



Simplified approach to modelling the catalytic degradation of low-density polyethylene (LDPE) by applying catalyst-free LDPE-TG profiles and the Friedman method

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Abstract

The course of the thermogravimetric degradation of LDPE in the presence of different aluminosilicate catalysts was modelled by applying a differential isoconversional Friedman approach. An analysis of catalyst-free PE-TG profiles confirmed that the degradation profiles predicted by various reaction models overlap over the entire conversion range once the data are analysed using a differential isoconversional Friedman approach. The results demonstrate that the catalytic degradation of LDPE can be predicted by a correlation twin, i.e. the two specific functional relations between the activation energy, pre-exponential factor and conversion. The crucial step for ensuring good agreement between the predicted and the measured profiles is to extrapolate the discrete values of the activation energies and pre-exponential factors to the zero conversion. It turns out that linear extrapolation and interpolation from the discrete values outperforms regression functions based on various order polynomials, and that apparent deviations from the global trend at lower conversions are not a consequence of the misinterpretation of the experimental results but are an experimental fact. The assumption about the compensation effect between the pre-exponential factor and activation energy holds within the conversion range from 10 to 90%. However, it is generally unsuitable for modelling purposes due to the uncertain extrapolation of the kinetic parameters to the zero conversion.

Keywords Catalytic degradation · Catalyst-free TG profiles · Isoconversional analysis · Polyethylene · Friedman

Introduction

The thermocatalytic degradation of various forms of pure polyethylene and/or waste mixtures containing PE has been the subject of many research projects whose main object was to either determine the kinetic parameters of degradation [1–5] or determine the influence of operating

parameters on the composition/distribution of degradation products [6–8]. These are gaseous and liquid hydrocarbons with a different degree of saturation (alkanes and alkenes), acting as recycled surrogates of oil. Since repeated experiments with the same catalyst sample [1, 9, 10] showed gradual deactivation, the economically and environmentally preferred catalysts (from the point of disposal after use) are those based on pre-treated natural aluminosilicates. Such deactivated catalysts can be deposited as backfill material for the re-cultivation of areas affected by various building interventions [11] once carbon content is below 3 mass%, which is practically achievable [12–15]. Owing to the lower acidity and activity of natural aluminosilicates compared to that of synthetic zeolites and other acidic catalysts, the mass ratio between natural aluminosilicates and PE must be higher in order to sustain the desired reactor activity. Consequently, the high catalyst content is reflected itself in TG profiles, where catalyst thermal transformation over the investigated temperature range leads to an apparent conversion over a temperature region

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where PE degradation is unlikely to take place [2, 15–18]. To annul this effect, we recently proposed a procedure for generating catalyst-free TG profiles [18], which were also used for the kinetic analysis in this work.

To date, the catalyst's effect on PE degradation has mostly been studied by integral analysis using an isoconversional approach. Here, the main concern was to determine the catalyst's effect on the apparent activation energy and the relationship between the apparent activation energy and conversion [1–3]. Catalyst modifications were studied in terms of product distribution [3, 19–21].

Kinetic investigations were focused on fitting experimental data into a different number of pseudo-kinetic reaction models, each containing varying numbers of parameters: from 11 [4] or up to 21 [5]. To avoid the need for model fitting, Samuelsson et al. [22] introduced an effective kinetic pre-factor to replace the kinetic parameters. In their approach, a pre-exponential factor and reaction model in the mathematical description were used for predicting the pyrolytic decomposition of cellulose.

To the best of our knowledge, no attempts have been made so far to interpret the catalysed PE degradation by differential Friedman analysis. We recently [23] demonstrated that isoconversional analysis based on a differential Friedman approach leads to the model-less description of the reacting system. It was shown that the thermal degradation of PE can be predicted by a system of two independent equations describing a functional relationship between the activation energy, pre-exponential factor and conversion. The proposed approach was applied here to predict catalytic LDPE degradation.

Materials and Experimental

A detailed description of the catalyst preparation method, catalytic degradation runs and catalyst characterization is given in our previous works [14, 18]. Therefore, only the basic nature of the catalysts used and experimental procedure applied is mentioned here to introduce the reacting system. For this study, three catalysts assigned as M300, MAI and ASA were used. M300 is a natural aluminosilicate containing heulandite, clinoptilolite and quartz, along with Al, Mg, Fe and K as the main impurities. By a zeolitization procedure, the chemical and physical properties of M300 were improved and the derived catalyst was assigned as MAI. The ASA catalyst is amorphous silica alumina and was produced according to the procedure proposed by Hensen et al. [24]. The powdered form of Merck LDPE was used in this study (physical properties: particle size 100 μm , density 0.906 g cm^{-3} , average M_w 35,000 g mol^{-1}). Catalytic degradation of LDPE was conducted in a PerkinElmer STA6000 thermogravimetric

analyzer. During all experiments, 9–10 mg of catalyst was ground in an agate mortar with an equivalent amount of LDPE to form a 1:1 mass ratio mixture. Since the natural aluminosilicates and their modifications synthesized and examined in this work exhibit relatively low acidity compared to synthetic zeolites (such as ZSM-5, beta and Y.), the catalyst–polymer ratio needs to be higher to obtain comparable degradation rates; based on our preliminary experiments, a 1:1 mass ratio is a reasonable compromise. Tests were carried out in the temperature range of 323–973 K under N_2 atmosphere (70 mL min^{-1}) with heating rates of 5, 10, 15, 20 and 25 K min^{-1} .

Analysis and Discussion

The kinetics of the thermocatalytic degradation of substances (LDPE in this particular case) during the TG analysis is expressed by the following equation:

$$\frac{d\alpha}{dt} = A \cdot \exp(-Ea/RT) \cdot f(\alpha) \quad (1)$$

where α corresponds to the degree of sample degradation and is defined as:

$$\alpha(t) = \frac{w_0 - w(t)}{w_0 - w(t_\infty)} \quad (2)$$

where w_0 , $w(t)$ and $w(t_\infty)$ correspond to the initial mass of the sample, to the mass of the sample at a specific time t , and to the mass of the sample at the end of the analysis. The function $f(\alpha)$ stands for a kinetic model.

Prior to quantitative interpretation of catalytic degradation runs, the catalyst's stability within the examined temperature range should be verified. Once the catalyst's mass losses are no longer negligible compared to the sample mass loss due to catalytic conversion, the catalyst's contribution to the overall degradation should be considered in order to unmask degradation of the examined material. Figure 1 shows TG profiles of the pure catalysts used in this research. It is obvious that they underwent thermal degradation and that, due to the high fraction of catalyst in the reaction mixtures, the catalyst transformation during the LDPE degradation should be considered.

Theoretically, the TG analysis of pure catalysts should be made for each heating rate, which would considerably increase the number of experiments required. We recently [18] proposed a procedure by which the number of required experiments with a pure catalyst is more than halved. The procedure is based on the reference TG profile (in our case, the TG profile measured at the heating rate of 10 K min^{-1}) which is shifted for the time proportional to the quotient between the temperature difference corresponding to a

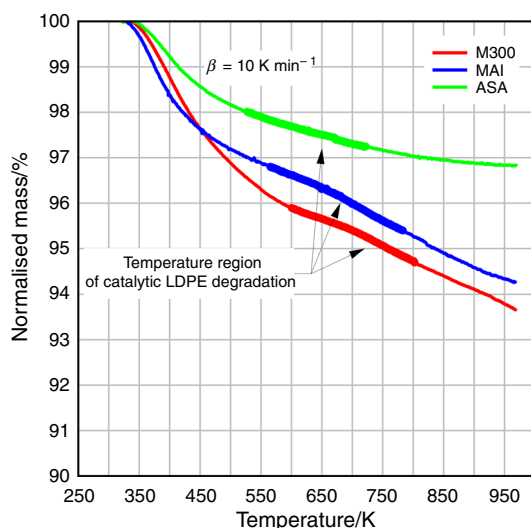


Fig. 1 Course of the thermal degradation of the applied catalysts with the temperature regions of the catalysed LDPE degradations being marked

50% sample conversion at a particular reference heating rate and a given heating rate (Eq. 3).

$$\Delta t = \frac{T_{\beta_i}^{50} - T_{10\text{K/min}}^{50}}{\beta_i} \cdot F \quad (3)$$

The proportional factor F compensates for the observed differences in the predicted and measured times along the TG curve measured at a heating rate of 5 K min^{-1} . Proportional factor F was calculated by a linear piecewise correction function based on tabulated values [18]. It was demonstrated that the correction function is independent of the heating rate, since good agreement was obtained between the predicted TG profiles at a heating rate of 25 K min^{-1} and experimentally measured ones at the same heating rate. It should be noted that all raw TG profiles were smoothed prior to any data manipulation in order to

prevent noise accumulation. The smoothing procedure applied is described in detail in our previous work [18].

Figure 2 shows unmasked PE-TG profiles along with raw ones for all catalytic runs. It is clear from the presented curves that subtracting of the mass losses associated with the catalyst transformation from the raw TG profiles generates TG curves with a shape that is typical of pure PE depolymerisation runs; i.e. the curves are flat outside the temperature region where PE depolymerisation did not take place. Due to the agglomeration of the LDPE powder and catalyst and due to the electrostatic forces, it was practically impossible to perfectly homogenize and dose the mixture into the TG pan, which resulted in the observed deviations between the final part of the unmasked PE-TG curve and the line showing 50% of the initial mass.

For the further analysis, normalized unmasked PE-TG curves were used since the final amount of carbonaceous deposits on all catalysts after the depolymerisation runs never exceeded 0.4 mass%.

For the purpose of the Friedman isoconversional analysis, Eq. (1) was converted into its logarithmic form:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A) - E_a/RT + \ln(f(\alpha)) \quad (4)$$

By plotting the isoconversional values of the corresponding pairs $\frac{d\alpha}{dt}$ versus $1/T$ calculated from the experiments carried out at different heating rates in $\ln\left(\frac{d\alpha}{dt}\right)$ versus $1/T$ plot, the isoconversional plots are obtained (SFigs 3–5). The values of the activation energies and pre-exponential factors of rate constants in the reaction rate models, which are summarised in Table S1, were calculated from the slopes and intercepts of the isoconversional lines with the ordinate axis.

Recently, we demonstrated [23] that an isoconversional analysis based on the Friedman differential approach leads,

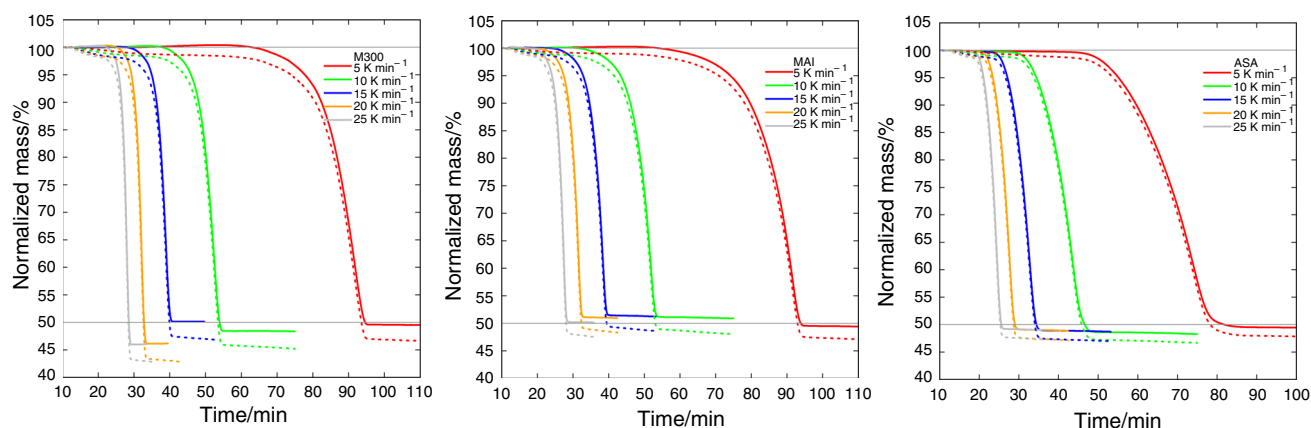
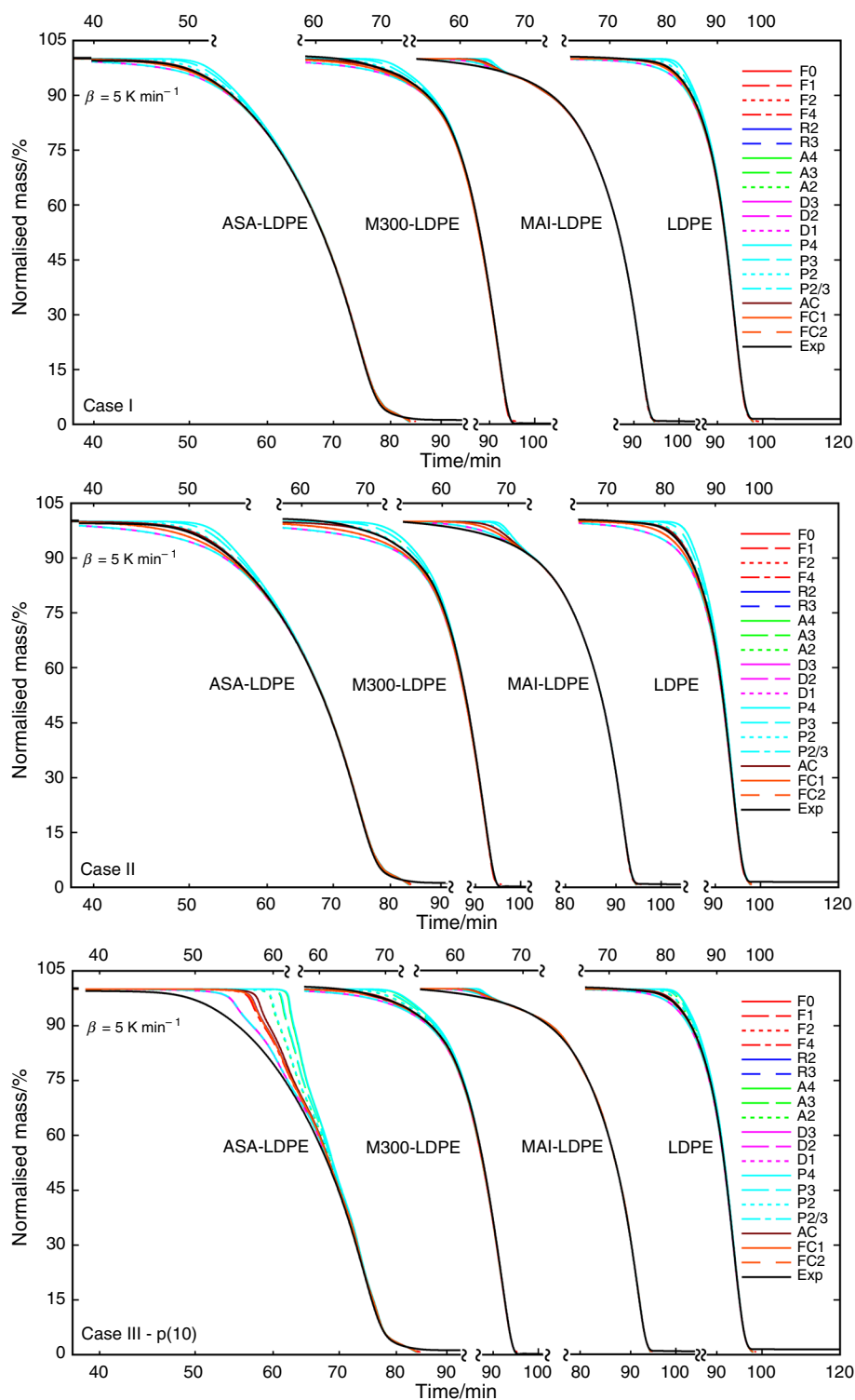


Fig. 2 Comparison between the raw TG profiles measured during catalytic LDPE degradation in the presence of different aluminosilicates (dotted lines) and unmasked catalyst-free PE-TG profiles (solid lines). (Reprinted from [18])

due to the coupled pre-exponential factor and reaction model, to an apparent zero-order reaction model since only in this case is the extrapolation of the calculated values of the pre-exponential factor to the zero conversion straightforward.

To confirm the previously derived conclusions, a visual comparison of the unmasked PE-TG profiles and the predicted ones for the kinetic models shown in Table S1 is presented in Fig. 3 and Figs. S2–S4. While Fig. 3 only shows extracted profiles for a heating rate of 5 K min^{-1} for all cases studied, Figs S2–S4 show a comparison of the

Fig. 3 Comparison of the predicted TG profiles for standard reacting models presented in Table S1 and the extracted experimental profiles for reacting systems being studied. The graph corresponds to different ways used to predict the kinetic parameters



predicted profiles and the extracted ones for other heating rates. For the purpose of generating simulated profiles, Eq. (1) was numerically integrated using the Runge-Kutta 56 integration method [25] applying the values of kinetic parameters determined for a particular catalyst by the isoconversional approach. The isoconversional analysis gives discrete values for the activation energies and pre-exponential factors over the measured conversional range. Therefore, for simulation purposes, the continuous values were generated by applying either a linear midpoint interpolation with an appropriate extrapolation or by applying polynomial approximations.

Two different approaches were used for the extrapolation to the zero conversion:

- (a) the values at zero conversion were calculated by a linear extrapolation from the values determined at conversions 0.025 and 0.05 (Case I):

$$E_a^{\alpha=0} = E_a^{\alpha=0.025} + (E_a^{\alpha=0.025} - E_a^{\alpha=0.05}) \quad (5a)$$

$$A^{\alpha=0} = \exp(\ln(A^{\alpha=0.025}) + (\ln(A^{\alpha=0.025}) - \ln(A^{\alpha=0.05}))) \quad (5b)$$

or

- (b) by prolongation of the slope determined from the measured conversions at 0.05 and 0.1 to the points at conversions 0 and 0.025 (Case II):

$$E_a^{\alpha=0} = E_a^{\alpha=0.05} + (E_a^{\alpha=0.05} - E_a^{\alpha=0.10}) \quad (6a)$$

$$E_a^{\alpha=0.025} = (E_a^{\alpha=0} + E_a^{\alpha=0.05})/2 \quad (6b)$$

$$A^{\alpha=0} = \exp(\ln(A^{\alpha=0.05}) + (\ln(A^{\alpha=0.05}) - \ln(A^{\alpha=0.10}))) \quad (6c)$$

$$A^{\alpha=0.025} = \exp((\ln(A^{\alpha=0}) + \ln(A^{\alpha=0.05}))/2) \quad (6d)$$

The values at 100% conversion were calculated for both cases by a linear extrapolation using the values determined for conversions 0.95 and 0.975.

$$E_a^{\alpha=1} = E_a^{\alpha=0.975} + (E_a^{\alpha=0.975} - E_a^{\alpha=0.95}) \quad (7a)$$

$$A^{\alpha=1} = \exp(\ln(A^{\alpha=0.975}) + (\ln(A^{\alpha=0.975}) - \ln(A^{\alpha=0.95}))) \quad (7b)$$

For midpoint conversions, the values of E_a and A were calculated by a linear interpolation from the values determined at a particular conversion interval.

In Case III, the values of the kinetic parameters were calculated using polynomials of different orders [25] (2nd to 10th order, 21 isoconversional points):

$$E_a = \sum_{i=0}^{10} a_i \cdot \alpha^i \quad \text{and} \quad \ln(A) = \sum_{i=0}^{10} b_i \cdot \alpha^i \quad (8)$$

Figures 4 and 5 present a comparison of the activation energies calculated by the isoconversional analysis of LDPE degradation runs carried out with and without a catalyst and the values of activation energies estimated by the applied approximation methods. The comparison of the presented results makes it clear that the predictions based on polynomial approximations oscillate around the experimental values; the magnitude of the oscillations depends on the distribution of the E_a values and the order of the fitted polynomials. Once E_a steadily changes (in the case of M300), the polynomials of an order higher than 4 are satisfactory for predicting the $E_a = f(\alpha)$ dependency. If the values of the activation energies on the boundary of the conversion range deviate considerably from the previous trend, larger oscillations are observed, which increase the spread of the calculated values for the activation energies in the extrapolation region, i.e. at zero and complete conversion values. Figure 6 shows a comparison of the experimental and predicted TG curves using the proposed approximations for all experiments carried out at a heating rate of 5 K. Fig. S5 shows results for other heating rates, i.e. 10, 15, 20 and 25 K min⁻¹, respectively. As may be expected from the $E_a = f(X)$ dependencies shown for the ASA catalyst in Fig. 5, a larger spread should be obtained for simulations showing LDPE degradation in the presence of the ASA catalyst once polynomial approximations were used in the calculation of the kinetic parameters.

From the comparison of the predicted profiles shown in Figs. 3 and 6 and from the presented efficiency of approximation methods used for the prediction of activation energies during the sample degradation (Figs. 4 and 5), it is evident that the linear extrapolation and interpolation from the discrete values obtained by the isoconversional analysis outperforms the regression functions based on the various order polynomials. Polynomial approximations of activation energy show, especially in the vicinity of border conversions, large deviations from the discrete values, which consequently reflect itself in the prediction spread shown in Fig. 6. Predictions made by the simple reaction models (1–6 and 17–19, Fig. 3) practically overlap with the experimentally measured TG profile due to straightforward extrapolation and determination of E_a values at zero conversion. The predicted TG profiles for the

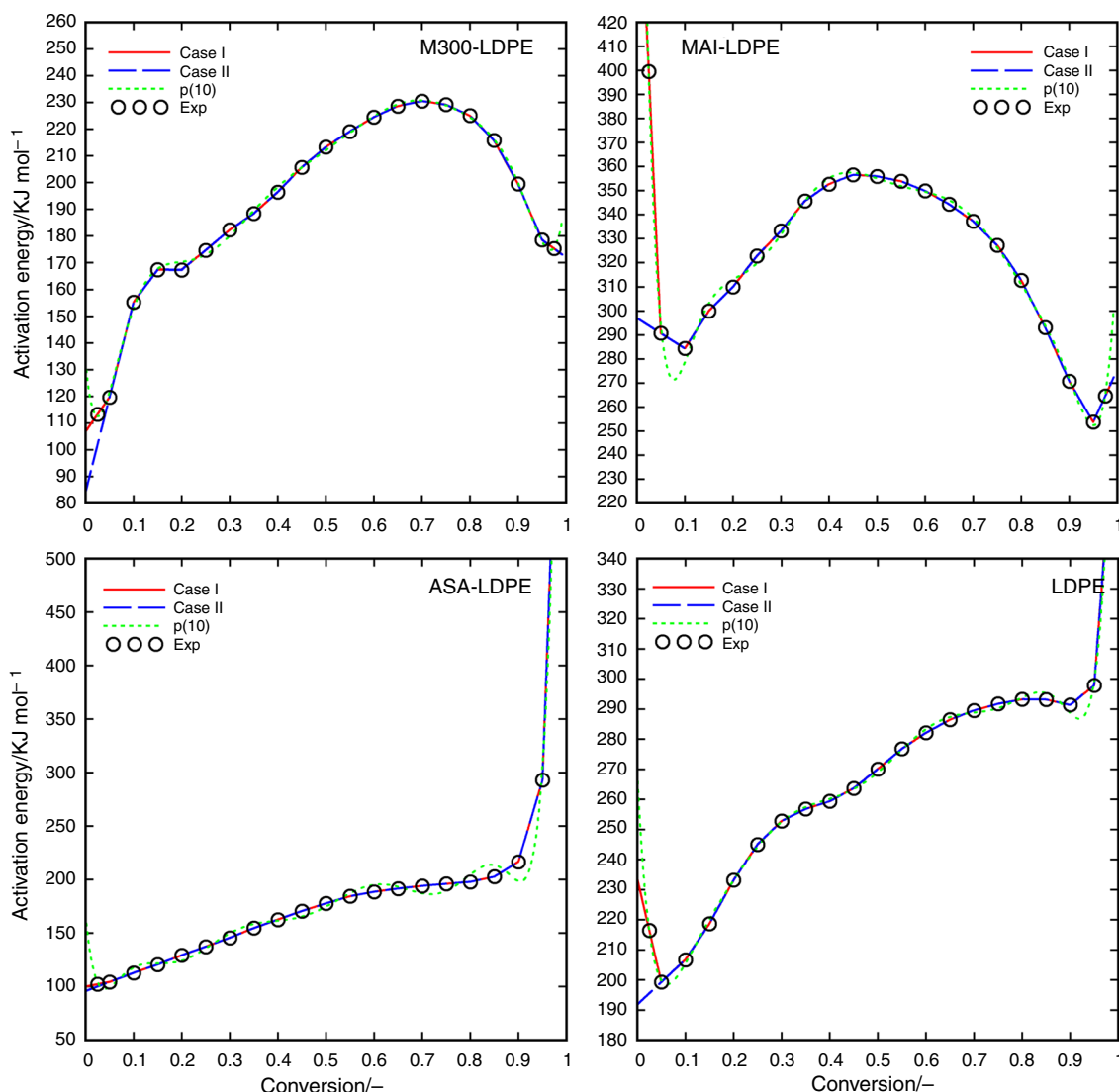


Fig. 4 Comparison of the values of the activation energies calculated by different interpolation/extrapolation methods and discrete values determined by isoconversional analysis

rest of the models show deviations due to approximation used for the determination of E_a values at zero conversion since models' values at zero conversion are undetermined or equal to zero. However, presented analysis revealed that once reaction parameters are determined by Friedman differential analysis coupled with the isoconversional method, the TG profiles could be predicted just by two functional relations between the apparent activation energy, apparent pre-exponential factor and conversion, i.e. without any reaction model.

The results presented in Figs. 4 and 5 reveal that the functional dependency between the activation energy and conversion cannot be linearized. The nature and reactivity of active sites, catalyst morphological and surface properties determine and influence degradation pathway and

product distribution, which all contributes to the relation between apparent activation energy and conversion. In this particular case, mostly the intrinsic acidity has a dominant effect. It is clearly seen in Fig. 4 that among the solids tested, the ASA sample which contains the strongest acid sites, followed by M300 and MAI [14], thus exhibits the lowest activation energy.

Similar conclusion may be drawn from published results showing thermal PE degradation [1, 2, 17, 26] and/or thermocatalytic PE degradation [1, 2, 17, 27, 28]. The observed functional dependency of isoconversionally determined activation energies versus measured conversions differs due to the diversities of the applied PE samples and catalysts.

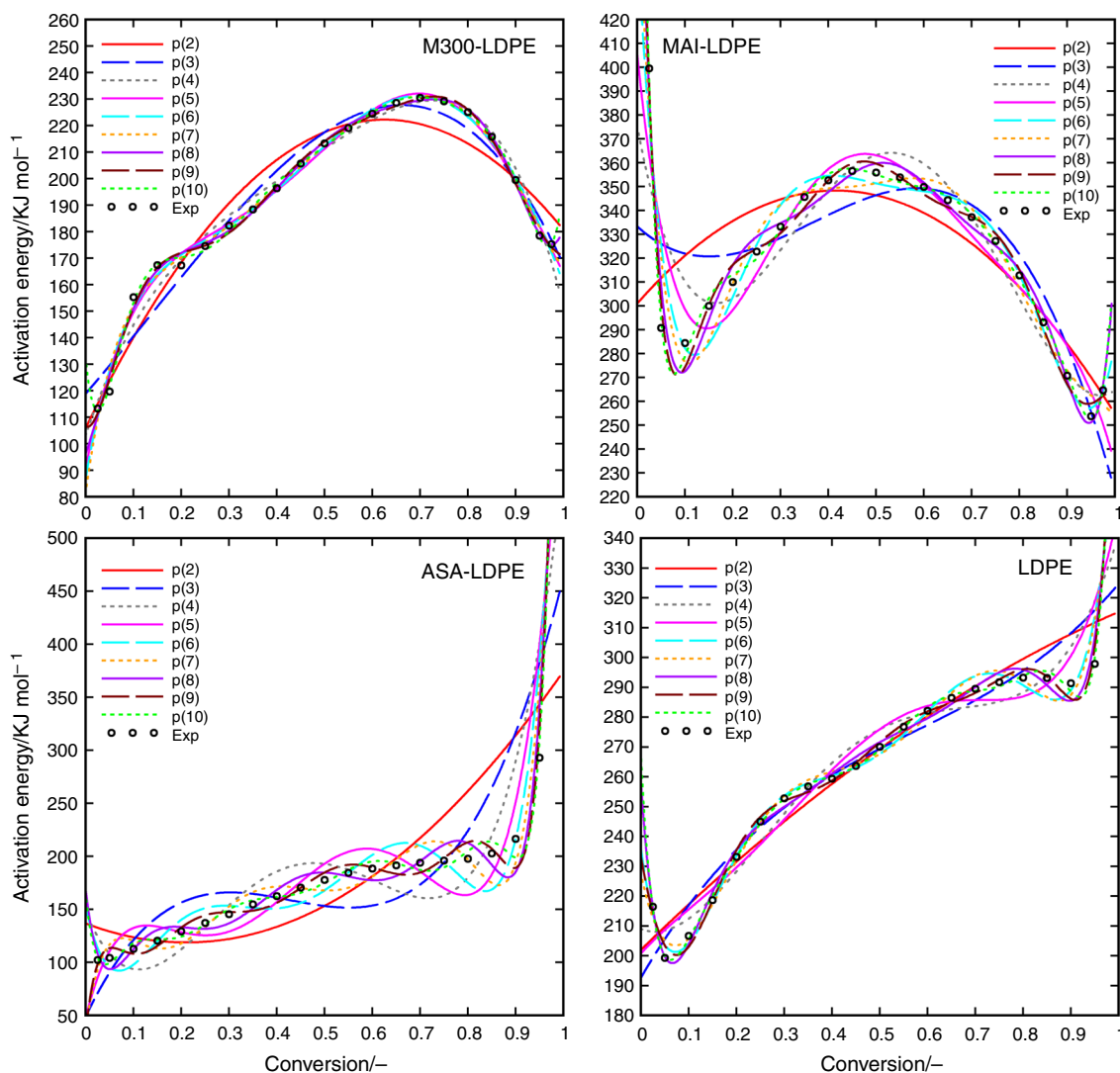
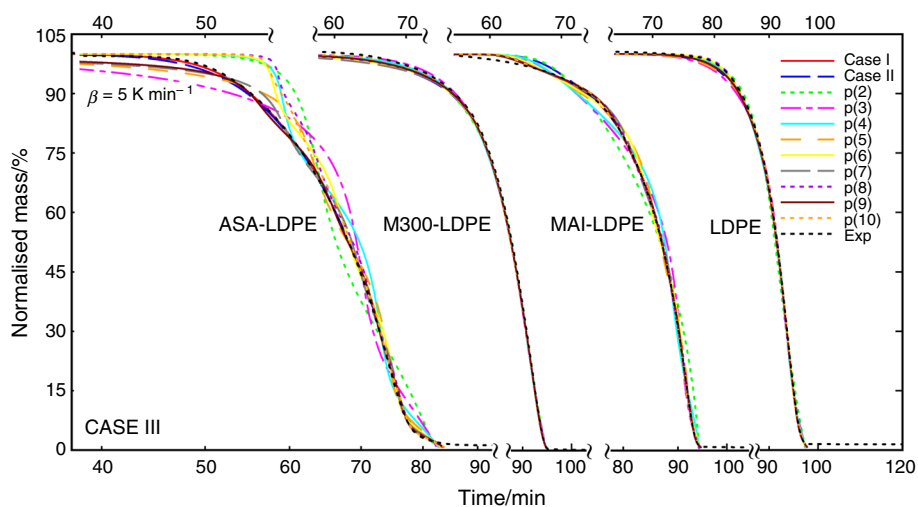


Fig. 5 Comparison of the values of the activation energies calculated by polynomials of different degrees and discrete values determined by isoconversional analysis

Fig. 6 Comparison of the calculated degradation profiles applying the polynomial approximations and the extracted TG profiles. For the whole range of heating rates, see Fig. S5



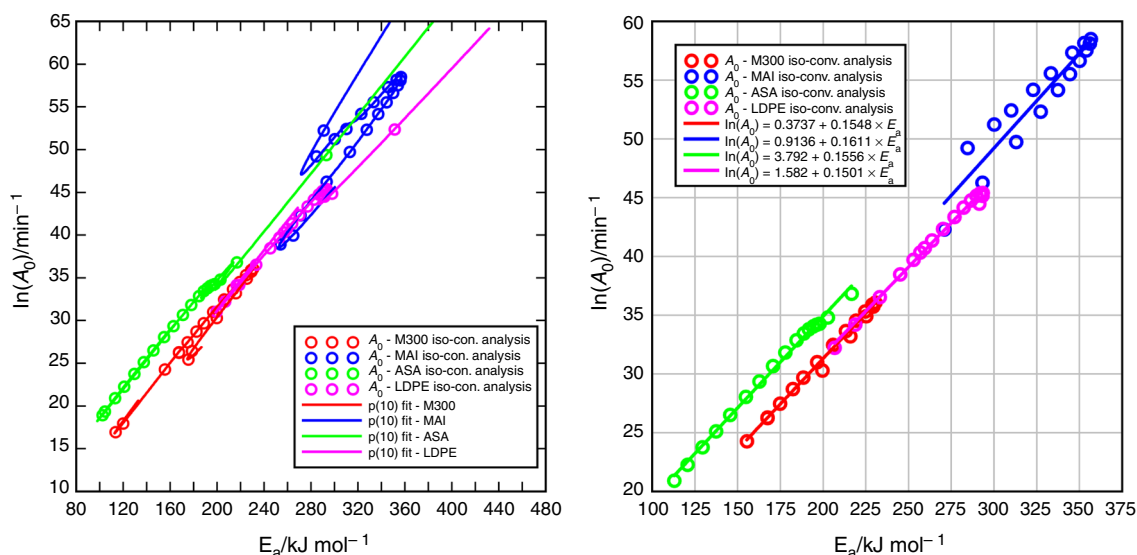


Fig. 7 Relation between the pre-exponential factors and the activation energies calculated by the Friedman isoconversional approach and the assumption of a zero-order reaction model. The right plot

shows linear fits for LDPE conversions between 10 and 90%. Enlarged plots for particular cases are shown in Fig. S6

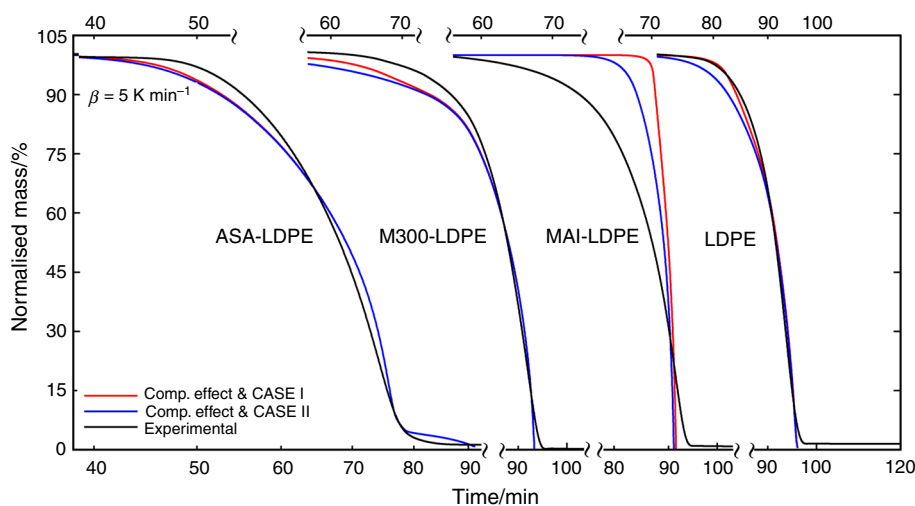
So far, the biggest concern has been deriving the functional dependency of the activation energy. Since similar relations were observed between the pre-exponential factors and the conversion, the hypothesis of the so-called compensation effect [29, 30] was also verified. The compensation effect is expressed by the following relation:

$$\ln(A) = a_A + b_A \cdot E_a \quad (9)$$

Figure 7 shows the corresponding relationship between the calculated pre-exponential factors for the zero-order reaction model and the activation energies for all cases studied. The calculated values fall within the range of published results elucidated from the measurements performed under the different operating conditions and interpreted by different kinetic equations [31]. From the

enlarged insert shown in Fig. 7, it is evident that the hypothesis about the compensation effect may be applied to the runs carried out with pure LDPE and a mixture of LDPE with the M300 or ASA catalyst, while for the case of the MAI catalyst the ‘S-shaped’ pattern is too conspicuous compared with the others. To determine the parameters in the compensation-effect Eq. (9), only the values of the midpoints between the 10 and 90% conversion were used in order to eliminate the possible effect of interpretation uncertainty regarding the TG profiles outside this region. The results presented in Fig. S6 show good correlation parameters ($R_{M300} = 0.996$, $R_{ASA} = 0.997$, $R_{PE} = 0.997$, $R_{Mal} = 0.953$), except for the case of the MAI catalyst. To verify the applicability of the compensation-effect equation for predicting the LDPE degradation profiles, Eq. (9) was

Fig. 8 Comparison of the experimental and calculated degradation profiles by compensation-effect equations coupled with assumptions for the calculation of activation energies as stated in the assumptions made in Case I and Case II. For the whole range of heating rates, see Figs. S7 and S8



coupled with the linear interpolation/extrapolation way described for calculating the activation energy under assumption Cases I and II. A comparison of the simulated results based on the compensation effect and the experimentally measured degradation profiles is shown in condensed form in Fig. 8 and for all heating rates in supplementary Figs. S7 and S8.

The presented comparison draws the conclusion that only for the case of thermal (uncatalysed) LDPE degradation was satisfactory agreement obtained, while for the other cases the deviations exceed those shown for the simulations where kinetic parameters (observed when pre-exponential factors) were calculated by the interpolation/extrapolation way described under the assumptions made in Case I. The main reason for the observed deviations lies in the linearization, which gives the wrong starting values for the pre-exponential factors. The initial deviations accumulate during the integration and, together with the assumed linear dependency, make the shape of the predicted profiles different to those of the measured ones. Despite these observed deviations, it is obvious that the assumption about the global compensation effect between the pre-exponential factor and the activation energy is valid within a conversion range of 10–90% for three out of four cases presented in this article, which is very surprising given that numerous chemical reactions are taking place during the degradation process.

Conclusions

The presented analysis demonstrates that for those cases when the catalyst underwent thermal degradation, i.e. its mass lose within the temperature range of the sample degradation, the previously proposed [18] procedure for generating catalyst-free TG profiles produces reliable TG profiles that were used to model a catalysed LDPE degradation process.

For modelling purposes, the isoconversional Friedman approach was applied. It was confirmed that the degradation profiles predicted by various reaction models overlap over the entire conversion range. The analysis reveals that the catalytic degradation of LDPE can be predicted by a correlation twin, i.e. the two catalyst's specific functional relations between the activation energy, pre-exponential factor and conversion. The crucial step to ensure good agreement between the predicted and the measured profiles is to extrapolate the discrete values of the activation energies and pre-exponential factors to the value at the zero conversion. It turns out that the linear extrapolation and interpolation from the discrete values obtained by the isoconversional analysis outperforms the regression functions based on the various order polynomials, and that apparent

deviations from the global trend at lower conversions are not a consequence of the misinterpretation of experimental results but are an experimental fact. The assumption about the compensation effect between the pre-exponential factor and the activation energy holds within the conversion range from 10 to 90%. However, it is unsuitable for the modelling purposes due to the uncertain extrapolation to the zero conversion.

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