensure isothermal conditions in samples. 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 never the same [37].

For these tests, samples have been previously dried in an oven at 103 °C for 48 h. The work under isothermal conditions allows studying the kinetic of reactions without being influenced by thermal effects caused by the temperature rise.

LDPE is heated in the furnace to the isotherm $T\varepsilon\{420; 430; 440; 450; 460; 470$ °C$\}$, according to analysis results obtained by non-isothermal analysis (see part 1). The program of temperature rise is as follows:

- Heating up from 40 to (T-20) °C at 50 °C min^{-1}
- Rise in temperature from (T-20) °C to (T-10) °C, 30 °C min^{-1}
- Rise in temperature from (T-10) to T °C at 10 °C min^{-1}
- Isotherm to T °C for a time t in min

This methodology is used to shorten the first thermal dynamic stage and to limit the sample degradation before isothermal step.

The maximum temperature for these tests was set at 470° C because at greater temperature, the mass loss during the heating period is very important (about 50 %) in order to exploit results.

Isothermal Kinetic Theory

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 [40]. Some authors have demonstrated the influence of experimental conditions (for example [41, 42]). In this work, simple step model and two steps model were studied in isothermal conditions.

Simple Step Reaction Model: Model 1

The reaction scheme assumed here for the thermal degradation of Solids was proposed by some authors [1, 6, 12, 43, 44]:

$$\mathrm{k} : \mathrm{A(LDPE)} \rightarrow \mathrm{B\ (Char)} + \mathrm{C(Volatile)}$$

The LDPE, noted A, is degraded by only one reaction. Gaseous products (C) and solid residue (B), called char are produced.

Single step kinetic for solid state decomposition takes the following kinetic equations:

$$\frac{dm_t}{dt} = -k(m_t - m_\infty)^n \quad (1)$$

$$k = K_0 e^{\left(-\frac{E_a}{RT}\right)} \quad (2)$$

where m_t is the sample mass at the time t, m_0 and m_∞ the initial and final mass of the sample during the reaction, k is

the Arrhenius constant; K_o the pre-exponential factor, E_a the activation energy, R gas constant (J mol^{-1} K^{-1}), T absolute temperature (K).

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

$$\frac{dm_t}{dt} = -k(m_t - m_\infty) \tag{3}$$

The integration of Eq. (3) gives:

$$\frac{m_t}{m_0} = \left(1 - \frac{m_\infty}{m_0}\right)e^{-k\tau} + \frac{m_\infty}{m_0} \tag{4}$$

$$\tau = t - dt \tag{5}$$

τ is the corrected time and dt is the difference between the experimental and modeling conditions.

Two Steps Reaction Model: Model 2

The degradation reaction of a solid in mathematical approach consists of the following two steps [44–46]:

1. LDPE (S) → Intermediate Solid (I) + Gaz (G_1)
2. Solid (I) → Solid (C) + Gas (G_2)

$$k_1 : S \rightarrow \alpha I + (1 - \alpha)G_1 \tag{6}$$

$$k_2 : I \rightarrow \beta C + (1 - \beta)G_2 \tag{7}$$

Solid *(S)* decomposes into solids *(I)* and gas *(G_1)*, simultaneously solid *(I)* decomposes into solid *(C)* and gas *(G_2)*, α and β represent the mass fractions of solids *(S)* and *(I)* respectively.

In a first reaction, the initial LDPE masse $m_S(t)$ is converted into an intermediate pseudo-species denoted $m_I(t)$ and gas. Then, the pseudo-species is converted into char, denoted $m_C(t)$, and gas through a second reaction. m_t: total mass of the sample at the time t is the sum of the masses of LDPE, intermediate pseudo-species and char; m_0: initial total mass; m_∞: final total mass.

The mathematical model, describing the time evolution of the different mass fractions during the pyrolysis process, is based on set first-order differential equations. The mass loss phenomenon of the cardboard pyrolysis is described by:

$$\frac{dm_S}{dt} = -k_1 m_S \tag{8}$$

$$\frac{dm_I}{dt} = -\alpha\frac{dm_S}{dt} - k_2 m_I = \alpha k_1 m_S - k_2 m_I \tag{9}$$

$$\frac{dm_C}{dt} = \beta k_2 m_I \tag{10}$$

$$k_1 = k_{01}e^{\left(-\frac{E_{a1}}{RT}\right)}etk_2 = k_{02}e^{\left(-\frac{E_{a2}}{RT}\right)} \tag{11}$$

$$m_S = -m_0 e^{-k_1 t} \tag{12}$$

$$\frac{m_I}{m_0} = \frac{\alpha k_1}{k_1 - k_2}\left(e^{-k_2 t} - e^{-k_1 t}\right) \tag{13}$$

$$\frac{m_C}{m_0} = \frac{\beta\alpha k_2}{k_1 - k_2}e^{-k_1 t} - \frac{\beta\alpha k_1}{k_1 - k_2}e^{-k_2 t} + \alpha\beta \tag{14}$$

$$m_t = m_S + m_I + m_C \tag{15}$$

With the following initial boundary conditions $m_s(0) = -m_o$; $m_I(0) = 0$; $m_C(0) = 0$.

Calculating 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 and 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. *Erf* is the instantaneous error on the results of DTG because it is the most sensitive parameter. The total error for each isotherm is $Erf(T)$

$$Erf(T) = \sum_{t=0}^{\infty}\left[DTG_{Experimental} - DTG_{model}\right]^2 \tag{16}$$

Values of E_{ai} and K_{oi} are evaluated using Excel solver by minimizing the sum Erf_T of $Erf(T)$ at different temperatures.

$$Erf_T = \sum_{T\in\{430;430;440;450;460;470\}} Erf(T) \tag{17}$$

Results and Discussions

Two of the most important causes of discrepancies in the results of kinetic parameters for polyethylene pyrolysis are a defective heat transfer to or in the sample and a complex degradation mechanism [21]. The heat transfer problems can be minimized using small amounts of sample and low heating rates, but a complex mechanism of decomposition can cause important differences in the parameters obtained from isothermal and non-isothermal experiments. Bockhorn et al. [21] suggest that both isothermal and non-isothermal experiments should be combined in kinetic studies. Taking this into account, the results obtained in both isothermal and dynamic (see part 1) experiments have

been analyzed in this work. Friedman method is used for kinetic study because it is very simple and don't need sophisticated mathematics models.

Kinetic Study

For determining the Arrhenius parameters in isothermal conditions, the models TG and DTG were calculated by Eqs. (1–5), for simple kinetic model (reaction numbers 1 and n) and Eqs. (8–15) for two steps kinetic. The constant values k were optimized independently to minimize the error function [Eq. (16)] between the experimental and theoretical conditions using the solver function of Microsoft Excel. The $k_{optimized}$ values were so determined for close the TG and DTG curves in experimental and theoretical conditions.

Thus, the Arrhenius parameters: Activation Energy E_a and Pre-exponential factor K_o were found by modeling of the plot of ln $k_{optimized}$ as function of $1/T$. Knowing that this curve is not a perfect line, it is noticeable that values of $k(T)$ will be different of $k_{optimized}(T)$ and that the accuracy of the model with these new values of k will not be as good as with $k_{otpimized}$. That is why a second step of optimization is proposed using a second error function [Eq. (17)] which is the sum of error functions for different reaction temperatures. In this second step, k are no longer optimized independently but K_o and E_a are both optimized to minimize the global error function for all experiments. By this way, model fits obtained at different temperatures give a best accuracy than after the first step of optimization. Values of k calculated from this new couple of kinetic parameters are named k_T for model 1, k_1 and k_2 for model 2. This numerical method is very simple and allows the use of simple software like Excel and does not require sophisticated mathematical skills (Fig. 1).

Simple Step Kinetic with Reaction Order n = 1

The results of simple step kinetic of pyrolysis of LDPE with reaction order n = 1 are given in Table 1. Thus, the

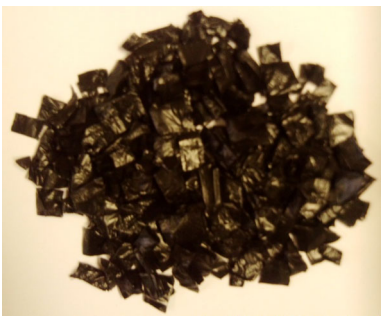

Fig. 1 Raw LDPE preparation

Table 1 Values of k_T (min^{-1}) at different isotherms

Temperature (°C)	k_T (min^{-1})	Erf_T
420	0.030	0.002
430	0.055	0.005
440	0.101	0.009
450	0.182	0.009
460	0.322	0.002
470	0.560	0.000

Arrhenius parameters: activation energy E_a and pre-exponential factor K_o were found by modeling of the plot of ln$k$ as function of $1/T$ (Fig. 2). The optimized value obtained are $E_a = 251$ kJ mol^{-1} and $K_0 = 2.45 \times 10^{17}$ min^{-1}. The lnk values calculated from these optimized values of Ea and Ko have produced the aligned points obtained on Fig. 2 (see Sect. 3.1 for details)

On Fig. 3, it is showed the experimental and calculated (using $K_{calculated}$ values found by the model and final optimization with [Eq. (17)] by solver function) TG plots versus times t(min) for each isotherm. Analysis of these curves shows that at first, the theoretical and experimental curves are shifted. We find that the experimental curve decreases slowly at first, accelerates from a time and then decreases slowly at the end. Furthermore, the theoretical curves are constant initially and decrease rapidly to the end. In conclusion, it is clear that this model does not explain the mass loss of LDPE correctly.

Simple Step with Reaction Order n

Order of Reaction n Linearization of Eq. (1) gives the Eq. 18 which allows to calculate the reaction order n.

$$\ln\left(-\frac{dm_t}{dt}\right) = \ln k + n\ln(m_t - m_\infty) \tag{18}$$

The value of reaction order has been calculated and the results obtained are shown in Table 2. Table 2 shows that the reaction orders are very similar. An average value $n = 0.667$ is obtained. These results are lower than those found by Ceamanos [47] (0.86–1) for kinetic of pyrolysis of HDPE in isothermal conditions. The differences may be due to the material used and the experiment conditions in each case.

Simple Step with Reaction Order n = 0.667 The kinetic of pyrolysis of LDPE was performed with $n = 0.667$. The Table 3 shows the optimized values of k by the Solver function of Microsoft Excel. Thus, the Arrhenius parameters: activation energy and pre-exponential factor were found by modeling of the plot of lnk as function of $1/T$ (Fig. 4). We have $E_a = 244$ kJ mol^{-1} and

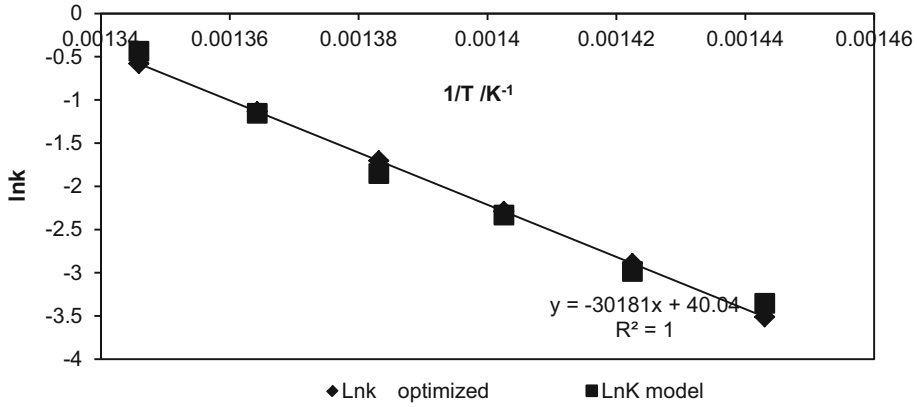

Fig. 2 Plots of Lnk as function of 1/T

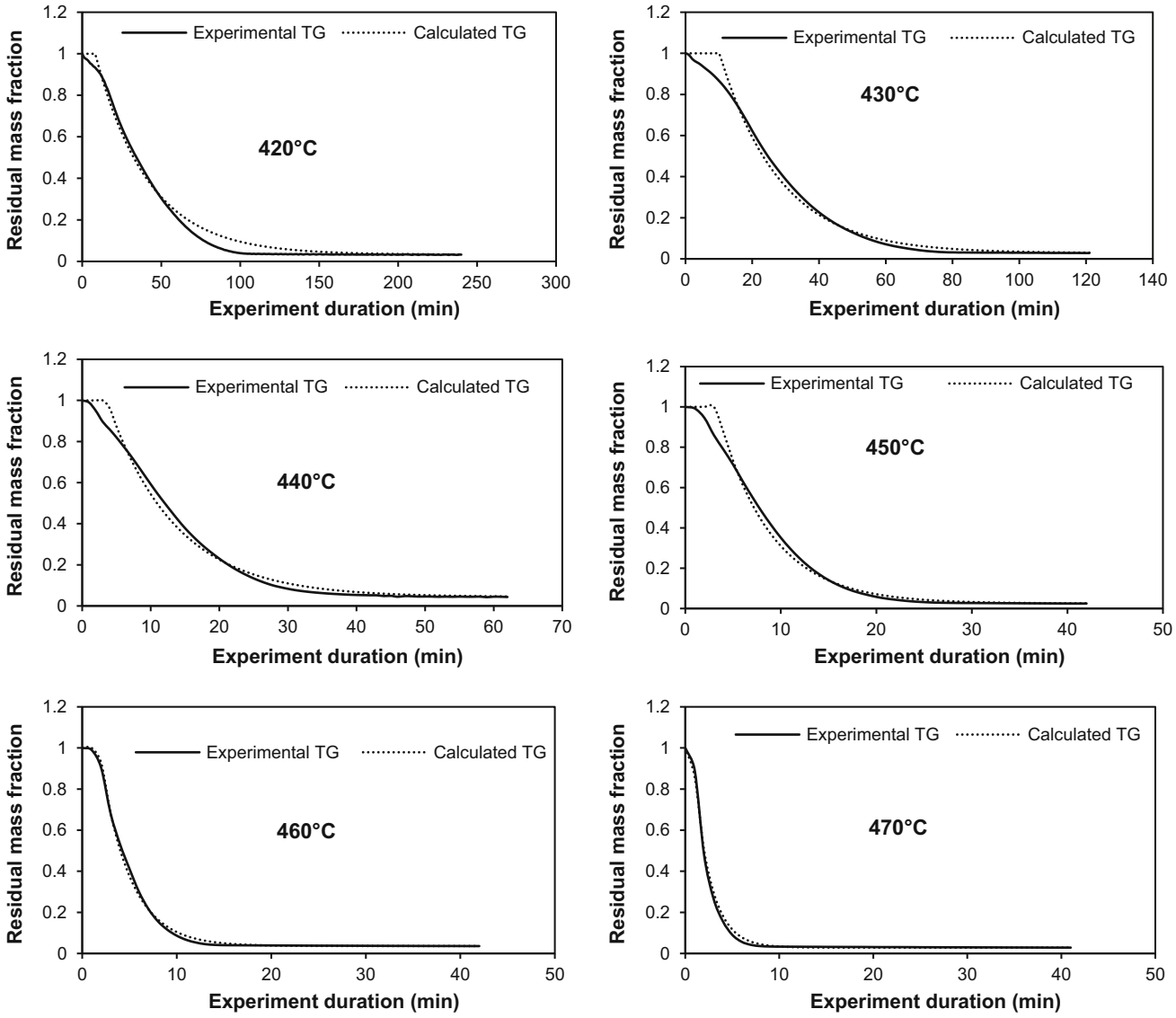

Fig. 3 Experimental and calculated TG results for each isotherm

Table 2 Expressions of lnr and n value at each isotherm

Temperature (°C)	n
420	0.667
430	0.668
440	0.665
450	0.666
460	0.679
470	0.657

Table 3 Values of k_T at different isotherms

Temperature (°C)	k_T (min^{-1})	Erf_T
420	0.021	0.002
430	0.039	0.003
440	0.070	0.004
450	0.124	0.005
460	0.215	0.045
470	0.369	0.140

$K_0 = 5.6 \times 10^{16}$ min^{-1}. On Fig. 5, the experimental and calculated TG (using $K_{calculated}$ values found by the model and final optimization with [Eq. (17)] by solver function) plots versus experiment duration (min) for each isotherm are shown with reaction order $n = 0.667$. Analysis of these curves show the same phenomenon that previously—for reaction order $n = 1$. In this case, the theoretical curves are improved and better approach with experimental conditions than the previous case. Therefore, the reaction order $n = 0.667$ more responsive to the mass loss of LDPE. It should also be noted that the values of Arrhenius parameters E_a and K_o are very similar in both cases.

Furthermore, the error functions which are much smaller in this second case confirm this assertion. However, regardless of the order of the reaction, it is concluded that a simple step model does not sufficiently explain the mass loss of LDPE. This may be due to the phenomenon of rise in temperature of the sample or can be also an over simplification of the model which is not representative of the reaction mechanisms of the pyrolysis of plastic bag.

Table 4 recapitulates the results of the present study and those found in literature for isothermal kinetic of polyethylene pyrolysis. This table shows the results typically obtained from the literature. Indeed, these results are very close to those obtained by other authors who have worked in similar conditions (isothermal)

Table 5 the results of simple step kinetic of LDPE with reaction order $n = 1$ in dynamic study (part 1). TG was performed in Argon atmosphere at the heating rates of 5, 10, 20, 30, 40 and 50 °C min^{-1}. Table 5 shows that the Arrhenius parameters change in function of heating rates β. Comparison with results obtained shows that E_a found in dynamic condition are higher than E_a in isothermal conditions. This difference may be caused by a temperature gradient of the resistance of heat conduction in the sample and the resistance of outer heat transfer [38]. In the other hand, in dynamic conditions, the reaction orders found in part 1 of this study are variables in function of heating rate and ranges from 0.8 to 1.5. Bockhorn et al. [21] suggest that both isothermal and non-isothermal experiments should be combined in kinetic studies. This suggestion is justified, because both studies are necessary and the one completes the other. However, the differences between the experiments conditions (isothermal and dynamic) don't allow to obtained similar results.

Two Steps Reaction Model: Model 2

Further to the previous results, the kinetics of the pyrolysis of LDPE was treated in two reaction steps. The results of the simulation are summarized in Table 6 and Fig. 6. k_i

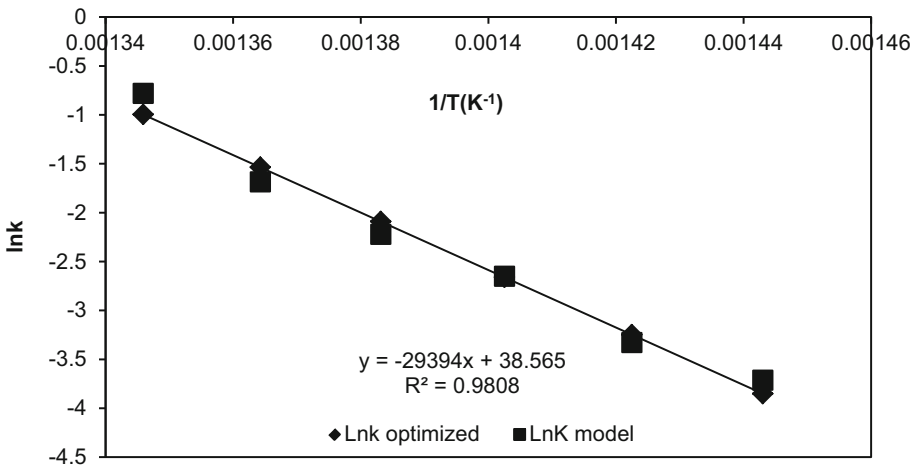

Fig. 4 Plot of Lnk as function of 1/T

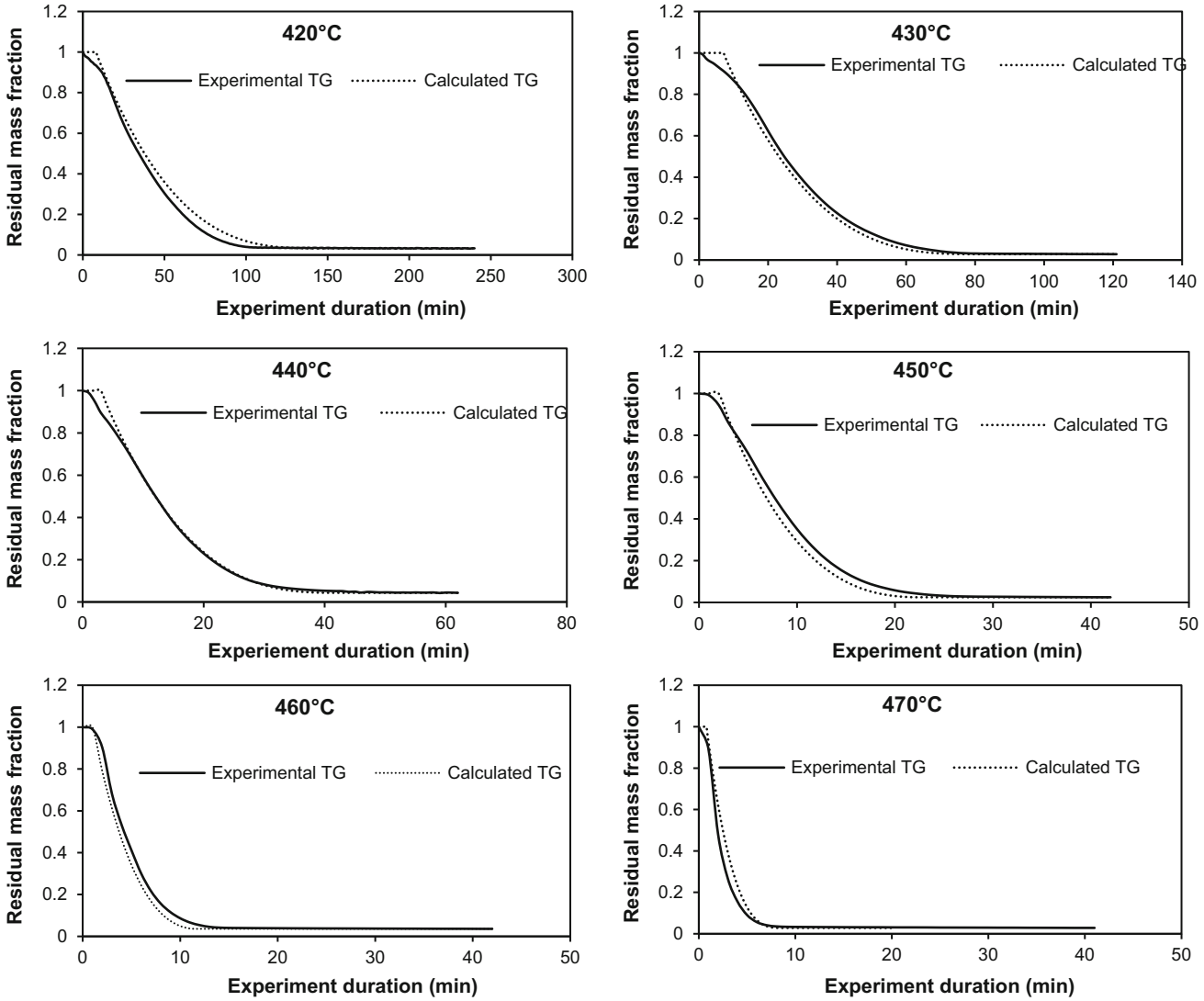

Fig. 5 Experimental and calculated TG results for each isotherm

Table 4 Comparison of results with literature

Authors	Material	Order n	T (°C)	Ea (kJ mol^{-1})	K_0 (min^{-1})
Present study	LDPE	1	400–500	251	2.45×10^{17}
		0.667	400–500	244	5.6×10^{16}
Kim [35]	HDPE	0.5	440–470	190	
Westerhout [10]	HDPE	1	400–450	220	1.9×10^{13}
	LDPE1	1	400–450	241	1.0×10^{15}
	LDPE2	1	400–450	201	9.8×10^{11}
Bockhorn [17]	PE	0.81	200–600	259	7.2×10^{13}
Klose [18]	PE	1	385–520	275	1.1×10^{18}
Madorsky [48]	PE		385–405	284	8×10^{19}
Wu [49]	HDPE	0.74	327–487	234	9.3×10^{13}
		0.63	327–487	206	1.2×10^{12}
Bockhorn [50]	HDPE	0.8–1.4	400–470	268	
Ceamanos [47]	HDPE	1	390–470	248.7	1.75×10^{17}

Table 5 Results of simple step kinetic study with reaction order n = 1

β/ °C min^{-1}	Material	Order	K_0 (min^{-1})	Ea (kJ mol^{-1})
5	LDPE	1	3.66×10^{21}	333
10			6.58×10^{29}	455
20			2.95×10^{28}	440
30			1.73×10^{25}	391
40			6.75×10^{24}	386
50			3.91×10^{24}	382

Table 6 Values of k at different isotherms

Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	Erf_T
420	0.035	0.045	0.0009
430	0.067	0.080	0.0010
440	0.128	0.141	0.0003
450	0.238	0.245	0.0009
460	0.437	0.418	0.0011
470	0.789	0.703	0.0005

were determined in the same manner as in the previous cases.

The Arrhenius parameters: Activation Energy and Pre-exponential factor were found by modeling of the plot of $\ln k_i$ as function of $1/T$ (Fig. 6). We have $E_{a1} = 268$ kJ mol^{-1}, $E_{a2} = 236$ kJ mol^{-1} and $K_{01} = 5.04 \times 10^{18}$ min^{-1}, $K_{02} = 2.64 \times 10^{16} min^{-1}$. On Fig. 7, the experimental calculated TG plots versus times t (min) for each isotherm are presented. Analysis of these curves shows that we predict much better the evolution of the mass loss in the first minutes of testing. We can conclude that this two-step model of reaction order $n = 1$ sticks better to the reality because it is closer to the real reaction mechanisms developed above. But we cannot be too emphatic about this because we cannot demonstrate that we are in thermal equilibrium (no thermal gradient in the sample) especially at the beginning of the test.

Reaction Mechanisms

The random scission mechanism as its name indicates the cutting position in the polymer chain random. This results in the formation of many different species lighter. Polyethylene is a polymer that behaves this way. When heated, one of the bonds in the polymer chain is producing two broken pieces of polymer having radical ends (Reaction 1).

Reaction 1: LDPE Random scission mechanism

$$CH_3 - [CH_2]_n - CH_2 - CH_2 - [CH_2]_m - CH_3 \rightarrow CH_3 - [CH_2]_n - CH_2 \cdot + \cdot CH_2 - [CH_2]_m - CH_3$$

Reaction 2: Radical termination

$$CH_3 - [CH_2]_n - CH_2 \cdot + \cdot CH_2 - [CH_2]_m - CH_3 \rightarrow CH_3 - [CH_2]_n - CH_2 - CH_2 - [CH_2]_m - CH_3$$

Reaction 3: β-Scission

$$CH_3 - [CH_2]_n - CH_2 - [CH\cdot] - CH_2 - [CH_2]_m - CH_3 \rightarrow CH_3 - [CH_2]_n - CH_2 \cdot + CH_2 = CH - [CH_2]_m - CH_3$$

Radicals can be recombined by capturing another radical to become a saturated molecule (see Reaction 2). The free electron which is on the carbon atom where the cleavage occurred can drag it to another carbon atom. Thus the radical is located more to the end of a molecular chain stabilized after a *β-Scission*. An unsaturated molecule and a new radical molecule (see Reaction 3) are thus produced; the remaining radical may disappear after an H abstraction reaction or a radical reaction termination.

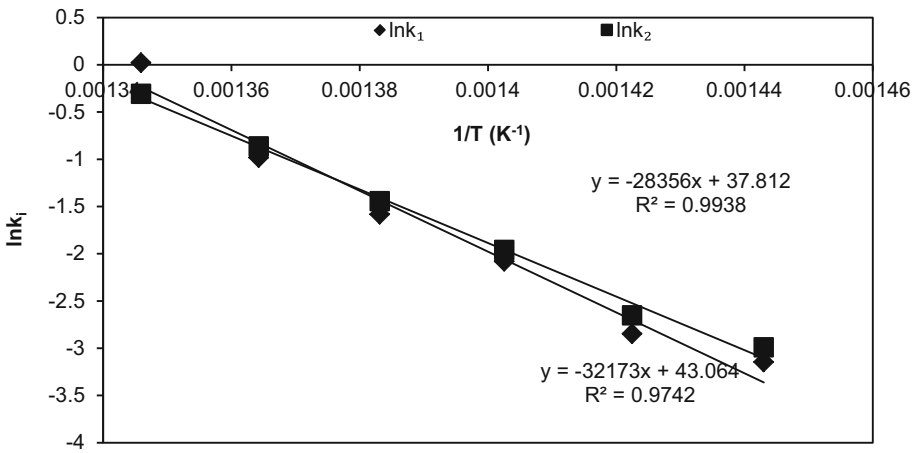

Fig. 6 Plot of Lnk_i as function of 1/T

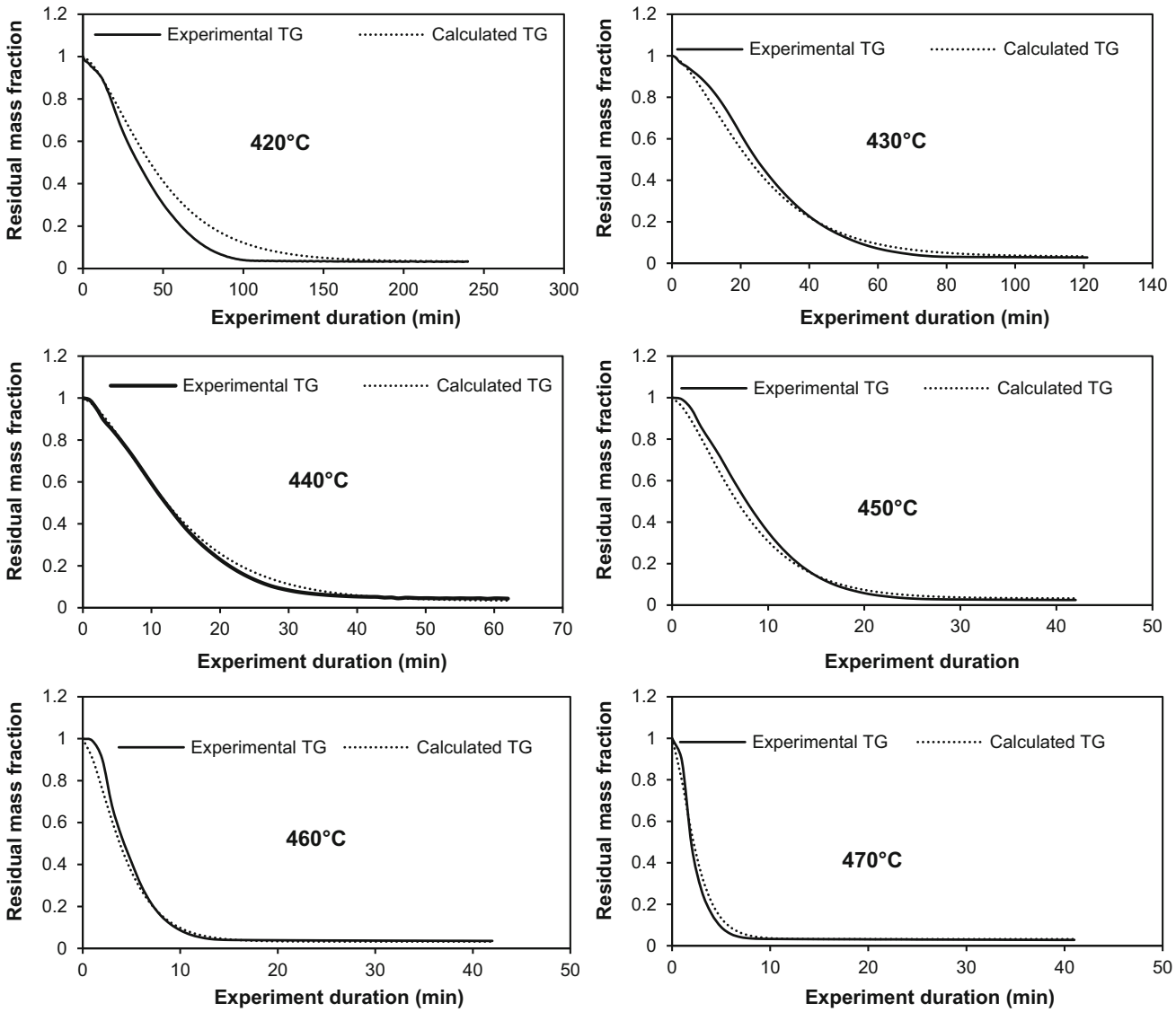

Fig. 7 Experimental and calculated TG results for each isotherm

The molecular chain of polyethylene is formed of thousands of carbon atoms. So the random cleavage mechanism has many solutions. The two pieces of polymer products are still subject to the same mechanism and so on until the molecules thus created are enough light to be stable under the conditions of the environment. The Fig. 9 explains this process. In fact, Fig. 9 shows the successive spectra of a minute apart obtained from the FTIR analysis of the pyrolysis product obtained by TG in dynamic study. The spectra are obtained by direct connection between the TG apparatus and FTIR in dynamic study of LDPE with 10 °C min^{-1} heating rate according to the Fig. 8.

These results show that the spectrum of gases from the degradation of the LDPE is the LDPE itself which is normal because the PE is a long chain composed of enormous simply C–C bond as gases generated during its degradation (Fig. 9).

It is also noted that cleavage generates a random statistical distribution of the types of items to the same species carbon number. Thus, the probability to form an alkene ($C=[C]_n–C$) is twice as large that the probability of forming an alkane ($C–[C]_n–C$) or a diene ($C=[C]_n=C$). The double bond alkenes, which can either be left or right of the molecule, this explains distribution observed including the LDPE pyrogram at 600° C in Fig. 10.

The discrepancies between isothermal and dynamic experiments and with the results of other authors will be considered to be a consequence of the complex degradation mechanism, as is generally accepted. Some kinetic equations have been suggested that do not consider a single step

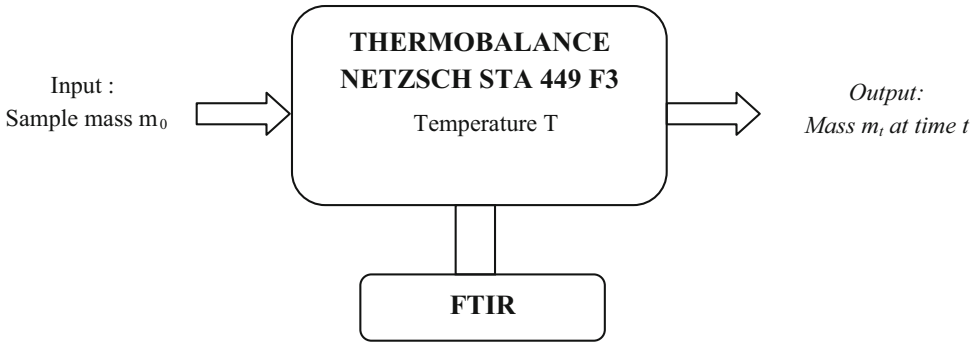

Fig. 8 Connection between TG and FTIR with $\beta = 10\ ^{\circ}C\ min^{-1}$

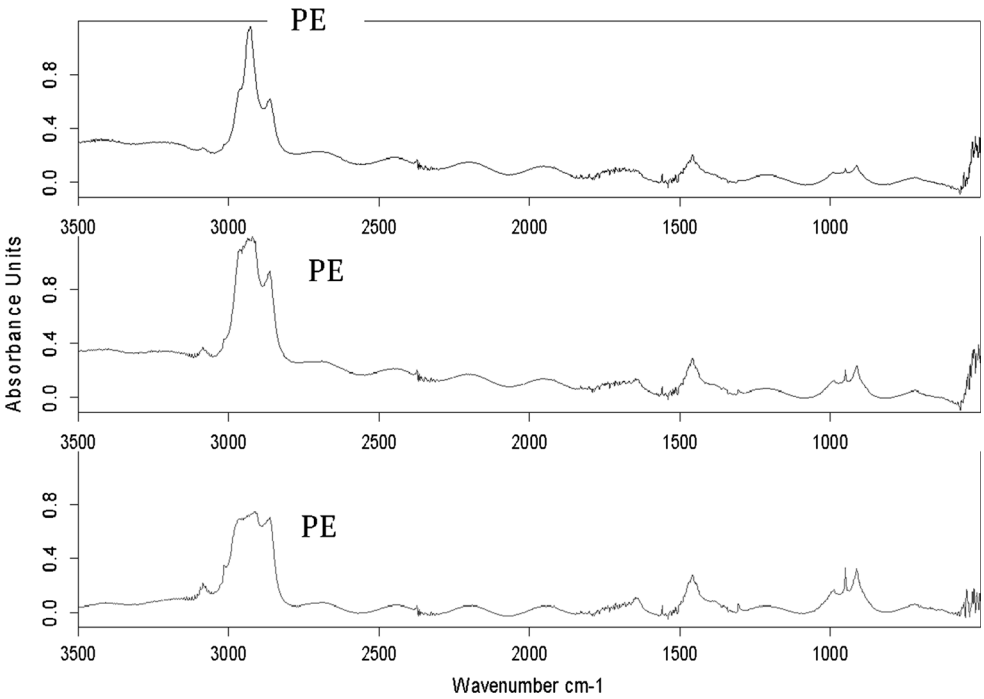

Fig. 9 TG/FTIR analysis of LDPE in dynamic study

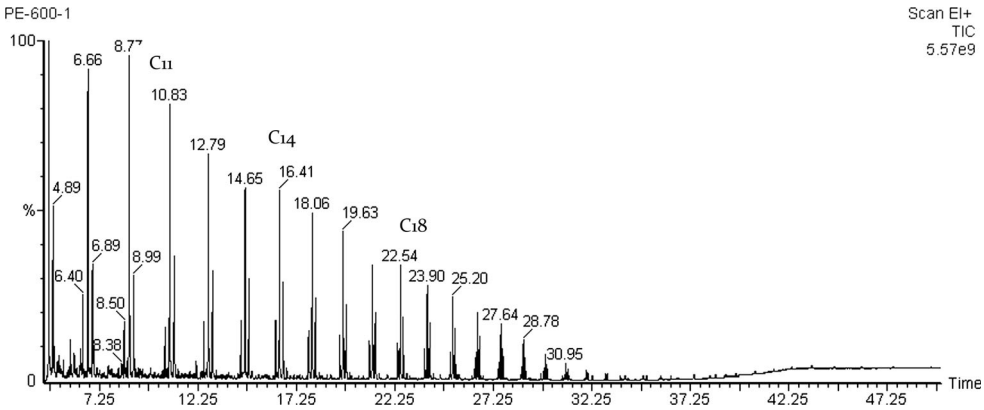

Fig. 10 GC/MS of LDPE at 600 °C

reaction [19, 50], and these can be perfectly useful for some applications. However, it is important to note the significant number of kinetic equations which considers a single step degradation [10, 17, 18, 49, 51]. The main advantage of a single step is its simplicity, but it is necessary to establish under which conditions this type of equation could be applied to the design of a non-isothermal reactor. The analysis of the results obtained by TG

according to the mechanism suggested by different authors [16, 20, 22, 24, 27, 29, 50, 52] requires taking into account only the steps involving volatile products. A simplified scheme of this mechanism is described by reactions of random scission.

Conclusion

The thermal decomposition and mass loss of low density polyethylene in an inert atmosphere has been studied by thermogravimetry. Isothermal and dynamic experiments using different heating rates have been carried out. Mechanism of decomposition of LDPE is complex and based on random β-scission. Thus, the reaction order was determined in both cases. In isothermal conditions, the reaction order is constant for all isotherms as 0.667 whereas in dynamic conditions, the reaction orders are variables in function of heating rate and ranges from 0.8 to 1.5. Determining the kinetic parameters also provides information to design more effective conversion systems and optimum pyrolysis regimes. The TG experiment shown 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 weight 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 in both cases with the n values determined. These results were better than those found with first order reaction in both cases but these models used do not explain the mass loss of LDPE correctly. Thus, the kinetics of the pyrolysis of PE was treated in two reaction steps under isothermal conditions with reaction order $n = 1$. The results show that this two-step model of reaction order $n = 1$ sticks better to the reality because it is closer to the real reaction mechanisms developed above. But we cannot be too emphatic about this because we cannot demonstrate that we are in thermal equilibrium (no thermal gradient in the sample) especially at the beginning of the test.

In conclusion, these numerical methods get the advantage to be easily scheduled without software or mathematic competences. The results obtained in this work are in agreement with those found in the literature. The kinetics parameters found are comparable with those described in literature. But mathematic models proposed for simple step reaction don't allow to predict the sample mass loss in both cases. A more complex kinetic model would be it better, it is the case of two steps reaction kinetic model.

Acknowledgments This work could not have been performed without financial support of CPER "Région Lorraine" for the equipment and instrumentation, financial support of Labex Arbre. The authors wish to thank these Organizations for their support.

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