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NON-ISOTHERMAL ANALYSIS OF THE KINETICS OF THE COMBUSTION OF CARBONACEOUS MATERIALS

R. López-Fonseca, I. Landa, M. A. Gutiérrez-Ortiz and J. R. González-Velasco[*]

Chemical Technologies for Environmental Sustainability Group, Department of Chemical Engineering,
Faculty of Science and Technology, Universidad del País Vasco/EHU, P.O. Box 644, 48080 Bilbao, Spain

Non-isothermal thermogravimetric data were used to evaluate the Arrhenius parameters (activation energy and the pre-exponential factor) of the combustion of two carbonaceous materials, selected as diesel soot surrogates. The paper reports on the application of model-free isoconversional methods (Flynn–Wall–Ozawa and Kissinger methods) for evaluating the activation energy of the combustion process. On the other hand, by means of the compensation relation between E and ln$A$, which was established by the model-dependent Coats–Redfern method, the value of the pre-exponential factor was estimated from the known value of the model-independent activation energy.

Keywords: *combustion, diesel soot, kinetics, non-isothermal thermogravimetry*

Introduction

Combustion of the soot, generally with the aid of a catalyst, is one of the solutions proposed for the reduction of diesel particulate emissions [1]. Consequently, the kinetics of the combustion of carbonaceous materials is of great interest for the modelling and design of catalytic converters of diesel engines. Prior to the design of the catalyst, it is required to get reliable information on the kinetics of non-catalytic combustion of the particulate matter generated in the diesel engine, the so-called diesel soot.

The kinetic studies of thermally induced reactions in solids, such as the combustion of carbonaceous materials, are traditionally performed by thermal analysis methods which measure a change in an extensive property, generally, mass (thermogravimetry, TG). The kinetics of thermal transformations studied by TG under non-isothermal conditions are usually described by the following equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=f(\alpha)k(T)=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where $f(\alpha)$ is the reaction model, α is the extent of reaction, $k(T)$ is the rate constant (A and E are the pre-exponential factor and the activation energy, respectively), T is the temperature, t is the time, and β is the heating rate. The temperature dependence of the rate constant is generally assumed to follow an Arrhenius-type dependence. The formal expression of $f(\alpha)$ depend on the conversion mechanism, and it represents the limiting step of the kinetic model.

Equation (1), as well as numerous approximations of its integral form (Eq. (2)), underlies most of the methods of kinetic processing.

$$g(\alpha)=\int_0^\alpha\frac{\mathrm{d}(\alpha)}{f(\alpha)}=\frac{A}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)\mathrm{d}T= =\frac{AE}{\beta R}\int_x^\infty\frac{\exp(-x)}{x^2}\mathrm{d}x=\frac{AE}{\beta R}\,p(x) \quad (2)$$

where $x=E/RT$ and $p(x)$ is the temperature integral, which cannot be exactly calculated. When operating under non-isothermal conditions, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and the determination of $f(\alpha)$, A and E (the so-called kinetic triplet) is an interlinked problem. A deviation in the determination of any of the three will cause a deviation in the other parameters of the triplet. Thus, it is highly recommended to start the analysis of non-isothermal experiments by determining one element of the triplet with high accuracy, such as the activation energy.

The methods of kinetics processing can be divided into two main categories [2]: those which employ data obtained under only one heating rate, and those based on performing a series of measurements under different heating rates (isoconversional methods). The attraction of isoconversional methods derives mainly from its ability to give activation energy values without the necessity of presuming the analytical form of the conversion model $f(\alpha)$. The basic assumption of model-free isoconversional methods is that the reaction rate at a constant conversion is only a function of temperature, and that the reaction model is

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[*] Author for correspondence: iqpgovej@lg.ehu.es

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not dependent on temperature or heating rate. These methods yield the dependence of the effective activation energy on the transformation degree. The existence of such dependence points to a complex character of the process (for a simple process the activation energy is constant at any transformation degree). The main disadvantage of isoconversional methods is that they do not suggest direct evaluation of the pre-exponential factor or kinetic model.

The so-called integral isoconversional methods differ according to the approximation used to calculate the temperature integral. The integral isoconversional method suggested independently by Flynn and Wall [3] and Ozawa [4] uses Doyle's [5] approximation of the temperature integral $p(x)$ to solve the Eq. (2). This method is based on the following equation:

$$\log\beta = \log\frac{AE}{Rg(\alpha)} - 2.315 - 0.457\frac{E}{RT} \qquad (3)$$

Thus, at a constant conversion the plot $\log\beta$ *vs.* $1/T$, obtained from a series of experiments performed at several heating rates, should be a straight line whose slope allows evaluation of the activation energy. The integral isoconversional method suggested by Kissinger–Akahira–Sunose [6, 7] is based on the Coats–Redfern approximation of the temperature integral $p(x)$ [8], that leads to:

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT} \qquad (4)$$

Thus, for α=const., the plot $\ln(\beta/T^2)$ *vs.* $1/T$, obtained from curves recorded at several heating rates, should be a straight line whose slope can be used to evaluate the activation energy. Obviously, the different isoconversional methods applied to the same non-isothermal data should lead to the same activation energy value, and to the same dependence of E on conversion [9, 10].

Among the methods that only consider a single thermoanalytical curve recorded at a single heating rate for determining E, and also A, the Coats–Redfern method [8] is probably the most employed in the literature. This method uses the equation:

$$\ln\frac{g_j(\alpha)}{T^2} = \ln\left[\frac{A_jR}{\beta E_j}\left(1-\frac{2RT}{E_j}\right)\right] - \frac{E_j}{\mathrm{RT}} \cong \ln\frac{AR}{\beta E_j} - \frac{E_j}{RT} \qquad (5)$$

The subscript *j* has been introduced to emphasise that substituting a particular reaction model in Eq. (5) results in evaluating the corresponding Arrhenius parameters. This method assumes that the Arrhenius parameters do not depend on α. By using this method, it is observed that the values of the activation energy and the pre-exponential factor, obtained for different analytical forms of $g(\alpha)$, are correlated through the following relation of compensation (Eq. (6))

$$\ln A_j = a + bE_j \qquad (6)$$

where the subscript *j* refers to one of the possible models $g_j(\alpha)$ considered to describe the process. This means that the rate of the process investigated can be satisfactorily described by Eq. (5) with practically any model $f(\alpha)$ and fitting $k(T)$ which compensates the error of the reaction model-choice. Therefore, an implication of the $f(\alpha)$–$k(T)$ compensation results in a linear correlation. Vyazovkin and Lesnikovich [11] proposed a procedure to calculate the value of the pre-exponential factor based on the use of the compensation effect. Thus, once the correlation parameters *a* and *b* have been evaluated, the model-free activation energy calculated by isoconversional methods is substituted for E_j in Eq. (6), and, subsequently A is estimated.

The objective of this paper is the study of the combustion of two carbon blacks selected as diesel-like materials by means of non-isothermal TG in order to evaluate the Arrhenius parameters of the process.

Experimental

Two carbon blacks, namely Flammruss 101 and Printex XE-2B (both kindly provided by Degussa AG), were selected as model diesel soot materials. The composition was established by chemical analysis in automatic Leco CHN-2000, Leco S-144-DR, and Leco CHNS-932 equipments. The textural properties were determined by N_2 adsorption-desorption at –196°C in a Micromeritics ASAP 2010 equipment in a relative pressure range from about 10^{-6} to 0.99.

The thermooxidative degradation of the carbonaceous materials was investigated by means of dynamic TG using a Perkin Elmer TGS-2 thermobalance under atmospheric pressure. The studies were carried out at constant heating rate of 1.5, 3, 5 and 7.5 K min^{-1} in the temperature range 50–950°C. The oxidant stream was dry air flowing at 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. The samples for TG analysis were prepared by simply mixing the corresponding carbonaceous material and SiC (silicon carbide) with a spatula in a mass ratio of 1/10. The addition of SiC decreased the flow resistance of the sample bed and provided a heat sink, which decreased temperature gradients in the sample. Employing sample sizes of 0.5 g carbonaceous material diluted with about 5 g SiC, thermal runaways as well as strong heat-up of the samples during thermogravimetric analyses were avoided. Thus, the sample for each TG run was 25 mg of the mixture (around 2.3 mg of carbonaceous material). The experimental conditions such as sample size, dilution ratio, atmosphere and gas flow rate were identical in all experiments.

Results and discussion

The elemental analysis of the samples revealed that the major component in both materials was carbon (>97 mass%), and the ash content was negligible. The textural properties, as revealed by N_2 adsorption analysis, were markedly different for both materials. Printex XE-2 sample showed a high surface area about 1170 $m^2\ g^{-1}$, while Flammruss 101 sample had a noticeably lower surface area around 30 $m^2\ g^{-1}$.

The normalised mass loss or conversion α was typically calculated from the corresponding TG curve as:

$$\alpha = \frac{M_0 - M_t}{M_0 - M_f} \tag{7}$$

where M_t is the mass of the sample at time t (or temperature T), M_0 and M_f are the mass of the sample at the beginning and at the end of the mass loss reaction, respectively. The TG analysis occurred with a negligible change concentration of oxidant, since dry air was fed in large excess with respect to the solid sample. During the TG experiment the oxygen concentration could be therefore considered constant as well as its effect on the reaction rate. The occurrence of both mass- and heat-transfer limitations can be decreased by decreasing the sample size spread thinly on the sample pan, diluting the sample by a proper, inert material having a high thermal conductivity such as silicon carbide, and employing a relatively high oxidant gas flow rate and a low heating rate [12].

The thermogravimetric data collected during non-isothermal combustion of the carbonaceous samples at several constant heating rates are shown in Fig. 1. It was found that Printex XE-2 sample was converted at temperatures noticeably lower than Flammruss 101 sample. The reaction occurred in a relatively narrow temperature range (around 150–170°C) between 440–650 and 565–810°C, respectively. When increasing the constant heating rate the TG curves were shifted to higher temperature regions without any appreciable distortion in the typical sigmoidal shape.

It is widely accepted that the oxidation of carbonaceous materials occurs on surface carbon sites that are capable of dissociatively chemisorbing oxygen [13]. These sites are primarily associated with edge or defects on the surface. The amount of these reactive sites is known to be strongly dependent on parameters such as the surface area [14]. Hence, carbonaceous materials having a high surface area are more reactive. The higher reactivity (lower combustion temperatures) of Printex XE-B2 sample was therefore associated with its larger quantity of carbon sites located at edge or defect sites on its surface.

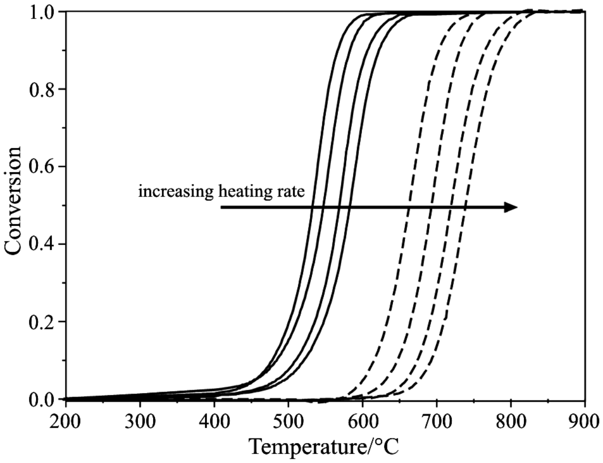

Fig. 1 Experimental mass kinetic curves obtained at different heating rates for Printex XE-2B and Flammruss 101 samples

The application of the isoconversional methods requires the determination of the absolute temperature at which a fixed extent of combustion from the several TG curves recorded at different heating rates. The conversion range between 0.1 and 0.9 was investigated. The Flynn–Wall–Ozawa method involves plotting logβ *vs.* 1/T. The slope of such plots gives the activation energy for the selected conversion degrees. Results from the application of this isoconversional method in the 10–90% conversion range are shown in Figs 2a and b for Printex XE-2B and Flammruss 101 samples, respectively. For constant α, the plot of $\ln(\beta/T^2)$ *vs.* 1/T, according to the Kissinger analysis, should be a straight line whose slope is the activation energy. The linear relationships are shown in Figs 2c and d for Printex XE-2B and Flammruss 101 samples, respectively. For all sets of α values (10–90% conversion range) in the isoconversional plots, the correlation coefficients for the linear regressions were higher than 0.95 for Printex XE-2B sample, and 0.98 for Flammruss 101 sample.

The results of isoconversional calculations are presented in Fig. 3 in terms of the activation energy as a function of the extent of conversion. The shape of this dependence may be very helpful in drawing conclusions on the kinetic scheme. As aforementioned, the same activation energy values and the same dependence of the activation energy on conversion should be predicted by each of the isoconversional methods evaluated in this work.

As for Printex XE-2B sample, both Flynn–Wall–Ozawa and Kissinger methods led to a relatively constant activation energy value irrespective of the conversion degree, with the Flynn–Wall–Ozawa method

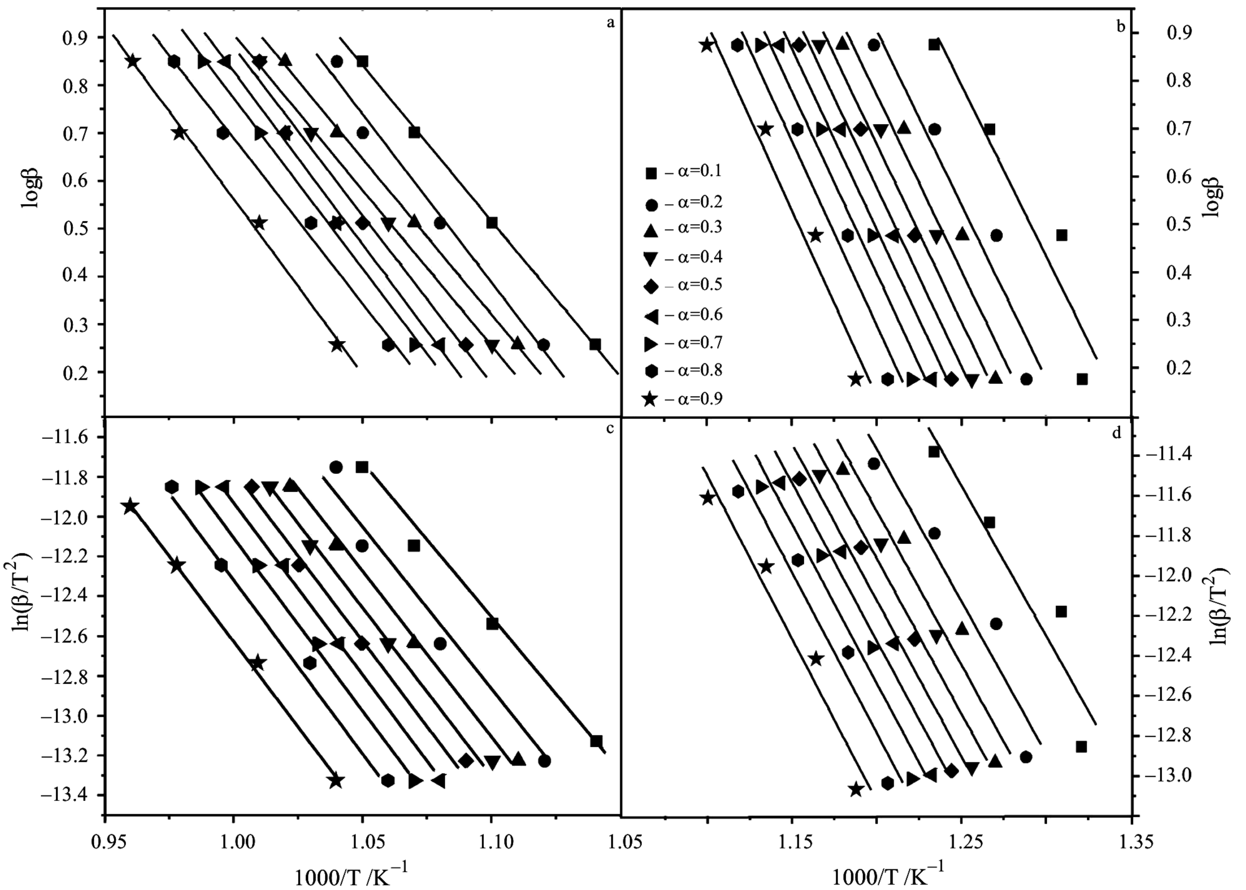

Fig. 2 Isoconversional plots at various conversion degrees for both carbonaceous materials (left-handed plots – Printex XE-2B; right-handed plots – Flammruss 101. a, b – Flynn–Wall–Ozawa method; c, d – Kissinger method)

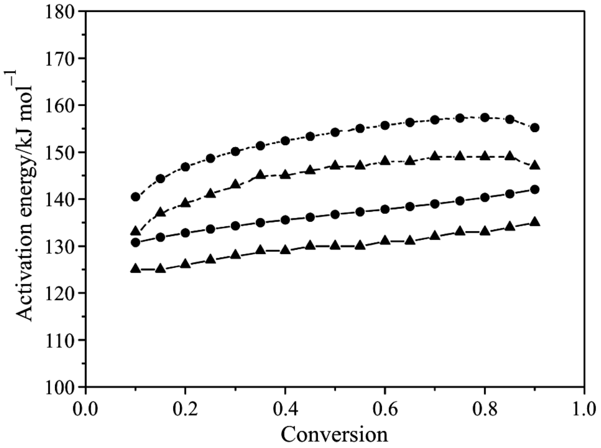

Fig. 3 Model-independent values of the activation energy as a function of the degree of conversion for the combustion of the carbonaceous materials calculated by isoconversional methods (—– Printex XE-2B; --- – Flammruss 101. ● – Flynn–Wall–Ozawa method; ▲ – Kissenger method)

yielding slightly higher values. Hence, averaged values of 136 and 129 kJ mol^{-1} were obtained with the Flynn–Wall–Ozawa and the Kissinger methods, respectively. A constant difference (around 7 kJ mol^{-1}) was observed for the values predicted by both models in the entire conversion range. If it is assumed that the activation of the combustion of Printex XE-2B is constant at any conversion degree, the process can be considered a single-step process. An averaged activation energy value of 132 kJ mol^{-1}, as calculated from the two isoconversional methods, was estimated for the combustion of this material.

As regards Flammruss 101 sample, both integral isoconversional methods led to nearly constant activation energy values in the conversion range investigated. Again, the Flynn–Wall–Ozawa yielded a slightly higher value, 151 kJ mol^{-1}, in comparison with 144 kJ mol^{-1}, obtained by the Kissinger method. A practically invariant difference (about 8 kJ mol^{-1}) was noted between both methods. From the application of the two isoconversional methods evaluated an averaged value of 150 kJ mol^{-1} was estimated for Flammruss 101 sample. The mean activation energy values, 132 kJ mol^{-1} for Printex XE-2B and 150 kJ mol^{-1} for Flammruss 101 sample, are in accordance with data reported in the literature for similar materials [15, 16].

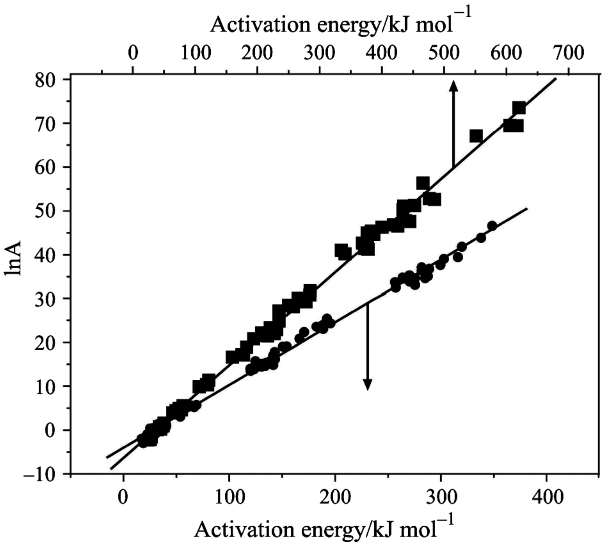

Fig. 4 ln*A* *vs*. *E* plot for the combustion of Printex XE-2B and Flammruss 101 samples

The Coats–Redfern analysis of the thermogravimetric data recorded at a single heating rate has been carried out by inserting various $g_j(\alpha)$ into Eq. (5) that results in a set of Arrhenius parameters determined from the plot $\ln[g_j(\alpha)/T^2]$ *vs.* $1/T$. It was found that each TG curve could be equally well described by several kinetic models resulting in correlation coefficients close to the unity. Hence, the Arrhenius parameters derived were highly variable, exhibiting a strong dependence on the reaction model chosen and a weak dependence on the heating rate. This extra flexibility in the fitting procedure allowed errors in the functional form of the reaction model to be concealed by making compensation errors in the Arrhenius parameters, sometimes by as much as one order of magnitude. Unfortunately, kinetic methods based on results obtained from single-rate run experiments did not permit an unambiguous determination of *E*. For a successful analysis at least one kinetic parameter must be a priori known. Thus, once the correlation relation was established and a model-free activation energy value was available, the value of the pre-exponential factor could be unambiguously determined. The compensation relations corresponding to Printex XE-2B and Flammruss 101 samples are plotted in Fig. 4. The following equations were derived, respectively:

$$\ln A=0.143E–3.571$$

$$\ln A=0.125E–3.507$$

Hence, the values of pre-exponential factor that could be derived were $2.9\cdot10^6$ and $2.0\cdot10^6$ min^{-1}, respectively.

Conclusions

The determination of the Arrhenius parameters (activation energy and pre-exponential factor) of the combustion of two carbonaceous materials, namely Printex XE-2B and Flammruss 101, was analysed by non-isothermal TG with the aid of a number of kinetics processing methods. The activation energy was determined by model-free integral (Flynn–Wall–Ozawa and Kissinger methods) isoconversional methods, which required thermoanalytical data obtained from a series of experiments at different heating rates. Despite the differences obtained by both methods, a certain averaged value of the activation energy could be estimated for the studied processes: 132 kJ mol^{-1} for Printex XE-2B sample, and 150 kJ mol^{-1} for Flammruss 101 sample. The combustion process of each material was assumed to be a single-step reaction. The compensation relation derived from the Coats–Redfern method was useful for the unambiguous determination of the pre-exponential factor once a model-free activation energy value was known.

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