



Theory and practice in the thermoanalytical kinetics of complex processes: Application for the isothermal and non-isothermal thermal degradation of HDPE

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ABSTRACT

The criterion according to which the best mechanism of a complex process and the associated kinetic parameters correspond to the best fitting of TG and DTG curves recorded at several heating rates is discussed. The main problem is if the application of such a criterion for a complex process will lead to the mechanism and corresponding kinetic parameters to be used for predictions. To this end, the thermal degradation of HDPE has been investigated by TG/DTG + DSC simultaneous analysis performed in Ar flow, at five heating rates as well as in four quasi-isothermal conditions. An algorithm for correct determination of the mechanism and the corresponding kinetic parameters of a complex process from non-isothermal and quasi-isothermal data was suggested.

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1. Introduction

Experimental data for kinetic analysis of heterogeneous reactions are often obtained in non-isothermal conditions, under linear temperature increase conditions over time ($\beta = dT/dt = \text{const.}$, where β is the heating rate, T is the temperature and t is the time). Under such conditions, the assessing methods for kinetic parameters in a single step reaction are based on the rate equation [1]:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (1)$$

or its integral form:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \left[\exp\left(-\frac{E}{RT}\right) \right] dT \quad (2)$$

where α is the conversion degree, A —the pre-exponential factor, E —the activation energy, $f(\alpha)$ —the differential conversion function, $g(\alpha)$ —the integral conversion function, and R —the gas constant.

According to the above equations, a kinetic triplet (E , A , $f(\alpha)$ or $g(\alpha)$) describes the progress of a physical or chemical change over time. Obviously, a complex process is described properly by a set of kinetic triplets.

The correct determination of non-isothermal kinetic parameters involves the use of experimental data recorded at several heating

rates, as has resulted from some relative critical analyses of the assessing methods for the kinetic parameters from non-isothermal data [2–18].

The following software packages only available for commercial use were drawn up particularly for kinetic analysis of non-isothermal data corresponding to a complex process: TA-KIN for Windows v. 1.6 (Anderson et al.) [19]; NETZSCH Thermokinetics software (Opfermann) [20]; KINETICS for Windows 95/98/NT (Burnham and Braun) [21]; ATKS for Windows 95–98 (Roduit) [22]. The best lie of TG, DTG, DTA or DSC experimental points on the corresponding calculated curves corresponds to the true mechanism and kinetic triplets. The accuracy of such procedures will be critically analyzed in the present paper. To this end, the kinetic analysis of the experimental non-isothermal and quasi-isothermal data corresponding to the complex process of thermal degradation of a sort of ultra high density polyethylene (HDPE) was performed. Based on the obtained results, the “algorithm for the kinetic parameter assessment from the non-isothermal data” suggested in a previous paper [13] is to be completed with a final step that will have to be performed at the kinetic analysis of a complex process.

2. Some remarks on the kinetic analysis of non-isothermal data

Criado and Morales [23,24] pointed out that a single α vs. T curve recorded at a certain heating rate can be satisfactory described by some different kinetic triplets. The inherent experimental errors determine the impossibility to discriminate the correct kinetic triplet by applying a statistical criterion. This state-

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ment has led to the main conclusion from some recent papers [2–18], especially of ICTAC 2000 Project [3] and the Workshop at ICTAC 13 [15], according to which the correct kinetic analysis of non-isothermal data corresponding to a heterogeneous process can be only performed by making use of the experimental data recorded at several heating rates. These data have allowed to apply the model-free methods in assessing the activation energy dependence on the conversion degree, that can be correlated with the investigated process mechanism. Therefore, the kinetic analysis of the non-isothermal data is to be started with the application of model-free methods, the most used being those suggested by Friedman [25] (FR method) and Ozawa, Flynn and Wall [26,27] (OFW method). There are the following two cases: (1) E is independent on α ; (2) E values are changed with α .

In the first case, with high probability, the investigated process is simple and it is described from the kinetic point of view by a unique kinetic triplet. In such a case, among the procedures for $f(\alpha)$ or $g(\alpha)$ (kinetic model) assessment from a pre-established set [28–41], we have focused ourselves to the DTG fitting method [34,38,39], as according to it the true values of kinetic parameters correspond to the best lie of DTG experimental points on the calculated DTG curves. The correlations between the shape parameters of DTG curves and the expression of $f(\alpha)$ pointed out by Dollimore et al. [32,33] have supported this criterion. Obviously, checking such a criterion involves a good agreement of experimental and calculated TG curves. The DTG curve shape is revealed to be more sensitive with the kinetic model and therefore, in some cases, a satisfactory agreement of the experimental and calculated TG curves has not always involved the check of the DTG curve fitting criterion.

In the second case (E values are changed with α), the investigated process is complex (successive, parallel, reversible reactions), and, consequently, it is described by a set of kinetic triplets. In such a case, the differential isoconversional FR method based on the logarithmic form of Eq. (1) is recommended as the results obtained by integral isoconversional OFW method are dependent on the history of the system in the $0-\alpha$ range [42]. The isoconversional methods are revealed to be based on Eqs. (1) and (2), which are forced applied for a complex process, and, therefore, in the cases of very complex processes, a high scattering of the E values assessed by an isoconversional method has been revealed [43,44].

For a complete kinetic description of the investigated process, all members of a kinetic triplet for a single step process or triplets for a multi-steps process should be determined. The final test of every kinetic analysis should involve the parameter determination to construct the calculated curves for comparison with the experimental results over a wide and representative range [15]. Some procedures for the kinetic parameter assessment from non-isothermal data, like the above mentioned software packages [19–22] and DTG fitting method [34,38,39] are based on this last necessary condition.

The application of isoconversional methods allows the direct determination of the activation energy but not the whole kinetic triplet. According to the relationships underlying the linear isoconversional methods, the pre-exponential factor could be only assessed by choosing the reaction model. For the single step process, Vyazovkin [45] has suggested an original procedure for assessing the pre-exponential factor and reaction model based on the data obtained by an isoconversional method and the apparent compensation effect (linear relationship between $\ln A$ and E) due to the analytical form of the conversion function.

For a complex process (consecutive, parallel and/or reversible reactions), the TG and DTG experimental points are expected

to have a satisfactory lying-out around corresponding to the calculated curves for some different mechanisms and kinetic triplets. Therefore, there are doubts on the results obtained by above mentioned software packages [19–22] applied in the kinetic analysis of complex processes. Such a case was revealed in a recent paper [46] dealing with the kinetic analysis of the poly(vinyl alcohol) thermo-oxidation. In such a case, the spreading of experimental data resulting from quasi-isothermal experiment on the calculated curve was obtained for the second mechanism in the order of decreasing of the first F -test on fit-quality for non-isothermal TG data. As in the cases of the single step processes, the mechanism and corresponding kinetic parameters of a complex process have resulted not to be assessed accurately from the non-isothermal data when applying a statistical criterion. This statement could be explained by the impossibility of the rigorous application of the statistical tests to TG and DTG experimental data because of the inherent measurement errors. Other reasons could be the relative high number of adjustable kinetic parameters characteristic for a complex process, the compensation effect between the activation parameters and the fact that the formal kinetic models in the considered set are too simple to account for all features of the actual process.

The application of the non-isothermal techniques, such as TG, DTA and DSC, for rapid prediction of thermal lifetime requires extrapolation of the test results over a large temperature range. Consequently, it appears the question if there is a similar degradation mechanism in both non-isothermal and isothermal conditions. This problem could be solved by comparing the activation energy values obtained by isoconversional (model-free) methods for non-isothermal data recorded at several heating rates and for isothermal data recorded at several temperatures.

According to the above mentioned software packages [19–22], the quick prediction of thermal lifetime outside the temperature range in experimental measurements requires the knowledge on the thermal degradation mechanism and the corresponding kinetic triplets. Another possibility for “isothermal predictions” from non-isothermal data was suggested by Vyazovkin [47,48] (“model-free prediction”), and it is based on the following equation:

$$t_{\alpha} = \frac{\int_0^{T_{\alpha}} [\exp(-E/RT)] dT}{\beta \exp(-E/RT_{iso})} \quad (3)$$

where t_{α} is the time required to reach a given conversion (α) and T_{iso} is the isothermal simulation temperature.

The application of this method for a single step process only requires the activation energy value determined by an isoconversional method, and the use of $\alpha=\alpha(T)$ curve recorded at a given heating rate. The form of Eq. (3) was also modified to employ data from arbitrary heating programmes [47]. When E varies with α , the assumption of constant activation energy only for small segments leads to the following relation [49,50]:

$$t_{\alpha} = \frac{\sum_0^{\alpha} \int_{t_{\alpha-\Delta\alpha}}^{t_{\alpha}} [\exp(-E_{\alpha}/RT)] dt}{\exp(-E/RT_{iso})} \quad (4)$$

The application of this last procedure for isothermal simulations raises the following problems: (a) the validity of integral rate Eq. (2) that grounds this method, even for a small segment of t or T ; (b) the high scattering of E values determined by an isoconversional method, obtained for some complex processes [43,44].

The above mentioned problems resulting from the kinetic analysis of thermoanalytical data corresponding to the complex thermal degradation of a sort of HDPE will be discussed and tried to be solved below.

3. The kinetic of HDPE thermal degradation

3.1. Experimental

3.1.1. Material

The thermal behaviour of a HDPE type of 800,000 average molecular weight, 0.935 g cm^{-3} density, 61% crystallinity degree

$20.0^\circ\text{C} \xrightarrow{5.15 \text{ K min}^{-1}} 352.9^\circ\text{C} \xrightarrow{-0.20 \text{ K min}^{-1}} 351.5^\circ\text{C} \xrightarrow{0.32 \text{ K min}^{-1}} 352.3^\circ\text{C} \xrightarrow{2.50 \text{ K min}^{-1}} 389.7^\circ\text{C} \xrightarrow{0.51 \text{ K min}^{-1}} 391.0^\circ\text{C} \xrightarrow{-0.03 \text{ K min}^{-1}} 390.0^\circ\text{C} \xrightarrow{342.5 \text{ min}} 390.0^\circ\text{C}$

quasi-isothermal program $T = 390^\circ\text{C}$:

quasi-isothermal program $T = 400^\circ\text{C}$:

$22.0^\circ\text{C} \xrightarrow{5.18 \text{ K min}^{-1}} 350.7^\circ\text{C} \xrightarrow{0.64 \text{ K min}^{-1}} 352.3^\circ\text{C} \xrightarrow{-0.36 \text{ K min}^{-1}} 351.4^\circ\text{C} \xrightarrow{2.47 \text{ K min}^{-1}} 399.8^\circ\text{C} \xrightarrow{0.47 \text{ K min}^{-1}} 401.0^\circ\text{C} \xrightarrow{-0.04 \text{ K min}^{-1}} 400.0^\circ\text{C} \xrightarrow{300.0 \text{ min}} 400.0^\circ\text{C}$

quasi-isothermal program $T = 420^\circ\text{C}$:

$22.0^\circ\text{C} \xrightarrow{5.13 \text{ K min}^{-1}} 382.3^\circ\text{C} \xrightarrow{-0.15 \text{ K min}^{-1}} 381.0^\circ\text{C} \xrightarrow{2.49 \text{ K min}^{-1}} 419.9^\circ\text{C} \xrightarrow{0.43 \text{ K min}^{-1}} 420.7^\circ\text{C} \xrightarrow{-0.04 \text{ K min}^{-1}} 420.0^\circ\text{C} \xrightarrow{82.0 \text{ min}} 420.0^\circ\text{C}$

quasi-isothermal program $T = 435^\circ\text{C}$:

$27.0^\circ\text{C} \xrightarrow{6.13 \text{ K min}^{-1}} 391.9^\circ\text{C} \xrightarrow{-0.07 \text{ K min}^{-1}} 391.2^\circ\text{C} \xrightarrow{2.48 \text{ K min}^{-1}} 435.5^\circ\text{C} \xrightarrow{0.21 \text{ K min}^{-1}} 435.7^\circ\text{C} \xrightarrow{-0.04 \text{ K min}^{-1}} 435^\circ\text{C} \xrightarrow{20.5 \text{ min}} 420.0^\circ\text{C}$

and 142°C melting point, produced by ARPECHIM–Pitesti–Romania was investigated.

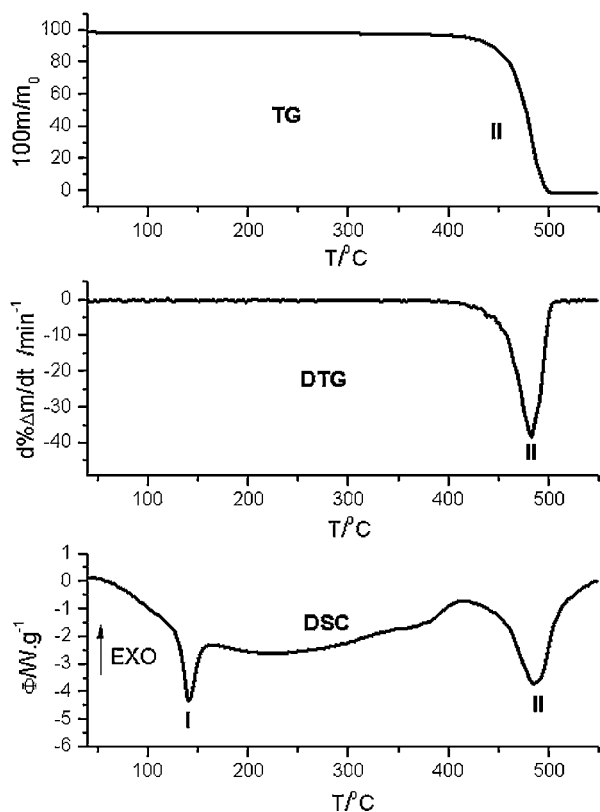


Fig. 1. TG, DTG and DSC curves for UHMWPE heated in Ar, at a heating rate of 12.36 K min^{-1} .

3.2. Thermal analysis

The heating curves (TG, DTG and DSC) of HDPE were recorded simultaneously with STA 490C apparatus produced by Netzsch–Germany, in argon flow (30 mL min^{-1} ; purity of argon: 99.999%), in the $25\text{--}600^\circ\text{C}$ temperature range, at the following heating rates: 2.99; 4.98; 7.44; 9.88 and 12.36 K min^{-1} , and making use of a Pt–Rh crucible. The sample mass was in the $5.00\text{--}5.30 \text{ mg}$ range.

The thermal analysis of HDPE was also performed in argon flow (30 mL min^{-1} ; purity of argon: 99.999%) and the following temperature programs:

quasi-isothermal program $T = 390^\circ\text{C}$:

quasi-isothermal program $T = 400^\circ\text{C}$:

quasi-isothermal program $T = 420^\circ\text{C}$:

quasi-isothermal program $T = 435^\circ\text{C}$:

3.3. Processing the experimental data

“Netzsch Thermokinetics–A Software Module for the Kinetic Analysis of Thermal Measurements” was used for processing the non-isothermal data and comparing the calculated and experimental curve corresponding to quasi-isothermal experiment. This program allows assessing the dependence of E on α by means of FR and OFW model-free methods, and the determination of the complex mechanism of the investigated process and the corresponding kinetic parameters. Recently [43,44,46,51–58] this program was used for kinetic analysis of some non-isothermal data.

To assess the E vs. α curve from isothermal data, the Friedman (FR-iso) and Galwey (G) [59] methods will be used. The FR-iso differential method is based on Eq. (1) that has led to:

$$\ln \frac{d\alpha}{dt} = \ln Af(\alpha) - \frac{E}{RT} \quad (5)$$

For $\alpha = \text{const.}$, the plot of $\ln(d\alpha/dt)$ vs. $(1/T)$ obtained from several degradation isotherms should be a straight line whose slope allows to assess the activation energy.

Galwey [59] has assumed that for a small α range, the reaction order of a heterogeneous process is zero. Consequently, for a given isotherm corresponding to temperature T_i and a comprehensive range of constant increment of conversion degree $\Delta\alpha_{mn} = \alpha_m - \alpha_n$, $(\Delta\alpha_{mn}/\Delta t_{mn})_i \approx k(T_i)$. The values of $k(T_i)$ are calculated for each experimental isotherm and E value corresponding to the conversion degree $(\alpha_m + \alpha_n)/2$ is determined from the slope of the $\ln k(T_i)$ vs. $(1/T_i)$ straight line.

3.4. Results and discussion

Fig. 1 shows the simultaneous TG, DTG and DSC curves obtained for HDPE, recorded at 12.36 K min^{-1} ; similar curves were obtained

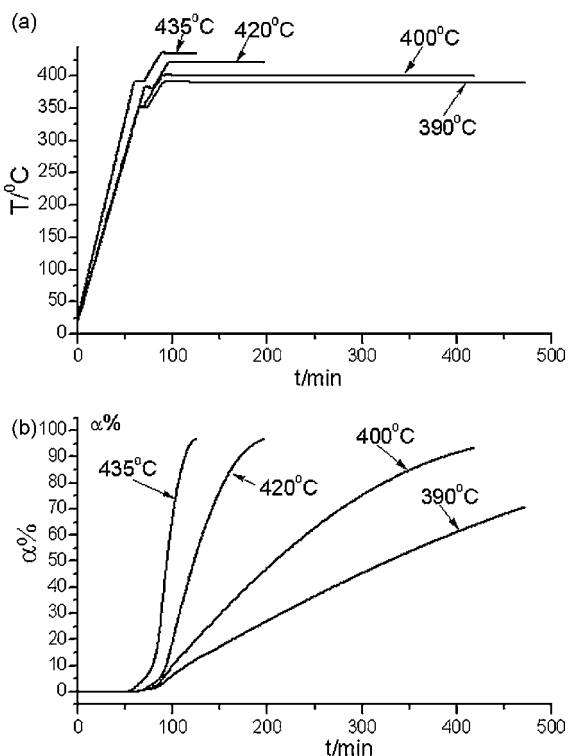


Fig. 2. Temperature programs (a) and conversion degree vs. time curves (b) for the quasi-isothermal experiments.

for all heating rates. Two successive processes occur at the progressive heating, namely the melting of the sample characterized by an endothermic peak in DSC curve (denoted by I), followed by an endothermic decomposition resulting in volatile compounds (denoted by II). The kinetic analysis will be performed for this last process, characterized by a mass loss of $99.6 \pm 0.3\%$. The suitability of such determination is supported by the good reproducibility of thermal analysis results. Some thermal analyses performed under identical conditions have shown the relative standard deviations of mass losses and temperatures lower than 0.3% and 0.25%, respec-

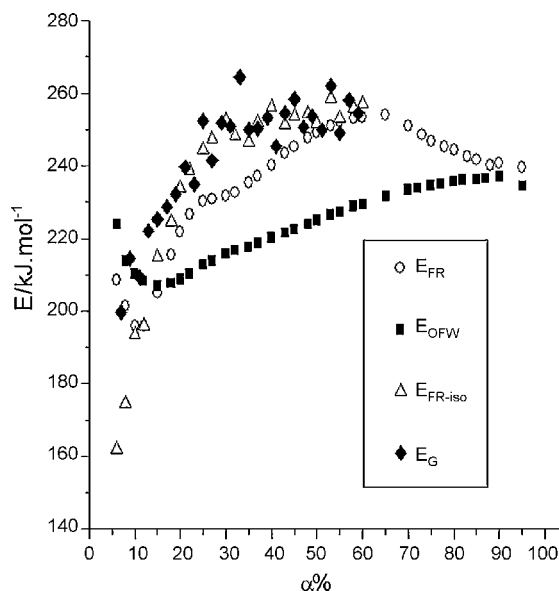


Fig. 3. Dependence of the activation energy assessed from the non-isothermal and quasi-isothermal data by isoconversional methods on the conversion degree.

tively. On the other hand, for different heating rates, the mass losses corresponding to process II were in a very good agreement (for 2.99; 4.98; 7.44; 9.88 and 12.36 K min^{-1} the mass losses were: 99.6%, 99.6%, 99.9%, 99.7% and 99.0%).

The results obtained in quasi-isothermal experiments are shown in Fig. 2.

For both isothermal and non-isothermal data, the relation used for percentage conversion degree assessment was:

$$\alpha\% = \frac{\% \Delta m}{99.6} \times 100 \quad (6)$$

3.4.1. Isoconversional (model-free) estimation of the activation energy

The results obtained by application of FR and OFW methods for non-isothermal data, and FR-iso and G for quasi-isothermal data are presented in Fig. 3. For $\alpha\% > 5\%$, both E_{FR} and E_{OFW} exhibit values

Table 1

Non-isothermal kinetic parameters after non-linear regression through the considered **t:f,f** mechanisms of decomposition of HDPE.

t:f,f with the kinetic models: Fn–Cn–Fn (mechanism 1)			t:f,f with the kinetic models: Fn–Fn–Fn (mechanism 4)		
Parameter	Value		Parameter	Value	
$\log A_1 \text{ (s}^{-1}\text{)}$	2.016		$\log A_1 \text{ (s}^{-1}\text{)}$	12.644	
$E_1 \text{ (kJ mol}^{-1}\text{)}$	64.8		$E_1 \text{ (kJ mol}^{-1}\text{)}$	200.0	
n_1	0.566		n_1	2.000	
$\log A_2 \text{ (s}^{-1}\text{)}$	15.781		$\log A_2 \text{ (s}^{-1}\text{)}$	15.456	
$E_2 \text{ (kJ mol}^{-1}\text{)}$	255.0		$E_2 \text{ (kJ mol}^{-1}\text{)}$	245.0	
n_2	0.589		n_2	0.599	
$\log K_{cut} 2$	0.100		$\log A_3 \text{ (s}^{-1}\text{)}$	15.938	
$\log A_3 \text{ (s}^{-1}\text{)}$	13.758		$E_3 \text{ (kJ mol}^{-1}\text{)}$	258.0	
$E_3 \text{ (kJ mol}^{-1}\text{)}$	255.4		n_3	0.449	
n_3	0.257		FollReact 1 ^a	0.100	
FollReact 1 ^a	0.034		FollReact 2 ^b	0.080	
FollReact 2 ^b	0.021				
Statistical parameters			Statistical parameters		
Correlation coefficient	F_{exp}	$F_{crit}(0.95)$	Correlation coefficient	F_{exp}	$F_{crit}(0.95)$
0.999779	1	1.38	0.998453	6.11	1.37

The share of step 3 ($C \rightarrow D$) is given by $1 - \sum(\text{foll Re act})$.

^a Share of reaction step 1 ($A \rightarrow B$) in the total process.

^b Share of reaction step 1 ($B \rightarrow C$) in the total process.

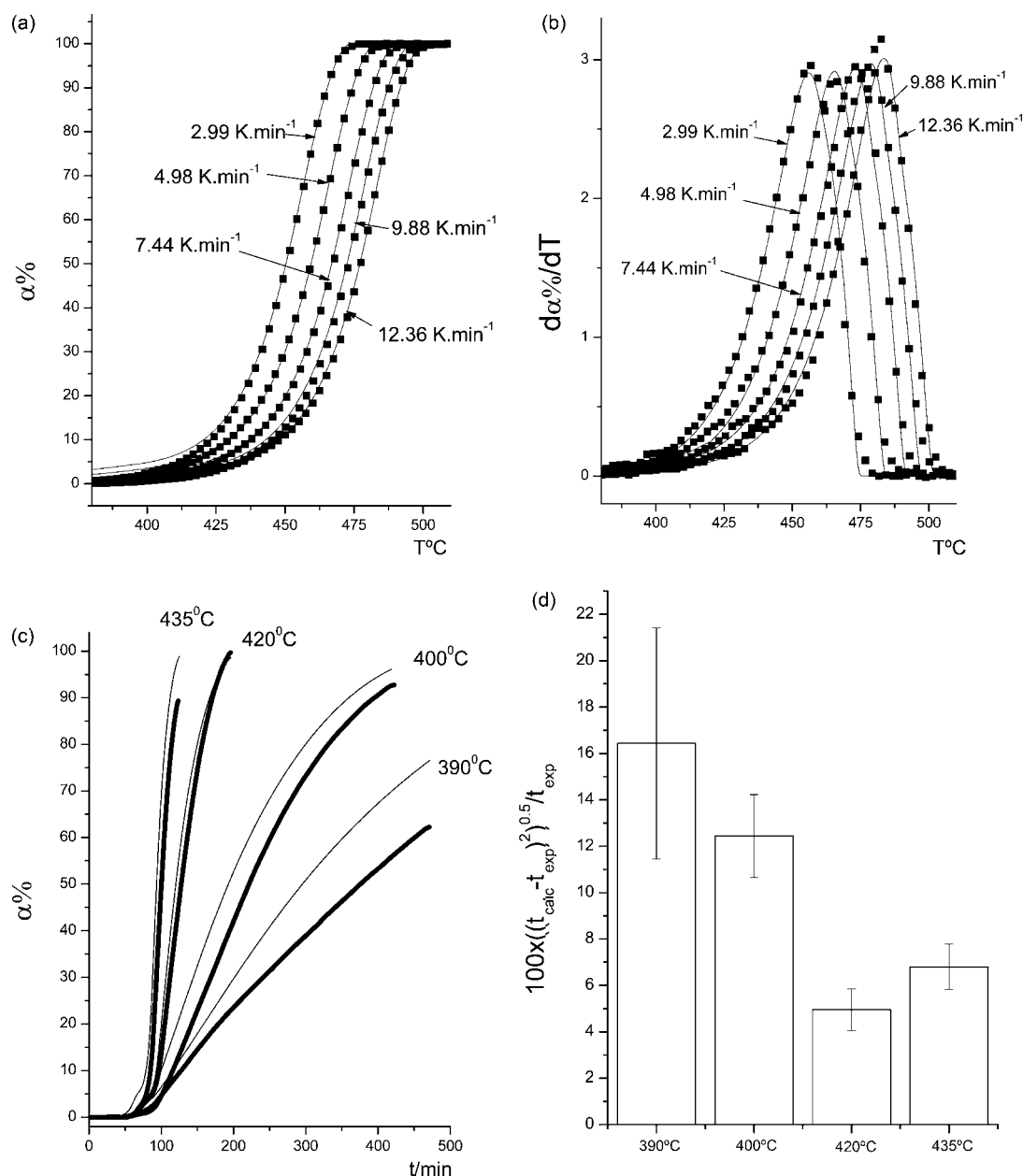


Fig. 4. Checking the validity of $t:f,f$ mechanism with the kinetic models $F_n-C_n-F_n$ and parameters given in Table 1: (a) (■) TG experimental values; (—) TG calculated curve; (b) (■) DTG experimental values; (—) DTG calculated curve; (c) $\alpha\%$ vs. t for quasi-isothermal conditions: thick line—experimental, and thin line—calculated; (d) absolute values of relative deviations for the calculated t in respect with experimental t .

of the relative standard deviation lower than 10% and are dependent on the conversion degree, especially in the $5\% < \alpha\% < 30\%$ range. For $6\% \leq \alpha\% \leq 95\%$, $\overline{E}_{FR} = 235.3 \pm 17.0 \text{ kJ mol}^{-1}$ and $\overline{E}_{OFW} = 223.4 \pm 10.1 \text{ kJ mol}^{-1}$, while for $30\% \leq \alpha\% \leq 95\%$, $\overline{E}_{FR} = 244.5 \pm 6.5 \text{ kJ mol}^{-1}$ and $\overline{E}_{OFW} = 228.3 \pm 7.2 \text{ kJ mol}^{-1}$. These average values are closed to those reported in Refs. [38,60–63]. On the other hand, for $\alpha\% \geq 10\%$, similar shapes of E vs. α curves obtained from non-isothermal data were reported in Refs. [64–69]. The differences between E_{FR} and E_{OFW} values were explained [5,6] by the relations underlying the isoconversional methods. The results obtained by FR method employing the point values of the overall process rate and, unlike OFW method, not including the history of the system in the $0-\alpha\%$ range by integration will be discussed below. The initially activation energy is shown to exhibit a high value and increasing function of conversion for $\alpha\% \leq 10\%$, then increasing for $10\% \leq \alpha\% \leq 55\%$, and then again slowly decreasing for $\alpha\% \geq 55\%$ (Fig. 3).

The thermal decomposition of polyethylene occurs through a random radical chain mechanism initiated by a homolytic scission reaction, followed by β -scission propagation reactions, radicals reactions leading to the formation of dienes and alkenes (random propagation), and finally the termination process consisting in consumption of radicals by formation of alkanes [60,65,67,69,70]. According to Saha and Ghoshal [69], the initial decreasing of E_{FR} with α could be associated with initiation at the weak links. The relative rapid increase of E_{FR} in the $10\% \leq \alpha\% \leq 30\%$ range corresponds to the consumption of weak links [65,69,70]. This process is followed by random scissions characterized by high values of the activation energy ($240\text{--}260 \text{ kJ mol}^{-1}$).

In the limits of inherent experimental errors, the activation energy values obtained from quasi-isothermal data (E_{FR-iso} and E_G) are in good agreement with those obtained from non-isothermal by FR method (for a given $\alpha\% \geq 10\%$, the absolute value of standard

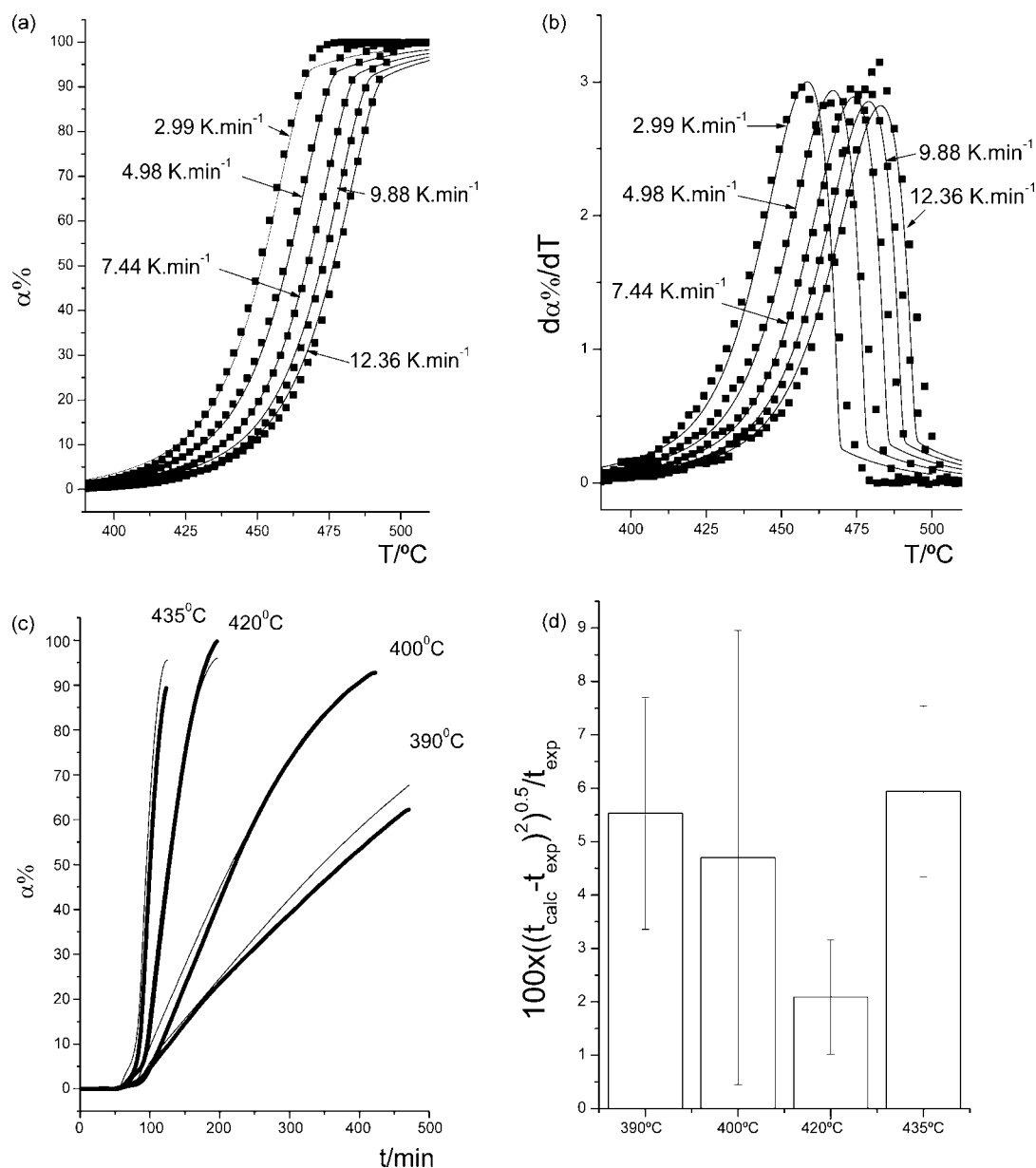


Fig. 5. Checking the validity of $t:f$ mechanism with the kinetic models F_n – F_n – F_n and parameters given in Table 1: (a) (■) TG experimental values; (–) TG calculated curve; (b) (■) DTG experimental values; (–) DTG calculated curve; (c) $\alpha\%$ vs. t for quasi-isothermal conditions: thick line—experimental, and thin line—calculated; (d) absolute values of relative deviations for calculated t in respect with experimental t .

deviation of E_{FR-iso} and E_G in respect with corresponding E_{FR} does not exceed 10%). This is an argument that the HDPE decomposition mechanism is the same in both isothermal and non-isothermal conditions.

3.5. Modeling as multiple step reaction

The dependence of E on $\alpha\%$ assessed by isoconversional methods for both isothermal and non-isothermal data has shown a complex decomposition process for the investigated HDPE, involving at least three elementary steps. From an analysis of the weight loss rate vs. time data in TG tests, Conesa et al. [71] also suggested that the HDPE decomposition could be modelled through three-reactions scheme. In order to find the mechanism of the investigated process and the corresponding kinetic parameters, we used the “Netzsch Thermokinetics” program—“Multivariate non-linear regression” based on the assumption that the kinetic parameters are identical for measure-

ments at all heating rates [20]. The procedure was performed to obtain the formal kinetic model to be used in predictions. This aim corresponds to the “technical aspect” of non-linear regression analysis, according to which the kinetic analysis is examined as a tool for data reduction [20]. The non-isothermal data recorded at the above mentioned five heating rates were brought together during analysis and the relevant differential equations of the reaction rates were solved numerically, and the kinetic parameters were optimized iteratively. The calculations were performed in the range of the $5\% \leq \alpha\% \leq 95\%$ conversion degree and considering the following conversion functions:

- reaction order model, F_n : $f(\alpha) = (1 - \alpha)^n$ (n is the reaction order);
- n th order reaction with autocatalysis, C_n : $f(\alpha) = (1 - \alpha)^n(1 + K_{cat}\alpha)$;
- Avrami-Erofeev model, A_n : $f(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{(1 - 1/n)}$ (n is a constant parameter).

Some reaction schemes given in the “Netzsch Thermokinetics” program and consisting in consecutive, parallel and/or reversible reactions were taken into account. The values of E vs. $\alpha\%$ obtained by FR isoconversional method were used as starting parameters for non-linear regression model-fitting procedure. After running the TG experimental data recorded at the above mentioned five heating rates and many reaction schemes, the HDPE decomposition was found to be satisfactorily described by the below schemes, presented in the order of decreasing of fit-quality of TG data:

- scheme coded by **t:f,f**: $A \rightarrow B \rightarrow C \rightarrow D$ with the kinetic models $F_n-C_n-F_n$ (mechanism 1);
- scheme coded by **h:f,f,f,f,f**: $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow F \rightarrow G$ with the kinetic models $C_n-F_n-F_n-F_n-F_n-F_n$ (mechanism 2);
- scheme coded by **q:f,f,f**: $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$ with the kinetic models $F_n-F_n-F_n-F_n$ (mechanism 3);
- scheme coded by **t:f,f**: $A \rightarrow B \rightarrow C \rightarrow D$ with the kinetic models $F_n-F_n-F_n$ (mechanism 4).

(the codifications are those used in “Netzsch Thermokinetics” program; A, B, C, D, E, F and G are solid compounds; 1; 2; ... 6 denote the mechanism steps).

We have noted that the choice of reaction scheme was based on F -test values, and therefore all reaction schemes that yield $F < F_{cr}$ are statistically equivalent fits of the data.

The corresponding kinetic and statistical parameters of mechanisms 1 and 4 are listed in Table 1.

The inspection of Table 1 shows that both mechanisms exhibit closed values of the activation energy and pre-exponential factor for 2nd and 3rd steps, but some differences between the corresponding reaction orders. This suggests a two stepped scheme. However, a satisfactory fitting of TG curves was not obtained when assuming such reaction scheme.

Taking into account the inherent errors in determination of TG curves for all considered mechanisms and corresponding kinetic parameters, experimental TG and DTG points laid out practically on the regenerated curves (see Figs. 4a and b, 5a and b in which these checkings are presented for mechanisms 1 and 4). Although there is a significant difference between E_1 and E_2 , both experimental and calculated DTG curves have only exhibited one peak each. A similar behaviour was also shown in other non-isothermal complex processes [46,55].

The obtained kinetic parameters data were also employed in obtaining the TG curves corresponding to the temperature programs where the quasi-isothermal experiments were performed. The results obtained for mechanisms 1 and 4 are shown in Figs. 4c and 5c. The absolute relative deviation values for the calculated degradation time (t) as compared to the experimental ones ($e\% = \text{mean absolute relative difference (ARD)} = 100 \times \left| \frac{t_{\text{calc}} - t_{\text{exp}}}{t_{\text{exp}}} \right|$; the mean value of $e\%$ is the mean absolute relative difference (ARD)), and the standard deviations of this quantity are presented in Figs. 4d and 5d for mechanisms 1 and 4, and in Fig. 6 for all four mechanisms, considering both all quasi-isothermal data and the data corresponding to quasi-isothermal experiment performed at 390 °C. All the four mentioned mechanisms have exhibited a good fitting of TG and DTG curves, and the mechanism 4 with the corresponding kinetic parameters has led to the best simulation of all quasi-isothermal data. Consequently, the only application of statistical criteria for processing of non-isothermal data recorded at several heating rates is not sufficient to obtain the actual mechanism of a complex process and the corresponding actual kinetic parameters that could be used for predictions. As was mentioned above, a similar result had been reported in a previous recent paper [46] presenting the kinetic analysis of

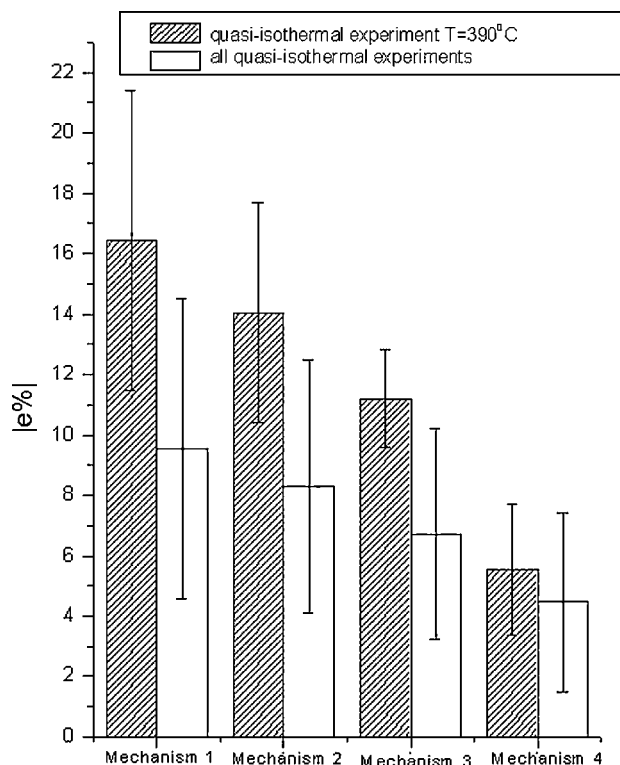


Fig. 6. Absolute values of relative deviations for calculated t in respect with experimental t , for all considered mechanisms.

poly(vinyl alcohol) degradation. Some possible explanations of a such statement were also specified in the previous section of this paper.

The “model-free prediction” method based on Eq. (4) was also applied for prediction of t_α values corresponding to quasi-isothermal data. To this end, E_{FR} vs. α and the integral temperature were assessed for a step of $\Delta\alpha\% = 1\%$. The t_α calculated values are not dependent practically on the employed non-isothermal curve, and exhibit values of $|e\%| = \left| \frac{t_\alpha(\text{calc}) - t_\alpha(\text{exp})}{t_\alpha(\text{exp})} \right| \times 100$ substantially higher than those given in Figs. 4 and 5. For example, for $T_{iso} = 390^\circ\text{C}$ and $20\% < \alpha\% < 50\%$, the values of $|e\%|$ calculated by “model-free prediction” method are in the 33.8–36.7% range, while the values of $|e\%|$ corresponding to mechanism 4 are in the 1.0–8.9% range. Relative high errors in assessing the t_α value by “model-free prediction” method were also reported previously by Saha and Ghoshal [69] who revealed a dependence of the calculated t_α value on the heating rate of the used non-isothermal data. This last result could be due to the relative high scattering of E values obtained by isoconversional method. As was mentioned above, the relative high $|e\%|$ values calculated by “model-free prediction” method have raised the problem of the integral rate Eq. (2) validity in the complex processes, and small segments of T or t .

The above mentioned results have shown that the branch corresponding to the complex processes from the previously suggested [13] algorithm for assessing the kinetic parameters from non-isothermal data, involving two successive steps (1: application of a differential isoconversional method (e.g. Friedman method) to assess the activation energy dependence on the conversion degree; 2: use of a non-linear regression program to assess the possible mechanisms and corresponding kinetic parameters) must be completed by the final step involving the check of the agreement between experimental and calculated α vs. t curves recorded in some temperature programs other than those used in assessing the kinetic parameters.

4. Conclusions

1. The application of the statistical criteria in the kinetic analysis of non-isothermal data recorded at several heating rates, and corresponding to a complex process was analyzed critically.
2. To this end, the TG/DTG data for the thermal HDPE decomposition, recorded in Ar flow, at five heating rates and in four quasi-isothermal conditions were processed.
3. The application of differential isoconversional methods has shown a good agreement between the E vs. α curves assessed from isothermal and non-isothermal data. This is an argument for the same HDPE decomposition mechanism in both conditions.
4. It was pointed out that there is the possibility that the four mechanisms of the complex HDPE decomposition involving consecutive reactions to describe relatively accurate the non-isothermal TG and DTG curves.
5. The check of these mechanisms for some quasi-isothermal data has shown only one of them being allowed to be used in accurate predictions.
6. An algorithm for the accurate determination of the mechanism and the corresponding kinetic parameters of a complex process from non-isothermal and quasi-isothermal data was suggested.

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