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Thermogravimetric analysis during the decomposition of cotton fabrics in an inert and air environment

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Abstract

The thermal degradation of samples of used cotton fabrics has been investigated using thermogravimetric analysis (TGA) between room temperature and 700 °C. Experiments were carried out with about 5 mg of sample in three different atmospheres: helium, 20% oxygen in helium and 10% oxygen in helium. Three different heating rates were used at each atmosphere condition. A kinetic model for the decomposition of used cotton fabrics explaining the behavior of all the runs performed has been proposed and tested. For the pyrolysis of the cotton, the model comprises two parallel reactions. For the combustion process, one competitive reaction was added to each parallel reaction of the pyrolysis model and four combustion reactions of the different solid fractions to obtain volatiles. One single set of parameters can explain all the experiments (pyrolysis, oxidative pyrolysis and combustion) at the three different heating rates used.

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1. Introduction

The growing interest in renewable energies is accompanied by intensified research and development of technical processes for the thermal conversion of biomass and wastes. Used cotton fabrics could be used as biomass, and in this way, offer a valid alternative to disposal in landfills. Although cotton fabrics are usually recycled in other ways, thermal decomposition only of the wastes is interesting for some industries that mainly focus on obtaining the potential energy by combustion.

The development of pyrolysis–combustion processes requires an optimization of the operating conditions in order to assure both acceptable gas outlet composition and an energy recovery, which makes the process economically satisfactory [1]. A good knowledge of the kinetics of the process is fundamental for the plant design and scale-up bases on process simulation.

Cotton is mainly comprised of cellulose. The pyrolytic degradation of cellulose has been the subject of extensive study, although in many instances, knowledge of the exact nature of

degradation and decomposition remains incomplete. Chatterjee and Conrad [2] studied the kinetics of cellulose decomposition in the temperature range of 270–310 °C with absorbent cotton and proposed two series reactions for the pyrolysis process. Dollimore and Hoath [3] used differential thermal analysis (DTA) to follow the degradation of cellulose in air products and obtained two and sometimes three exothermic peaks. Antal and Várhegyi [4] reviewed the literature of cellulose pyrolysis and concluded that the pyrolysis of a small sample of pure cellulose is characterized by an endothermic reaction governed by a first order rate law with a high activation energy. Völker and Rieckmann [5] investigated the influence of the final mass on modelling results and evaluated the applicability of established kinetic models for engineering purposes.

Cotton fabrics, which have a major share of the textile market, are highly inflammable and the development of successful flame retardant systems for cotton is of major interest. For this reason, many authors have studied the mechanism of pyrolysis of untreated and flame retardant treated cotton fabrics. For instance, Farooq et al. [6] carried out the thermogravimetric analysis of the mechanism of pyrolysis of untreated cotton fabrics and cotton fabrics finished with various flame retardant, considering the fraction decomposed as between 0.1 and 0.9. These authors evaluated the activation

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energies obtaining values of 155–158 kJ mol⁻¹ for the thermal decomposition of untreated cotton. In addition, they proposed a second order decomposition mechanism as the most suitable. Wanna and Powell [7] studied the thermal decomposition of untreated and treated cotton fabric with selected salts in oxidative and inert atmospheres using TGA-FTIR. On the other hand, no papers considering the overall decomposition kinetics of cotton cellulose or cellulose have been found.

It is clear that the n -th order kinetic model can be correct for homogeneous gas phase kinetics, in accordance with the collision theory and the transition state theory developed for elemental reactions and normally with $n = 1, 2$ or 3 . The pyrolysis of polymers it is a non-homogeneous reaction and consequently the n -th model should not be valid. In literature, we can find mechanisms for the pyrolysis of different polymers with parallel and series reactions. Considering only one elemental reaction for the decomposition of a solid, the proposal of a kinetic expression based on the elemental reaction is not easy because the decomposition takes place in a solid phase. Font and García [8] proposed the application of the transition state theory to the pyrolysis of biomass considering the similarity between the pyrolytic reaction that take places in the outer surface and the first order uni-molecular catalytic surface reactions. In accordance with the model developed, it is possible to obtain n -th models as a consequence of the increase or decrease of the surface with active centres where the decomposition can take place, and with fractional values of the reaction order n .

The n -th order reaction has been used extensively by different researchers when studying the mechanisms of decomposition of several polymers, no matter the mechanisms of reactions comprises parallel or series reactions. Nevertheless, in spite of the proposal of a model that could explain fractional reaction orders, the models obtained from the TG runs must be considered as correlation ones, and from the analysis of the activation energy, it can be deduced if the model is related satisfactorily to a controlling decomposition elemental step or must be only considered valid for correlation.

The present work, which is included in a wider project whose objective is to study the combustion of different industrial and municipal wastes, studies the thermal decomposition of used and waste cotton fabrics from the thermogravimetric point of view, including the kinetic analysis in a thermobalance in inert atmosphere and with different amounts of oxygen, proposing a kinetic model.

2. Experimental

2.1. Raw material

Used cotton fabrics were simulated by using a used blue T-shirt made of 100% cotton. Prior to the runs, the T-shirt was cut into small pieces with an average size of 1 cm × 1 cm.

Table 1 shows some characteristics of the material studied. Elemental analysis of the major components was carried out in a Perkin-Elmer 2400. The moisture was determined by the weight loss at 105 °C for 12 h. The calorific value was obtained

Table 1
Characteristics of the material used

C (wt.%)	45.5
H (wt.%)	6.6
N (wt.%)	0.3
S (wt.%)	<0.1
O% by difference (wt.%)	47.5
Cl (wt.%)	0.12
Ash content (wt.%)	<0.1
Net calorific value (kJ kg ⁻¹)	17100
Moisture (wt.%)	5.0

in an AC-350 calorimetric bomb from Leco Corporation. Chlorine was measured using an automatic sequential spectrometer X-ray Fluorescence model TW 1480. Ash residue was obtained by calcination at 850 °C.

2.2. Thermobalance

The thermogravimetric experiments were carried out in a Setaram thermobalance model DSC92 controlled by a PC system. The atmosphere used for pyrolysis was helium with a flow rate of 60 ml min⁻¹ (STP), according to the specifications of the equipment. In the combustion runs, two mixtures of helium and oxygen: 9:1 (10% oxygen) and 4:1 (20% oxygen) were used, with the same total flow rate. The sample temperature was measured with a thermocouple directly at the crucible, i.e., very close to the sample. Because a water-cooled microfurnace was used, the temperature could be lowered rapidly.

Before the runs with used cotton fabrics, an experiment with a heating rate of 5 °C min⁻¹ using Avicel PH-105 microcrystalline cellulose was done to check the good performance of the equipment. The results obtained showed good agreement with the kinetic evaluation of Avicel Cellulose TG curves at this heating rate presented by Grønli et al. [9] in their round-robin study of cellulose pyrolysis kinetics by thermogravimetry.

The experiments were carried out with heating rates of 5, 10 and 20 °C min⁻¹ over a variety of temperatures that included the entire range of solid decomposition, 80–700 °C. Experiments without a sample were carried out, and used as background in order to subtract the buoyancy effect. The mass of the samples used was approximately 5 mg, and under these conditions the heat transfer limitations can be neglected.

3. Results and discussion

3.1. Thermogravimetric study

Figs. 1–3 show in detail the experimental curves for used cotton fabrics pyrolysis (helium) and combustion (helium:oxygen, 4:1 and 9:1) at different heating rates. The calculated curves of the kinetic models are also shown. In the figures, w is defined as the residual mass fraction of the solid (including residue formed and non-reacted initial solid), i.e., the ratio between the solid mass at any time (m) and the initial solid mass (m_0). In all the processes, we can be observed the general shift to higher temperatures when the heating rate is increased.

Fig. 1. Cotton pyrolysis at several heating rates: 5, 10 and 20 °C min⁻¹. Experimental and calculated curves.

Fig. 3. Cotton combustion at several heating rates and 10% oxygen. Experimental and calculated curves.

Fig. 4 compares the results obtained in the different atmospheres at a constant heating rate. As can be seen, the presence of oxygen accelerates the decomposition (taking place at lower temperatures) and a final combustion process is observed. On the other hand, there is not a great difference between the runs performed under 10% oxygen and those at 20% oxygen.

3.2. Kinetics of the process

3.2.1. Pyrolysis model

Most of the papers published corresponding to the pyrolysis of cellulose and cotton consider only one fraction when correlating the experimental data of the primary decomposition, in spite of the parallel and series mechanisms proposed in literature [4]. In the cotton fabrics used in this work, and considering that we have extended the temperature range until high temperatures, a second decomposition process has been considered in order to improve the correlation.

The kinetic model proposed for the decomposition of the used cotton fabrics in an inert atmosphere could be interpreted

considering this waste formed by two independent parts, each one following an independent reaction, as follows:

where C_1 and C_2 refer to different parts of the solid material to be decomposed (cotton in this case). " V_i " are the gases + volatiles evolved and " S_i " are the solid residue formed in the decomposition. The uncapsalized variables " c_n " are the amount of each material that is in the sample.

It is very useful to introduce the concept of the conversion degree for each reaction:

$$\alpha_i = 1 - \frac{C_n}{C_{no}} = \frac{V_i}{V_{i\infty}}, \quad i = n = 1, 2 \quad 193$$

(Two different subscripts have been used, because in the combustion model presented also in this model there are competitive reactions for the same solid.)

In the previous equations, $V_{i\infty}$ represents the maximum obtainable amount of volatiles via reaction ' i ' at time infinity,

Fig. 2. Cotton combustion at several heating rates and 20% oxygen. Experimental and calculated curves.

Fig. 4. Experimental TG plots for pyrolysis and combustion with 20 and 10% oxygen, all carried out at 20 °C min⁻¹ heating rate.

198
199 C_n refers to the non-decomposed material at each time, and C_{no}
200 is the initial contribution of fraction 'n' to the total weight. Note
201 that at $t = 0$ the value of α_i is zero, and that $V_{1\infty}$ equals the yield
202 coefficient v_1 and that $V_{2\infty}$ equals the yield coefficient v_2 .

203 The kinetic equations associated with the parallel reaction
204 for the pyrolysis runs, taking into account the mass balance
205 between products and reactants and the degree conversions, can
206 be expressed as:

$$\left. \begin{aligned} -\frac{d\left(\frac{C_n}{C_{no}}\right)}{dt} &= \frac{d\left(\frac{V_i}{V_{i\infty}}\right)}{dt} = \frac{d\alpha_i}{dt} = k_i \left(\frac{C_n}{C_{no}}\right)^{n_i} = k_i (1 - \alpha_i)^{n_i} \\ k_i &= k_{i0} \exp\left(-\frac{E_i}{RT}\right) \end{aligned} \right\}, \quad n, i = 1, 2$$

206
207 By integration of these reactions it is possible to calculate α_1
208 and α_2 at each time; the relationship between these two values
and the weight fraction measured in the thermobalance (w) is:

$$209 \quad w = 1 - V = 1 - (V_1 + V_2) = 1 - (V_{1\infty}\alpha_1 + V_{2\infty}\alpha_2)$$

212 The values of $V_{1\infty}$ and $V_{2\infty}$ are related with the total
volatiles at time infinity (V_∞), that is a known amount:

$$213 \quad V_\infty = V_{1\infty} + V_{2\infty}$$

216 The pyrolysis data and the combustion data have been
217 correlated together, in order to obtain a single set of parameters
218 for the thermal decomposition of used cotton fabrics in different
219 atmospheres: pyrolysis, oxidative pyrolysis and combustion.

220 3.2.2. Combustion model

221 Similarly to the kinetic models found in literature to explain
222 pyrolytic processes, different authors propose different models
223 to explain decomposition mechanisms under oxidative atmo-
224 spheres. Obviously, if the model proposed satisfactorily fits
225 experimental data generated under a wide selection of
226 conditions, the model can be considered representative of
227 the process analyzed [10]. However, literature that includes
228 detailed kinetic studies, fitting experimental curves at different
229 heating rates and oxygen content is extremely sparse. Different

models have been found in literature, concerning the
decomposition of tannery waste under oxygenated atmosphere
[11], polycoated materials such as milk cartons [12],
polytetrafluoroethylene [13] and also of tire wastes [14]. No
models for combustion of cotton or used cotton fabrics have
been found, as commented previously.

The kinetic model proposed for the combustion runs could
be interpreted considering, that the presence of the oxygen

introduces a new competitive process for the decomposition of
each fraction and in this way this model explains the fact
observed in Fig. 4, where the first weight loss in combustion
runs reaches a lower value than in pyrolysis runs.

Figs. 5 and 6 show the TG and DSC plots for pyrolysis
and combustion at 5°C min^{-1} heating rate. As seen in Fig. 5,
an endothermic peak appears for the pyrolysis process
and in the combustion process besides two exothermic peaks
appear.

Taking into account the behavior commented above, the
oxygen to be included in the decomposition law has been
considered, as has been done with other materials [15–16].

The following scheme represents the combustion model
proposed to explain the behaviour obtained at two different
helium: oxygen atmospheres and three heating rates:

Fig. 5. Experimental TG and DSC plots for pyrolysis at 5°C min^{-1} heating rate.

Fig. 6. Experimental TG and DSC plots for combustion with 20% oxygen at 5°C min^{-1} heating rate.

Reactions 1 and 2 are the same as in pyrolysis. Furthermore, as a final new process appears in combustion runs, the combustion reactions to the chars formed has been considered:

V_{ci} refers to the volatiles produced through the combustion reaction with solid S_i .

Conversion degrees are considered for each reaction:

$$\alpha_i = 1 - \frac{(C_n)_{\text{reacted by reaction } i}}{C_{n0}} = \frac{V_i}{V_{i\infty}},$$

$$i = 1, 2, 3, 4; n = 1 \text{ (for } i = 1, 3); n = 2 \text{ (for } i = 2, 4)$$

$$\alpha_{ci} = \frac{(S_i)_{\text{burnt}}}{s_i} = \frac{V_{ci}}{V_{ci\infty}},$$

$$i = 1, 2, 3, 4; n = 1 \text{ (for } i = 1, 3); n = 2 \text{ (for } i = 2, 4)$$

where $V_{i\infty}$ and $V_{ci\infty}$ represent the maximum amounts of volatiles evolved if the whole solid fraction decomposes only through the reactions that lead to the corresponding volatiles, without competitive reaction. Note that in this case $V_{i\infty}$ equals the yield coefficient v_i and that $V_{ci\infty}$ equals the yield coefficient s_i .

Reactions 1 and 3 are competitive with respect to the same solid C_1 , so it is possible that none of the two values of degree conversion α_1 and α_2 can reach the value 1 at time infinity, although the sum α_1 and α_2 logically must be equal to 1, when the reactant C_1 is exhausted. In this case, the ratio between the non-reacted solid C_1 and the initial solid C_{10} , taking into account the degree conversions α_1 and α_3 , can be expressed as:

$$\frac{C_1}{C_{10}} = 1 - \alpha_1 - \alpha_3$$

and consequently the kinetic laws for the decomposition of the solid fraction C_1 can be written as

$$-\frac{d\left(\frac{C_1}{C_{10}}\right)_{\text{by reaction } i}}{dt} = \frac{d\alpha_i}{dt} = k_i \left(\frac{C_1}{C_{10}}\right) = k_i (1 - \alpha_1 - \alpha_3)^{n_i},$$

$$i = 1, 3$$

Similarly for reactions 2 and 4, the following expression can be obtained:

$$-\frac{d\left(\frac{C_2}{C_{20}}\right)_{\text{by reaction } i}}{dt} = \frac{d\alpha_i}{dt} = k_i \left(\frac{C_2}{C_{20}}\right) = k_i (1 - \alpha_2 - \alpha_4)^{n_i},$$

$$i = 2, 4$$

For the combustion of the residue S_1 (formed by the first reaction) in accordance with the scheme:

The degree conversion α_{c1} is

$$\alpha_{c1} = \frac{(S_1)_{\text{burnt}}}{s_1} = \frac{V_{c1}}{V_{c1\infty}}$$

The kinetic law for the combustion of S_1 can be written as:

$$-\frac{d(S_1/s_1)_{\text{burnt}}}{dt} = k_5 \left(\frac{S_1}{s_1}\right)^{n_5}$$

In this way, the kinetic constant of this second decomposition does not depend on the initial mass fraction, and consequently the kinetic constant k_5 with distinct mass fractions.

On the other hand, it can be deduced that:

$$\left(\frac{S_1}{s_1}\right)_{\text{at any time}} = \left(\frac{S_1}{s_1}\right)_{\text{formed reaction 1}} - \left(\frac{S_1}{s_1}\right)_{\text{burnt}} = \alpha_1 - \alpha_{c1}$$

Consequently, it can be written that:

$$\frac{d\alpha_{c1}}{dt} = k_5 (\alpha_1 - \alpha_{c1})^{n_5}$$

Another way of obtaining similar expressions can be found elsewhere [17]. This procedure can be applied to the other three combustion reactions. Consequently, the reaction model can be solved considering the following equations:

$$\frac{d\alpha_i}{dt} = k_i (1 - \alpha_1 - \alpha_3)^{n_i}, \quad i = 1, 3$$

$$\frac{d\alpha_i}{dt} = k_i (1 - \alpha_2 - \alpha_4)^{n_i}, \quad i = 2, 4$$

$$\frac{d\alpha_{1i}}{dt} = k_5 (\alpha_i - \alpha_{1i})^{n_5}, \quad i = 1, 2, 3, 4$$

$$v_1 = V_{1\infty}; \quad v_2 = V_{2\infty}; \quad v_3 = V_{3\infty}; \quad v_4 = V_{4\infty}$$

$$s_1 = V_{c1\infty}; \quad s_2 = V_{c2\infty}; \quad s_3 = V_{c3\infty}; \quad s_4 = V_{c4\infty}$$

$$v_1 + s_1 = v_3 + s_3$$

$$v_2 + s_2 = v_4 + s_4$$

Note that the same kinetic constant and reaction order are considered for the decomposition of S_i .

The total weight fraction is related to the other variables by:

$$w = 1 - V$$

$$= 1 - (V_1 + V_2 + V_3 + V_4 + V_{11} + V_{12} + V_{13} + V_{14})$$

$$w = 1$$

$$- (\alpha_1 V_{1\infty} + \alpha_2 V_{2\infty} + \alpha_3 V_{3\infty} + \alpha_4 V_{4\infty} + \alpha_{c1} V_{c1\infty} + \alpha_{c2} V_{c2\infty} + \alpha_{c3} V_{c3\infty} + \alpha_{c4} V_{c4\infty})$$

To take into account the effect of the partial pressure of oxygen (which equals 0.10 and 0.20 atm for helium:oxygen 9:1 and 4:1, respectively), since different behaviour is observed when comparing corresponding thermograms, the pre-exponential factors for reactions with oxygen have been considered to consist of two terms, one a typical pre-exponential factor k'_{io} and the other one the partial pressure of oxygen P_{O_2} raised to the power of an order b_{io} :

$$k_{io} = k'_{io} (P_{O_2})^{b_i}, \quad i = 3, 4, 5$$

348 The parameters optimized were: five orders of reaction, five
 349 pre-exponential factors, five activation energies and v_1 , v_2 , v_3 ,
 350 v_4 , s_1 , s_2 , and the values of b_3 , b_4 , b_5 . A simplification made in
 351 the model is to assume the same dependency of the constants
 352 with the partial pressure of oxygen, in the combustion of the
 353 chars.

354 The objective function (OF) to minimize was the sum of the
 355 square differences between experimental and calculated weight
 loss values

$$\text{OF} = \sum_{m=1}^3 \sum_{j=1}^N (w_{mj}^{\text{exp}} - w_{mj}^{\text{calc}})^2, \quad m, \text{ heating rates; } j, \text{ points}$$

359 The model validity has been tested calculating the variation
 coefficient (VC):

$$\text{VC} = \frac{\sqrt{\text{OF}/(N-P)}}{\bar{w}_{\text{exp}}} \times 100$$

362 where N and P are the number of data and parameters fitted,
 363 respectively, and $\bar{w}_{\text{exp}}$ is the average of the experimental
 364 weights. According to the procedure suggested by Martín-
 365 Gullón et al. [18], the great interrelation existing among the
 366 pre-exponential factor, the apparent activation energy and the
 367 reaction order can be decreased when optimization is per-
 368 formed in terms of a ‘comparable kinetic constant’ K_i^* instead
 369 of optimizing k_{oi} . This constant is calculated in a temperature
 370 around the maximum decomposition rate (T_{max}). Since K_i^* , E_i
 371 and n_i are optimised the pre-exponential factor k_{oi} is calculated
 using the following expression:

$$K_i^* = k_i(0.64)^{n_i} = k_{oi} \exp\left(\frac{-E_i}{RT_{\text{max}}}\right) (0.64)^{n_i}$$

375 Conesa et al. [19,20] came to a conclusion in their study of
 376 TG-DTG curves that at least three TG curves with different
 377 heating rates must be adjusted simultaneously in order for a
 378 kinetic model to be considered as potentially correct.

379 The kinetic parameters have been optimized in order to
 380 minimize the differences between experimental and calculated
 381 weight loss. Table 2 presents the values of the optimised
 382 parameters. Note that all the data of the three atmospheres
 383 (pyrolysis, oxidative pyrolysis, and combustion) and the three
 384 heating rates have been simultaneously fitted.

385 As can be seen in Figs. 1–4, the model is able to explain
 386 all the experimental data collected, at all the heating rates
 387 studied and in the presence and absence of oxygen. Bear in
 388 mind that all the runs are fitted with no variation of the
 389 parameters.

390 On analysing the values of the parameters in Table 2, some
 interesting conclusions can be obtained:

392 1. Considering the pyrolysis parameters, it can be observed that
 393 fraction 1 has a value of v_1 , that equals a $V_{1\infty}$, around 0.75,
 394 indicating that this fraction is the most important, although
 395 there is a small but significant second fraction, with a value
 396 v_2 around 0.11. Analysing the TG data of some papers
 397 concerning the pyrolysis of cellulose, this second fraction is
 398 also present [21,5].

Table 2

Kinetic parameters obtained for the thermal decomposition of used cotton
 fabrics (k'_{io} in $\text{s}^{-1}\text{atm}^{-b_i}$, E_i in kJ mol^{-1})

Pyrolysis	
k'_{10}	9.76×10^{10}
E_1	161.1
n_1	0.57
v_1	0.749
s_1	0.103
k'_{20}	1.32×10^3
E_2	65.2
n_2	2.62
v_2	0.124
s_2	0.024
Oxidative pyrolysis	
k'_{30}	2.70×10^{11}
b_3	0.39
E_3	159.4
n_3	0.29
v_3	0.589
s_3	0.263
k'_{40}	1.33×10^{23}
b_4	0.57
E_4	306.4
n_4	1.49
v_4	0.148
s_4	0
Combustion of char	
k'_{50}	4.47×10^6
b_5	0.31
E_5	126.8
n_5	0.64
VC (%)	2.628

- Concerning the kinetic parameters of the main fraction in the
 pyrolysis decomposition, activation energy around
 161 kJ mol^{-1} and reaction order around 0.57 are obtained,
 that are similar to the values proposed by Antal et al. (1980)
 when considering all the runs. The activation energy E_1
 obtained is also very similar to the values calculated by Farooq
 et al. [6] using two different methods: the iso-conversional
 technique and the most probable mechanism.
- With respect to the minor fraction in pyrolysis, a low value of
 activation energy around 65 kJ mol^{-1} and a reaction order
 equal to 2.77 are obtained, as a consequence of the slow
 decomposition of this fraction at high temperatures, and
 consequently these values can be considered as correlation
 parameters with no physical meaning.
- The oxidative pyrolysis of the main fraction has activation
 energy (159 kJ mol^{-1}) similar to that of pyrolysis
 (161 kJ mol^{-1}), and the reaction order (0.29) is somewhat
 lower than in pyrolysis (0.57). An order reaction less than
 unity can be due to an increase of the active surface with the
 reaction extension [8], so it is possible that in the oxidative
 process, the active surface increases more intensively than in
 pyrolysis. The value of v_3 (0.569), that equals $V_{3\infty}$, is less
 than the value ($V_{1\infty} = 0.755$) corresponding to the main
 fraction in pyrolysis. This fact could be explained as a

consequence of the partial oxidation of the molecular organic chains to ketones, aldehydes, carboxylic acids, etc., causing a weight loss lesser than in the case without oxygen. Therefore, all these parameters can be considered as acceptable and logical from a physical–chemical point of view.

5. In the oxidative pyrolysis of the minor fraction, the activation energy is around 150 kJ mol^{-1} , the reaction order is 0.97 and there is no formation of residue solid. These parameters must only be accepted for correlation of the data.
6. In the combustion of the chars, assuming the same kinetics for the three residue solids formed (S_1 , S_2 and S_3), the apparent activation energy is around 126 kJ mol^{-1} . The apparent activation energy obtained for the combustion of the char formed (126 kJ mol^{-1}) is similar to that obtained by other researchers. Haji-Sulaiman and Aroua [22] proposed values around 135 kJ mol^{-1} for the oxidation of Malaysian coal chars. Henrich et al. [23], also obtained values of apparent activation energy around 140 kJ mol^{-1} are for oxidation in pure oxygen of soot, graphite, activated charcoals and chars of municipal waste and electronic scrap. Nevertheless, Walker et al. [24] suggested apparent activation energy around $209\text{--}242 \text{ kJ mol}^{-1}$ for the reaction: $\text{C} + 1/2 \text{O}_2 \rightarrow \text{CO}$. A reaction order (0.57) less than unity is obtained. This latter aspect could also be explained as a consequence of the increase of the active surface with the reaction extension.
7. The reaction orders with respect to the oxygen for the oxidative pyrolysis are 0.39 for the main fraction and 0.45 for the smaller fraction, indicating a low dependence of this with respect to the oxygen. For the combustion of char the reaction order with respect to oxygen is 0.31, that is a low value in comparison with respect to the reaction order between 0.7 and 1 considered in the gasification of the carbon [25]. The experimental data shown in Fig. 4 shows the small dependence of the oxygen on the TG runs. On the other hand, it is possible that the simplification of the model, considering that the three combustion reactions follow the same kinetic law causes the correlation parameters to be somewhat different to those expected.

A study of the main by-products formed in the pyrolysis and combustion of used cotton fabrics, was carried out in a very recent paper [26]. More than 90 compounds, including carbon oxides, light hydrocarbons and PAHs, have been identified and quantified. In the gas phase some of the main components obtained were methane, ethene and benzene. The main semivolatile compounds detected were styrene, phenol, naphthalene, acenaphthylene and phenanthrene.

The evolution of the different fractions throughout the heating process can be observed in Figs. 7 and 8, that show the experimental and calculated mass fraction of volatiles v and conversion factors α at $5^\circ \text{C min}^{-1}$ in He:O_2 4:1. The kinetics parameters for reaction 2 show that there is a second order reaction with a low activation energy, and this could explain that the decomposition of the fraction C_2 occurs in a wide range of temperatures, as seen in the big separation between the curves of α_2 and α_4 (Fig. 8).

Fig. 7. Calculated conversion factor (α_i , α_{ij}) at $5^\circ \text{C min}^{-1}$ in He:O_2 4:1.

It must be emphasised that the parameters obtained must be considered as correlation ones, some of them with physical–chemical significance. There is a great interrelation between them, so other sets of parameters could be also valid for the correlation of the data with a very small increase of the objective function. In spite of this great interrelation of the parameters, it must be indicated that the objective function has been minimized reducing the great interrelation that exists between the pre-exponential factor, the activation energy and the reaction order.

The correlation of the three pyrolysis runs and six combustion runs have been done simultaneously, so 26 parameters were optimized for minimizing the objective function. No papers have been found in literature where pyrolysis and combustion runs were optimized simultaneously, so the correlation work presented in this paper can be considered as original. As a result, an acceptable set of parameters is obtained, that correlates the nine TG runs

Fig. 8. Calculated mass fraction of volatiles (v_{ij}) at $5^\circ \text{C min}^{-1}$ in He:O_2 4:1.

satisfactorily, as can be seen in Figs. 1–3 that show the conversion degrees versus temperature for a run, observing a logical variation in accordance with the parameters deduced.

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References

- [1] J.A. Caballero, R. Font, M.M. Esperanza, *J. Anal. Appl. Pyrol.* 47 (1998) 165.
- [2] P.K. Chatterjee, C.M. Conrad, *Text. Res. J.* 36 (1966) 487.
- [3] D. Dollimore, J.M. Hoath, *Thermochim. Acta* 45 (1981) 87.
- [4] M.J. Antal, G. Várhegyi, *Ind. Eng. Chem. Res.* 34 (1995) 703.
- [5] S. Völker, Th. Rieckmann, *J. Anal. Appl. Pyrol.* 62 (2002) 165.
- [6] A.A. Farooq, D. Price, G.J. Milnes, *Polym. Degrad. Stab.* 44 (1994) 323.
- [7] J.T. Wanna, J.E. Powell, *Thermochim. Acta* 226 (1993) 257.
- [8] R. Font, A.N. García, *J. Anal. Appl. Pyrol.* 35 (1995) 249.
- [9] M. Grønli, M.J. Antal, G. Várhegyi, *Ind. Eng. Chem. Res.* 38 (1999) 2238.
- [10] J.A. Conesa, R. Font, A. Marcilla, J.A. Caballero, *J. Anal. Appl. Pyrol.* 58–59 (2001) 619.
- [11] J.A. Caballero, R. Font, M.M. Esperanza, *J. Anal. Appl. Pyrol.* 47 (1998) 165.
- [12] J.A. Reyes, J.A. Conesa, A. Marcilla, *J. Anal. Appl. Pyrol.* 58–59 (2001) 747.
- [13] J.A. Conesa, R. Font, *Polym. Eng. Sci.* 41 (2001) 2137.
- [14] J.A. Conesa, R. Font, A. Fullana, J.A. Caballero, *Fuel* 77 (1998) 1469.
- [15] S. Vossoughi, Y.M. El-Shoubary, *Thermochim. Acta* 157 (1995) 37.
- [16] I. Martín-Gullón, M. Esperanza, R. Font, *J. Anal. Appl. Pyrol.* 58–59 (2001) 635.
- [17] R. Font, I. Martín-Gullón, M. Esperanza, A. Fullana, *J. Anal. Appl. Pyrol.* 58–59 (2001) 703.
- [18] I. Martín-Gullón, M.F. Gómez-Rico, A. Fullana, R. Font, *J. Anal. Appl. Pyrol.* 68–69 (2003) 645.
- [19] J.A. Conesa, J.A. Caballero, A. Marcilla, R. Font, *Thermochim. Acta* 254 (1995) 175.
- [20] J.A. Conesa, A. Marcilla, R. Font, J.A. Caballero, *J. Anal. Appl. Pyrol.* 36 (1996) 159.
- [21] M.J. Antal, G. Várhegyi, E. Jakab, *Ind. Eng. Chem. Res.* 37 (1998) 1267.
- [22] M.Z. Haji-Sulaiman, M.K. Aroua, *J. Inst. Energy* 70 (1997) 52.
- [23] E. Henrich, S. Bürkle, Z.I. Meza-Renken, S. Rumpel, *J. Anal. Appl. Pyrol.* 9 (1999) 133.
- [24] P.L. Walker, F. Rusinko, L.G. Austin, *Adv. Catal.* 9 (1959) 133.
- [25] Z. Du, A.F. Sarofim, J.P. Longwell, in: J. Lahay, P. Ehrburger (Eds.), *Fundamental Issues in Control of Carbon Gasification*, 1992, p. 91.
- [26] J. Moltó, J.A. Conesa, R. Font, I. Martín-Gullón, *Environ. Sci. Technol.* 39 (14) (2005) 5141.