Application of the distributed activation energy model to blends devolatilisation

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Abstract

In this study, an investigation was carried out into the thermal behaviour of coal, petcoke and their blend as a generic feedstock in combustion and IGCC plants for energy production. The samples were pyrolysed in a TG analyzer in nitrogen atmosphere (constant flow of 0.0335 m/s) at several heating rates with temperatures ranging from 300 to 1223 K. The distributed activation energy model was applied to study the effects of heating rates on the reactions of single solids. The results obtained were used in the calculation of curves mass loss vs. temperature at more realistic heating rates. The algorithm used to obtain the distribution of reactivities for single solids was successfully implemented to allow the prediction of blends performance.
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Keywords: Coal; Petcoke; Devolatilisation; Kinetics; Modeling

1. Introduction

The pyrolysis produces remarkable changes in chemical structure, surface morphology and porosity of the solid particle, which have an important effect on the char reactivity [1]. These changes are produced during devolatilisation of volatiles as a first step of pyrolysis itself but also combustion or gasification that can even accelerate ignition by increasing the temperature of the gas phase. Although much work has been conducted to study coal pyrolysis, extensive research on a definitive mechanism is still the subject of much discussion.

It is generally assumed that gasifiers or combustors operate at very high temperatures and the devolatilisation process will be completed instantaneously [2]. These conditions are very difficult to reproduce in conventional experimental systems, therefore, modeling is necessary to obtain parameters in more accessible conditions to know the particularities of the samples and lately extrapolate to real conditions. This way, effects of different heating rates in changes in the temperature in the particle and in the oven can be taken into account in the model.

Reactions of practical interest often involve a complex set of sequential and parallel unimolecular and bimolecular reactions that are often impossible to characterize at any significant level of detail. A kinetic analysis must capture the essence of the exceedingly complex reaction set in a tractable mathematical way [3]. Simple models have been described in the literature where it is assumed that the decomposing material is constituted by only one hypothetical chemical compound that reacts in a broad temperature interval [3]. However, other more realistic approximation to the decomposition kinetics of complex materials is the parallel reaction model. This model assumes that the distribution of reactivity caused by the reaction complexity can be represented by a set of independent, parallel reactions. The reactivity distribution of these reactions, described by a distribution of frequency factors and activation energies, can be solved mathematically. Specific mathematical forms appearing in the literature are the Gaussian, Weibull and Gamma distributions [3].

The distribution can also be a finite discrete distribution of arbitrary form. The key to the widespread usage of this last routine is its flexibility to fit almost any reactivity distribution and an efficient nested nonlinear-constrained linear regression routine first used by Burnham et al. [4]. Other examples of previous papers dealing with this subject are, among others, works of Miura [5], Maki et al. [6] and Arenillas et al. [7].

This work aims to find the characteristics of coal and petcoke pyrolysis process in order to obtain operative parameters. These parameters will be used to calculate their behaviour at real

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Nomenclature

$A(E)$	pre-exponential factor related to a specific activation energy (s^{-1})
A_i	pre-exponential factor (s^{-1})
DAEM	distributed activation energy model
E	activation energy (kJ/kg)
E_i	specific activation energy (kJ/kg)
$f_{i,0}$	fraction of M_0 which decomposes with a specific activation energy, dimensionless
m	mass of volatile matter (kg)
$m_0(E)$	initial mass of volatile matter with a specific activation energy (kg)
$M(T)$	mass of the sample (kg)
M_f	final mass of sample (kg)
$M_v(t)$	total mass of volatile matter (kg)
M_0	initial mass of the sample (kg)
R	ideal gas constant (kJ/mol K)
t	time (s)
T	temperature (K)
TGA	thermogravimetric analyzer
w	fraction of inert material, dimensionless
X	fraction of mass remaining

conditions as single components and to predict their behaviour once blended as a generic feedstock in plants for energy production.

2. Experimental

Three different materials have been used in this study, Puertollano coal, petcoke and a mixture of them (50:50 ratio with limestone in 2.46% weight) used as feedstock in a plant for energy production. Their ultimate and proximate analyses appear in Table 1. The samples were pyrolysed in a thermobalance CAHN TG-2151 that can work from ambient pressure to 100 bar depending on the final temperature. The reactant gas is introduced into the system through the bottom with a predefined composition and total flow. In this study all the tests were run at ambient pressure and a constant flow of nitrogen of 0.0335 m/s. The sensitivity of this apparatus is 1 μg. The sample is placed in a platinum basket forming a small fixed bed with different initial mass depending on the sample, 35 mg for coal, 110 mg for petcoke and 45 mg for the mixture. The particle size of coal ranges from 0.5 to 1.6 mm, for petcoke ranges from 0.25 to 0.5 mm and for feedstock has and average value of 0.05 mm. Sets of experiments at different heating rates of 5, 10 and 20 K/min were performed with every sample.

The fraction of mass remaining (X) was calculated according to Eq. (1), where M_0 is the initial sample weight, $M(t)$ is the sample weight at any time and M_f is the final weight (the weight stable after reaction).

$$X = \frac{M(t) - M_f}{M_0 - M_f} \tag{1}$$

3. Results and discussion

Usually, mathematical models to describe overall decomposition of complex solids consider independent parallel reactions. Coal is a very complex solid with a large volatile content which is mainly released during first steps of pyrolysis, gasification and combustion processes. It has been proven that the reaction rate in the devolatilisation step in gasification and combustion processes is very high due to very high temperatures in the reaction chamber. Therefore, it is fairly difficult to perform *in situ* measurements in order to find kinetic parameters under these severe conditions. However, these reactions can be studied at mild conditions to develop models which take into account the effect of different variables in the reaction. Afterwards, and taking into account this information, it is possible to predict the behaviour of the solids at real conditions.

To study this complex process on coal and petcoke, the distributed activation energy model (DAEM) to experiments in thermogravimetric analyzer (TGA) has been applied. This model assumes that a complex fuel is a mixture of components, each of which decomposes following a first-order reaction. The complex composition produces a wide variety of chemical groups and a continuous distribution of reactions with characteristic activation energy during pyrolysis [8].

Thus, the total mass, $M_v(t)$, of volatile matter is

$$M_v(t) = \int_0^\infty m(E, t)\,dE \tag{2}$$

Assuming that the material in the interval E to $E + dE$ of activation energy decomposes via a first-order reaction, with a pre-exponential factor $A(E)$

$$\frac{dm(E, t)}{dt} = -A(E)\,\exp\left(\frac{-E}{RT}\right) m(E, t) \tag{3}$$

so

$$m(E, t) = m_0(E)\,\exp\left[-A(E)\int_0^t \exp\left(\frac{-E}{RT}\right)dt\right] \tag{4}$$

Here, $m_0(E)$ is the initial mass of volatile material decomposing with an activation energy in the interval E to $E + dE$. In practice, the quantity $m(E,t)$ cannot be measured; only the total amounts, $M(t)$, or the total rates of decomposition are measured. Hence by integrating over all energies for a first-order reaction the expression becomes

$$\frac{M(t)}{M_0} = w + \sum_{\text{Reactions},\,i} f_{i,0}\,\exp\left[-A_i\int_0^t \exp\left(\frac{-E_i}{RT(t)}\right)dt\right] \tag{5}$$

where $M(t)$ is the mass of the sample, which contains a fraction w of inert material; M_0 is the initial value of M; $f_{i,0}$ is the fraction of M_0 which decomposes with an activation energy E_i and pre-exponential factor A_i. Using experimentally measured $M(t)$, the problem is to find $f_{i,0}$, A_i and E_i. There are several approximations to the DAEM for pyrolysis of coal [9], in this work the algorithm recently developed by Scott et al. [8] has been implemented in a Fortran subroutine to solve this equation. This model assumes increasing rate of mass loss at increasing temper-

Table 1
Proximate and ultimate analyses, and calorific value of the samples

Sample	Proximate analysis (wt%)				Ultimate analysis (wt%)				
	Moisture	Ash	V.M.	F.C.[a]	C	H	N	S	O[a]
Coal	4.2	39.3	23.8	36.9	45.2	3.1	1.0	0.9	49.8
Petcoke	0.4	0.4	10.6	89.0	87.7	3.7	1.6	5.7	1.3
Feedstock	0.9	23.9	17.8	58.3	64.5	3.3	1.2	3.3	27.7

All data, except moisture, are expressed in dry basis. V.M., volatile matter. F.C., fixed carbon.

[a] Calculated by difference.

atures with increasing heating rates which is a general case for coal pyrolysis. This model also needs enough experimental data to produce a proper description of the conversion–temperature dependency in order to generate the activation energy and pre-exponential factor distribution.

This algorithm was applied to the results of thermogravimetric experiments of the pyrolysis of the two different raw materials, coal and petcoke. To introduce the thermogravimetric experiments data into the model Eq. (1) has been used which takes into account the effect of inert material so, in this case, w is zero. Two experimental sets of data obtained at low heating rates (5 and 10 K/min) were used to calculate the distribution of activation energies and pre-exponential factors for every material. Subsequently three theoretical curves were generated at 5, 10 and 20 K/min and compared with experimental data in order to produce a robust test of how well the kinetics extracted by the algorithm reproduce the original data and extrapolate to different heating rates. In addition, one more theoretical curve was produced for a heating rate of 10,000 K/min close to the conditions of devolatilisation as a first step in gasification or combustion processes [10]. In this study the inversion algorithm evaluated E and A at 50 equally spaced intervals of conversion, corresponding to an unreacted fraction in the range 0.05–0.95. Therefore, the global reaction is mathematically described as composed by 50 reactions with different activation energies. We also evaluate the reactions at 100 equally spaced intervals of conversion finding no difference in results but in computing time. Mass fractions reacted at the very beginning of the reaction, mass fraction remaining more than 0.95, or at the end, mass fraction remaining less than 0.05, are not taken into account in this study since for all the samples studied the reaction is mainly placed between 0.9 and 0.1 fractions of mass remaining.
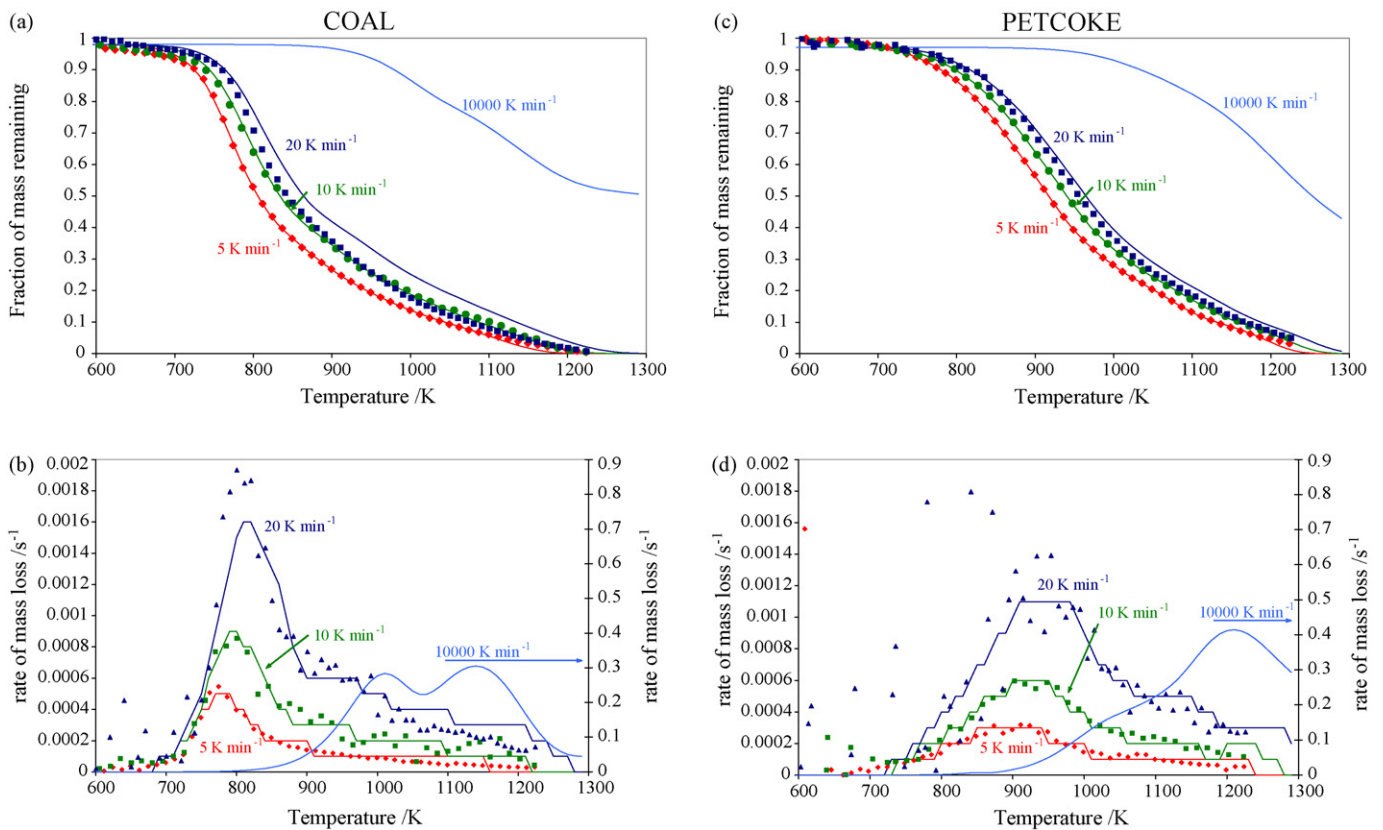

Fig. 1. Comparison of the progression of pyrolysis for the samples studied. The variables shown are fraction of mass remaining and devolatilisation rate for coal and petcoke. Experimental results are points. The lines show the curves generated using the parameters recovered by the algorithm using kinetic parameters deduced from the experimental results at 5 and 10 K min^{-1}.

Results of evolution of the remaining mass fraction and rate of mass loss vs. temperature for coal and petcoke are compiled in Fig. 1. For both samples, experimental and calculated results generated by the program are compared. It is observed that the experiments performed at heating rates of 5 and 10 K/min were successfully fitted by the model. These results were used for predicting the 20 and 10,000 K/min curves. The axes are kept constant to facilitate the comparison.

In both cases, for coal and petcoke, the algorithm produces exactly the data of fraction of mass loss vs. temperature obtained at heating rates of 5 and 10 K/min. These data were used to calculate the set of activation energies and pre-exponential fractions of each of the 50 possible reactions involved in the devolatilisation process. Regarding to the evolution of the fraction of

mass loss with temperature and heating rate, the model is able to describe properly the experimental data and, therefore, the shift in the rate of mass loss to higher temperatures as well as the general increase of rate of mass loss with the heating rate shown in the experiments. This behaviour can be explained on the basis of heat transfer and medium diffusion.

In the case of coal, when comparing experimental and predicted data obtained with a heating rate of 20 K/min, the program is able to predict the exact starting temperature for pyrolysis but for higher temperatures the model under-predicts the fraction of mass remaining. This fact can be due to the under-prediction of the maximum of rate of mass loss at around 800 K because for higher temperatures the model accurately predicts the experimental rate of conversion. Thus, the predicted starting
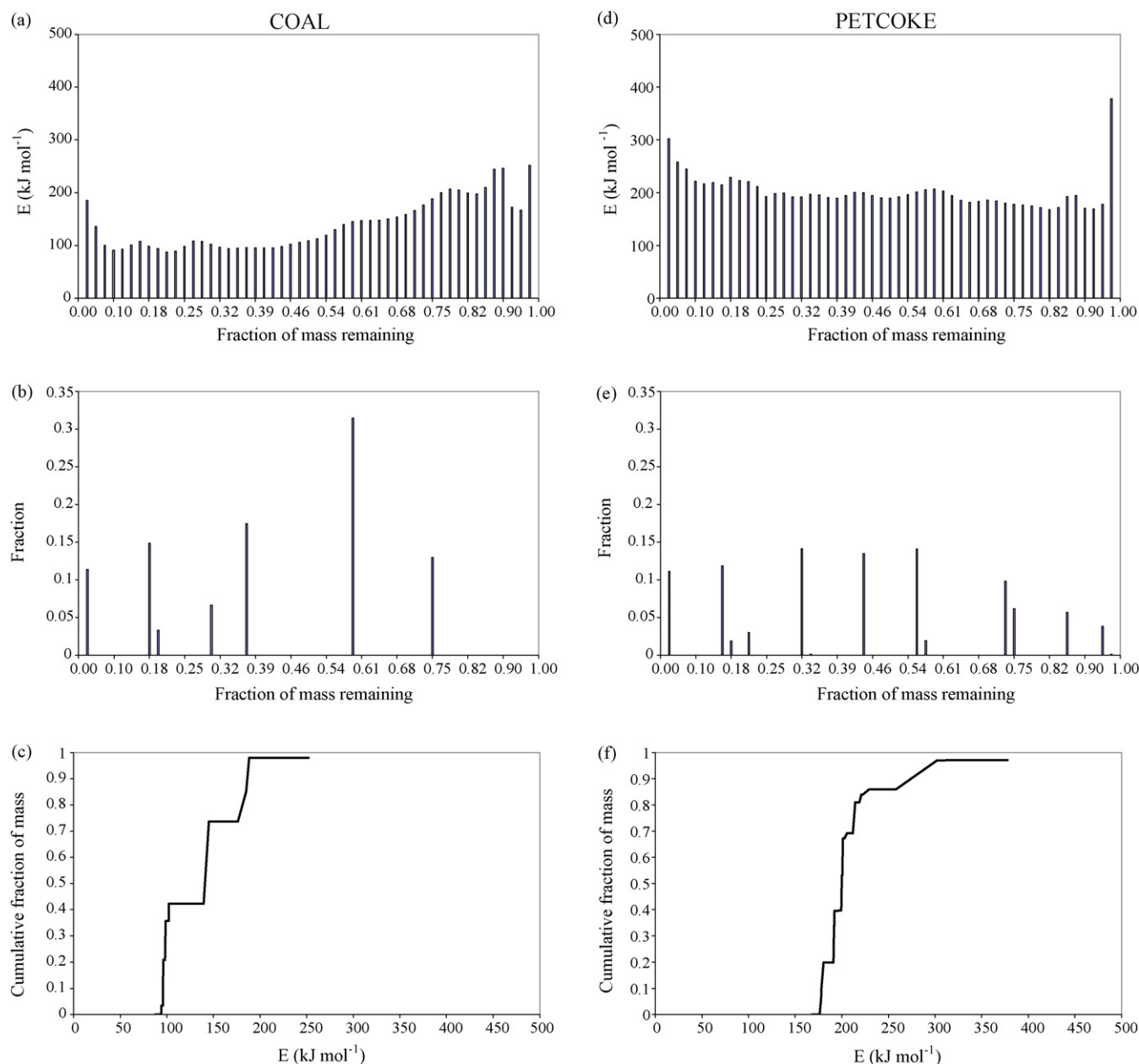

Fig. 2. Comparison of variables activation energy mass fraction allocated to each of the 50 possible reactions and cumulative mass fraction depending on the activation energy for the pyrolysis of coal and petcoke.

temperature of coal pyrolysis with a heating rate of 10,000 K/min should be close to the real one although the real process could be faster than the predicted.

In the case of petcoke, the peak of rate of mass loss is lower and wider than the one of coal. Therefore, petcoke reaction is slower and more gradual, i.e. there are more reactions involved in petcoke devolatilisation, than the one of coal. This sort of reaction seems to be easier to be treated by the model. Hence the comparison between experimental and predicted data for a heating rate of 20 K/min is better than the one of coal because the predicted evolution of the fraction of mass remaining with temperature is closer to the real one. Generally speaking, the model gives a very good approximation of the temperature range where the reaction will take place at the high heating rates of gasification or combustion processes.

The most relevant point of the distributed activation energies model is the capacity of analysing the devolatilisation process in a distribution of reactions with different activation energies. In Fig. 2 the distributions of activation energies for coal and petcoke are shown related to the fraction of sample allocated to each reaction and cumulative mass fraction depending on the activation energy. Regarding to the distribution of activation energies, coal and petcoke have opposite trends. For coal the highest activation energies, therefore, the less favoured reactions, occur at the very beginning of the process. However, following the reaction (see Fig. 2a), the activation energies decrease to reach a

minimum at a fraction of mass remaining of 0.2. On the other hand, for petcoke the activation energies increase slowly with reaction and the reactions related to smaller fractions of mass remaining are less favoured.

Comparing the fraction of mass allocated for every reaction for coal and petcoke, there are less relevant reactions for coal than petcoke and they are described by smaller activation energies (see Fig. 2b and d). In Fig. 2b, it is shown that more than 30% of the reaction takes place through the reaction described at a fraction of mass remaining of 0.6 while none of the reactions of petcoke have allocated fractions higher than 0.15. In addition, on one hand, the activation energies for coal are low compared to petcoke. The smallest activation energy is around 100 kJ/mol in coal and 175 kJ/mol in petcoke but, on the other hand, the range of activation energies is wider before reaching a relevant fraction of mass reacted, from 100 to 200 kJ/mol for coal and from 175 to 225 kJ/mol to reach 80% conversion for petcoke.

To sum up, the model describes two factors involved in accelerate or slow down a reaction, the amount of mass allocated to a reaction and its activation energy. In our study these two factors favour the devolatilisation of coal compared to petcoke due to lower activation energies and higher fractions of mass allocated to reactions.

In commercial gasification processes it is not unusual to feed mixtures of coal and other feedstock in order to increase the process sustainability. In this work, the algorithm proposed by
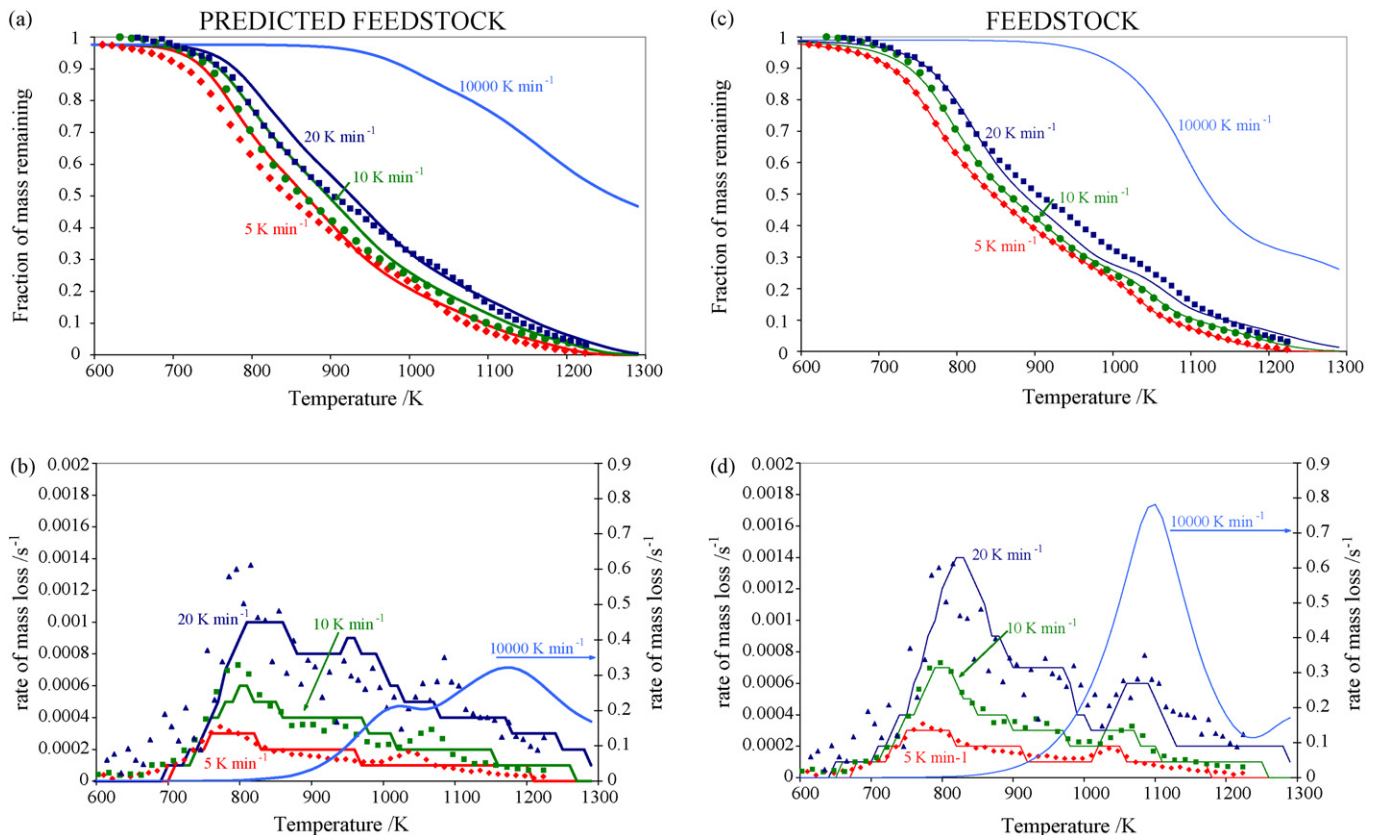

Fig. 3. Comparison of the progression of pyrolysis for the samples studied. The variables shown are fraction of mass remaining and devolatilisation rate for predicted feedstock and real feedstock. Experimental results are points. The lines show the curves generated using the parameters recovered by the algorithm using kinetic parameters deduced from the experimental results at 5 and 10 K min^{-1}.

Scott et al. [8] has been improved in order to deal with feed mixtures comprised of several components. A coefficient that takes into account the fraction of mass allocated for every reaction for every component has been introduced in order to calculate the evolution of total mass remaining with temperature. Thus, Eq. (5) becomes:

$$X_m = \sum_{ai} a f_{a,i,0} \exp\left[-A_{a,i} \int_0^t \exp\left(\frac{-E_{a,i}}{RT(t)} \right) dt \right]$$
$$+ \sum_i b f_{b,i,0} \exp\left[-A_{b,i} \int_0^t \exp\left(\frac{-E_{b,i}}{RT(t)} \right) dt \right] \quad (6)$$

where a and b are the fractions of components a and b in the feed mixture. To use the model with a mixture 50/50 of coal and petcoke the coefficients a and b take a value of 0.5.

In Fig. 3 there is a comparison of the predicted and the experimental data for the devolatilisation of a gasifier feedstock. The initial temperature predicted by the model is higher than the experimental one so the real feedstock is more reactive. However, at higher temperatures the predicted reaction seems to accelerate and both finish at a very similar temperature. Regarding to the evolution with temperature of mass loss rate compared with the experimental results (see Fig. 3b and d), the model under-predicts the first peak of reaction rate and make it wider keeping higher rates for higher temperatures. Therefore, the model produces a conservative prediction of the process for high heating rates around 10,000 K/min; although with higher starting temperatures, the evolution of mass remaining, both calculated and experimental converge at high temperatures. Since pyrolyisis of blends seem to have a clear additive behaviour of properties of both components [11], a possible influence of the particle size could explain the differences found. The particle size of the feedstock is 0.05 mm in average one order of magnitude lower than the one of coal or petcoke alone which are around 1 mm and 0.35 mm, respectively. Although it has been reported in the literature that there are not significant effects of transport expected on kinetics for fine particles lower than 1.5 mm, at the same time, the conversion is dependent on the outcome of competition between mass transfer and secondary reactions, so there is less probability of reaction between the volatiles generated for smaller particles [10].

In addition, in a thorough analysis of the experimental data, a perturbation appears around 1000 and 1100 K for all the heating rates that does not appear in the prediction, neither in coal or petcoke curves (see Fig. 3c). These perturbations shift to higher temperatures with increasing heating rates.

In Fig. 4 there is a comparison between the evolution of the mass fraction remaining vs. temperature for coal, petcoke and feedstock, both predicted and experimental values. Since the main points of the comparison appear for the 3 heating rates studied experimentally, only the case of the 10 K/min heating rate is shown. When generating this curve from the implemented algorithm, the result is an average of data from coal and petcoke because the mixture is 50/50 (see Fig. 4a). Looking at the evolution of mass loss rate this averaging produces a similar initial peak to the one of coal but lower rates and slightly shifted to
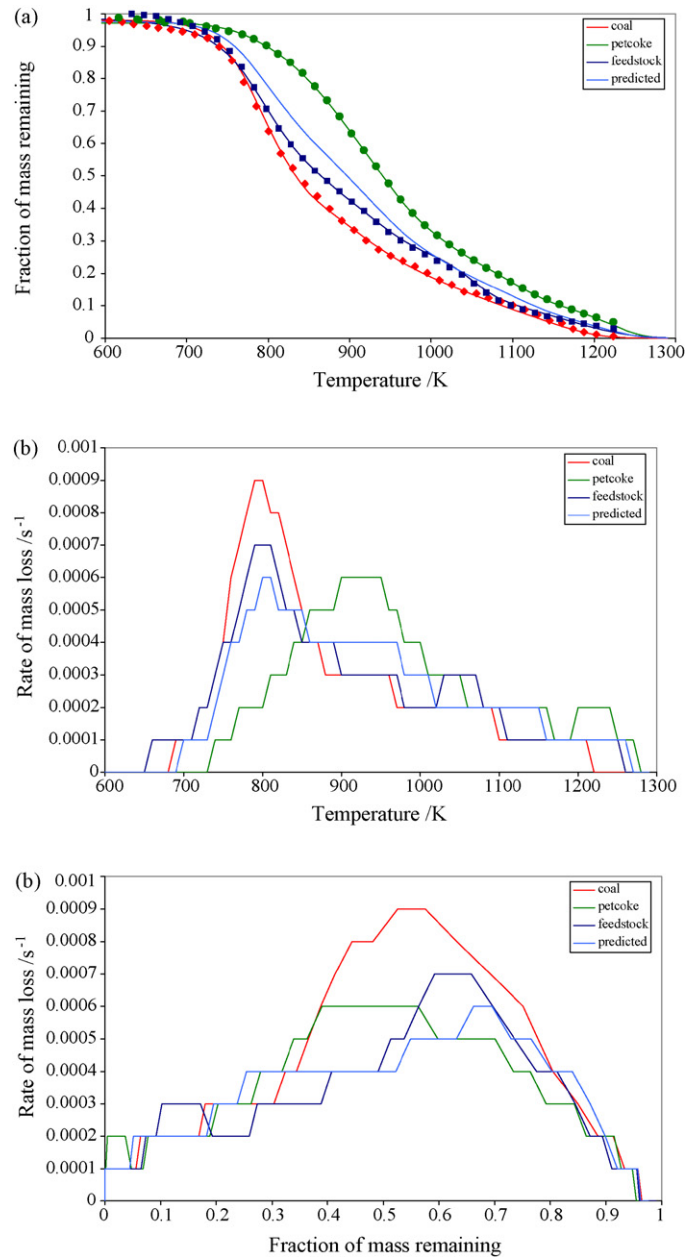

Fig. 4. Comparison of the progression of pyrolysis for the samples studied with a heating rate of $10\,\mathrm{K\,min^{-1}}$. The variables shown are fraction of mass remaining and devolatilisation rate for coal, petcoke, predicted feedstock and real feedstock. Experimental results are points. The lines show the curves generated using the parameters recovered by the algorithm using kinetic parameters deduced from the experimental results at 5 and $10\,\mathrm{K\,min^{-1}}$.

higher temperatures at the same time that the reaction rate widen to higher temperatures to assimilate petcoke influence (Fig. 5).

Regarding to the relationship between the experimental data for the real feedstock and the experimental data of coal and petcoke, feedstock seems to be more reactive than any of the components at the lowest temperatures studied. At higher temperatures, the pyrolysis of feedstock slow down related to the one of coal and finishes at an average temperature between coal and petcoke. In this case, like the one predicted, this first peak is lower than the one of coal but, unless the predicted one, it
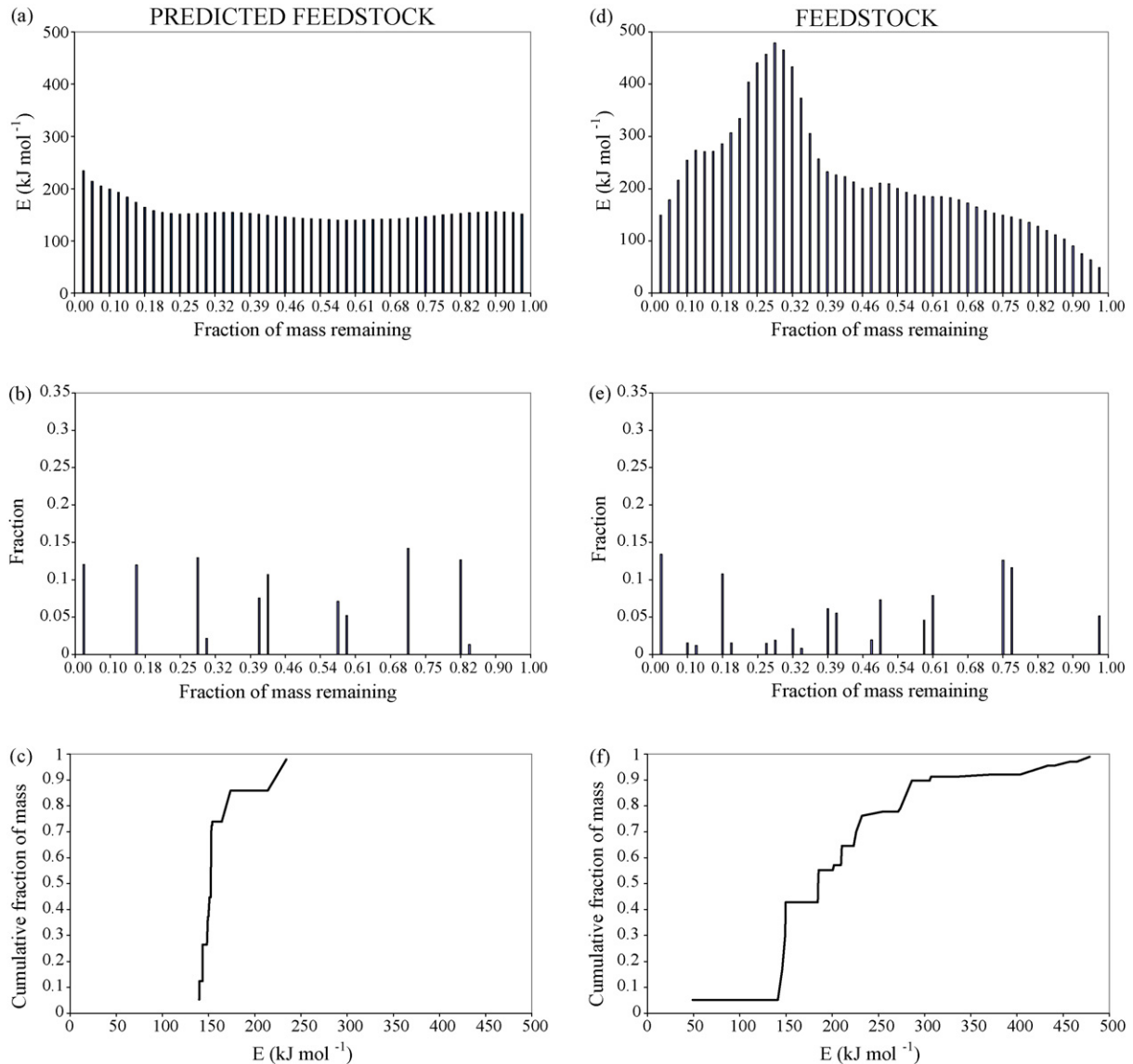
Fig. 5. Comparison of variables activation energy, mass fraction allocated to each of the 50 possible reactions and cumulative mass fraction depending on the activation energy for the pyrolysis of predicted feedstock and real feedstock.

is almost at the same temperature in both the mixture and the coal alone. This peak, as the predicted, is longer than the one of coal but not so clearly to finish at a similar temperature to the predicted.

In the curve rate of mass loss vs. temperature produced by the real feedstock there is an extra peak in reaction rate between 1000 and 1100 K compared with the other curves (see Fig. 4b). This peak is related to the perturbation pointed out above. The most possible explanation is the reaction of the limestone presented in the real mixture hence from literature [12] its calcination reaction under inert atmosphere takes place at temperatures around 1000 K with low CO_2 concentration. Calcination of limestone is:

$$[CaCO_3]_s \Leftrightarrow [CaO]_s + [CO_2]_g$$

so, there is a decrease in weight added in the reaction to the loss of weight due to the devolatilisation. Initially the pyrolysis reaction

could be thought not to be sensible to the calcination of limestone because it is a 2.5% in weight of the sample, nevertheless its calcination takes place in a limited range of temperatures than the pyrolysis and when only remains 0.2 of the mixture coal–petcoke (see Fig. 4c) (now the unreacted limestone is around 15% of the sample), which confirms that the perturbation is due to the calcination of limestone.

However, the most significant difference between predicted and experimental behaviour of the feedstock are exposed when comparing the activation energy distributions. On one hand, the treatment of the components in the mixture to obtain the theoretical behaviour of the sample, homogenise the activation energies along the global devolatilisation reaction. On the other hand, the distribution of activation energies for the real feedstock devolatilisation show low initial activation energies related to a fast start. At a fraction of mass remaining around 0.3 appears a high peak of activation energy to decrease immediately related

to the calcination of limestone pointed out above. It is a short perturbation because the fraction of mass related to this energy is small. Finally, there are also differences between the predicted and real ranges of activation energies. While the predicted ones are in a narrow range from 140 to 175 kJ/mol to reach a mass fraction of 0.8, in the real case, it is a wide range from 50 to 250 kJ/mol to reach the same mass fraction.

The devolatilisation of a predicted (from its components assuming no interaction between them) and experimental mixture has been analysed with a distribution of activation energies model. From the comparison of the results, it can be concluded that exists an influence of the particle size even for sizes smaller than 0.25 that makes it more reactive at lower temperatures, but, for higher temperatures, the reaction slows down probably due to heat transmission difficulties, in the sample bed because of the different thermodynamic and heat transfer properties of coal and petcoke. It has been also proven that the initially neglected influence of limestone calcination can produce perturbances when compared to a very different reaction as coal–petcoke devolatilisation.

The distributed activation energy model can be used to produce a very good approximation to the mixture behaviour from its main components but there are some deviations from the ideal behaviour that are not implemented yet in the model.

4. Conclusions

A new algorithm of DAEM developed by Scott et al. has been applied to study coal and petcoke devolatilisation. By fitting two sets of data obtained in TGA with different heating rates the main parameters are calculated and will be used to calculate a new set of data in a different heating rate.

The comparison of experimental and calculated data allows the use of this model to generate good approximations of the temperature ranges where the reaction will take place at the high heating rates in gasification or combustion processes. The model describes as well the influence of the activation energies and fraction of mass allocated to every reaction. Comparing the results obtained for theses variables for coal (faster reaction) to petcoke (slower reaction), the devolatilisation of coal is favoured by lower activation energies and higher fractions of mass allocated to these reactions.

In addition, the model was implemented to predict the behaviour of coal and petcoke blends, generic feedstock in energy generation plants. As a result of the comparison of predictions and experimental data, the DAEM can be used to produce a very good approximation to the mixture behaviour from its main components, but, since trace components are not taken into account, there are some deviations from the ideal behaviour that should be upgraded.

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