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Application of the Distributed Activation Energy Model to Biomass and Biomass Constituents Devolatilization

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In this study, an investigation about the thermal behavior of four different woods was carried out. The distributed activation energy model was applied to study the effect of heating rate on the reaction of single solids. Results obtained were used in the curve prediction of fraction of mass remaining and rate of mass loss vs. temperature at more realistic heating rates. The possible calculation of biomass samples behavior in pyrolysis conditions as the summation of their constituents, lignin, cellulose, and hemi-cellulose is also explored. All the samples show a weak interaction between the constituents which produce slight differences between experimental and calculated behavior. However, differences between experimental and calculated data lower than 2% offer a robust test of the applicability of the model on kinetic studies of a wide range of biomass samples, heating rates, data input format and equipment layout. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2700–2715, 2009
Keywords: biomass, cellulose, devolatilization, kinetics, DAEM

Introduction

Sustainable heat and power generation from biomass are at the centre of scientific and industrial interest due to the increasing awareness about the continuous diminution in the availability of fossil fuels and the higher sensibility towards environmental preservation.[1] In the context of climate change a lot of solutions have been proposed to reduce pollutant emissions in power generation as, for example, the use of biomass combustion, gasification or pyrolysis to produce heat, electricity or even biofuels. Within these three thermochemical processes it is fairly interesting to point out that pyrolysis is the less pollutant since COx, SOx, and NOx production is reduced compared to combustion and gasification. Many kinds of biomass species have been subjected to pyrolysis conditions to produce fuels, solvents, chemicals, and others.[2] This use is favored by the possibility of using residual biomass from forests maintenance or wood companies because of the quality of their residues. In addition, the study of biomass pyrolysis is also favored since it is the first step of biomass conversion processes such as gasification, liquefaction, carbonization, and combustion.[3]

It is well-known that biomass referred to plant matter consists mainly of three major components (cellulose, hemicellulose, and lignin) together with the trace amount of extractives and minerals. Normally, cellulose, hemicellulose, and lignin cover 40–60, 20–40, and 10–25 wt % of biomass materials on dry basis, respectively.[4] Previous studies indicated that it is important to distinguish the behavior of the three components for a better understanding of the biomass pyrolysis process.[4] At low heating rates (<100°C/min), biomass materials decompose in well-described stages of moisture evolution, hemicellulose decomposition and cellulose decomposition, while lignin is decomposed very slowly and

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Table 1. Proximate and Ultimate Analyses and Calorific Value of the Samples

Sample	Proximate Analysis (wt %) Moisture	Ash	VM	FC[a]	Ultimate Analysis (wt %) C	H	N	S	O[a]
Cellulose					65.02	5.78	0.19	0	29.01
Lignin					42.47	6.03	0.03	0	51.47
Hemicellulose					40.64	5.91	0.05	0	53.40
Pinus sylvestris 1	6.21	0.39	78.52	14.88	48.28	6.34	0.12	0	45.26
Pinus sylvestris 2	6.36	0.35	78.76	14.53	48.29	6.28	0.12	0	45.31
Pinus halepensis	8.96	1.72	73.82	15.5	46.05	6.08	0.12	0	47.75
Woods blend	9.43	0.94	73.5	16.13	46.47	6.17	0.12	0	47.24

All data, except moisture, are expressed in dry basis.
VM, volatile matter; FC, fixed carbon.
[a]Calculated by difference.

at minor level.[5] Moreover, it has been observed that there is no significant interaction among the three components in biomass pyrolysis.[4]

Flexibility in the supply of biomass to the energy conversion facility, in terms of seasonal availability, is considered as one of the keys to guarantee their continuous operation and the yield investments.[6] Therefore, to find a reliable kinetic model based on simply technical data analysis for different biomass origin is very important. Moreover, this model can help optimize pyrolysis performance of the different biomass components (cellulose, hemicellulose, and lignin), which can play an important role not only to scale up this process, but also in future integrated biomass systems such as biorefineries.

There are numerous works devoted to study the kinetics of different biomass pyrolysis as one-component mechanisms of primary pyrolysis but a more general approach to allow copyrolysis of biomass is to study the effect of the three different components in the biomass pyrolysis kinetics.[1,2] In this way, numerous works have also been devoted to use mechanisms comprised of several reactions, generally three reactions coinciding with hemicellulose, cellulose, and lignin. These mechanisms are usually parallel reactions, although consecutive reactions can also be applied[7] due to significant reaction time overlap, all of them acting as if there were no interactions.

Last review published on biomass pyrolysis to our knowledge[1] already introduces the distributed activation energy models (DAEM), as models always proposed starting from treatments already used for coal. This approach avoids the low values of activation energies which result when a single-step reaction is applied to fit a temperature dependence that arises from the occurrence of different temperature intervals.[8] Several approaches have been used, all combining the activity of both primary and secondary reactions in the estimated parameters using specific mathematical forms to describe the frequency factors and activation energies distributions like Gaussian, Weibull, and Gamma distributions.[9] For instance, Becidan et al.[10] used a simple DAEM with the distribution of activation energy approached by a Gaussian distribution to describe the pyrolysis behavior of wastes from breweries, industrial coffee roasting and fibreboard furniture.

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. Miura and Maki[11–13] also developed a model to obtain the distribution curve of activation energies and activation energy dependent frequency factors from three sets of data obtained under different heating profiles and applied it to 19 different coals to study the influence of coal rank on the model parameters. This model was applied by other authors to analyse kinetics pyrolysis of coal[14] and biomass samples like rice, rice straw, and corncob[3] or sawdust and biomass constituents.[3,15] With a different approach of the model Cai et al.[16,17] used the DAEM describing the global reaction following a distribution of reactions of *n*th-order. Finally, Burnham et al.[18]used an efficient nested nonlinear-constrained linear regression routine to develop a model based in only two sets of data at different heating rates.

This work aims to find the characteristics of wood pyrolysis process from four different samples to obtain operative parameters. Their components hemicellulose, cellulose, and lignin are also studied. These parameters will be used to calculate wood behavior at real conditions as single feedstocks and from its contituents as a generic feedstock in plants for energy production.

Experimental

Four different wood samples and samples of lignin (Organosolve 37017 Sigma-Aldrich), cellulose (cellulose fibrous, long C6663 Sigma-Aldrich) and xylose (Xylan from breech wood, xylose residues >90% 0502 Sigma-Aldrich) as hemicellulose model compound have been used in this study. The wood samples were obtained from different Mediterranean forest areas and consisted of softwood from two different pine species: Scots pine (*Pinus sylvestris*) and Aleppo Pine (*Pinus halepensis*). The samples were classified according to their origin in four categories: *Pinus sylvestris* 1, *Pinus sylvestris* 2, *Pinus halepensis* and a mixture of the three of them designated Woods blend. Their ultimate and proximate analyses are shown in Table 1.

The samples were pyrolysed in a thermobalance SETARAM Setsys Evolution. The inert 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 a constant flow of nitrogen of 8.33×10^{-5} m^3N/s in a reactor with 20 mm of internal diameter to produce a normal surface flow rate of 2.65×10^{-3} m/s. The sensitivity of this apparatus is 1×10^{-6} kg. The sample was placed in a platinum basket forming a small fixed bed with initial mass of 6 mg approximately for biomass, lignin, cellulose, and hemicellulose. The particle size of the samples was in all cases lower than 0.250 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 and $M(t)$ is the sample weight at any time.

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

Results and Discussion

Sample pyrolysis comparison

Wood is mainly comprised of cellulose, hemicellulose, and lignin. Cellulose is only composed of anhydrous glucose. Hemicellulose is a bunch of xylose, mannose, galactose, rhamnose, and arabinose ordered by the usual percentage present in biomass. While cellulose and hemicellulose are composed of sugar monomers, lignin from biomass is composed of three different monolignol monomers methoxylated to different degrees.

Figure 1 shows the behavior under pyrolysis conditions of four different wood samples and their main constituents (cellulose, lignin, and xylose as hemicellulose). The results obtained at three different heating rates 5, 10, and 20 K/min are also compiled. It is observed that cellulose, lignin, and hemicellulose present a different behavior. Cellulose starts to decompose at higher temperatures, around 600 K, with a very steep decrease of fraction of mass remaining to a high extent of around 4%. Lignin and hemicellulose start to decompose at the same temperature, around 450 K, but with a different behavior, while lignin decomposes slowly mainly in a range of 250° (450–700 K) and to a high final weight (∼40%), hemicellulose decomposes only in 150°, until 600 K to a final weight of ∼20% of the initial weight. The different behavior of lignin could be due to a more heterogeneous composition than the one of cellulose or hemicellulose that are composed by anhydrous glucose and xylose respectively.

Regarding to the four biomass samples, all of them show a very similar behavior in pyrolysis. It is observed that for the different heating rates, the fraction of mass remaining of all samples is very close. Wood decomposition takes place between 450 K and 650 K with a slight shift to higher temperatures with higher heating rates. All samples also reach a similar final weight between 15 and 18% of the initial one. They produce three steps, initially wood decomposition takes place like the one of lignin, at 550 K shows a steep decrease like hemicellulose and, at 600 K there is a second decrease like in the case of cellulose. Comparing the results of wood pyrolysis with pyrolysis of their constituents, biomass pyrolysis starts with lignin pyrolysis, secondly wood reaches temperature for hemicellulose to pyrolyse and lately it is the cellulose the one decomposing with a fast decrease of mass remaining. Finally, the remaining part of the lignin present in wood, which was reacting throughout the devolatilization process, undergoes its pyrolysis.

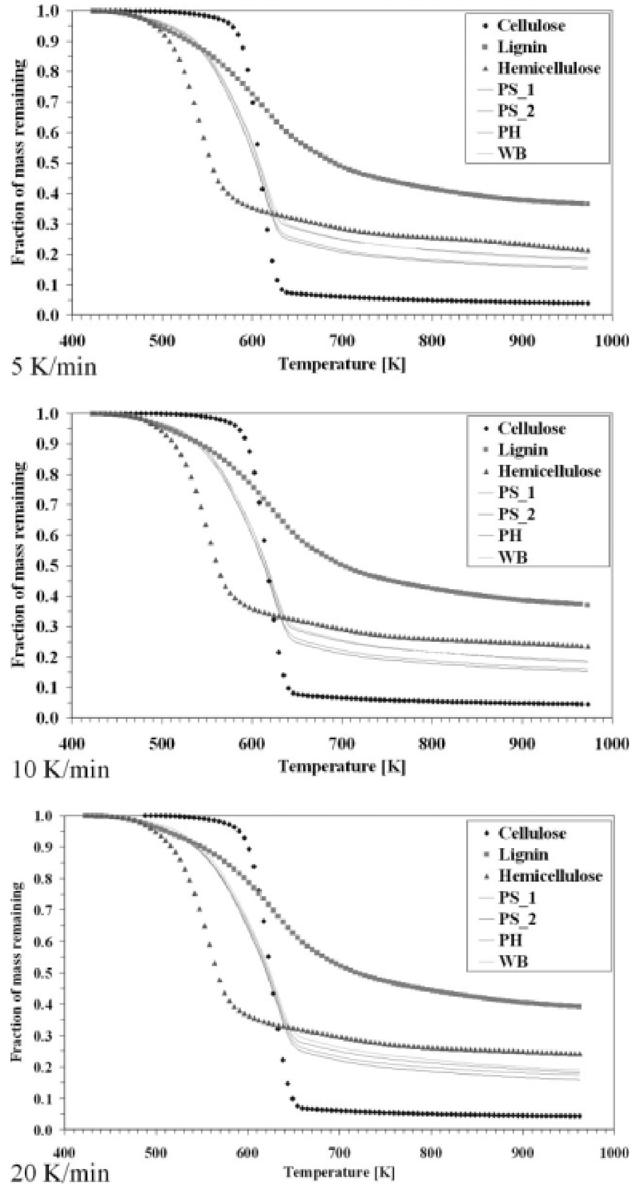

Figure 1. Fraction of mass remaining vs. temperature for three different heating rates.

Samples: PS_1 is *Pinus sylvestris* 1, PS_2 is *Pinus sylvestris* 2, PH is *Pinus halepensis* and WB is woods blend.

DAEM application

Usually, mathematical models to describe overall decomposition of complex solids consider independent parallel reactions. Wood is a complex solid with a large volatile content which is mainly released during first steps of pyrolysis, flash pyrolysis, carbonization or gasification. Products of these processes are obtained in three fractions, char, biooil, and gas which proportions depend on the process conditions. Parameters like temperature or residence time influence the products through the kinetics of the reaction, therefore a thorough knowledge of the kinetics is a key factor to predict product fractions. To study this complex process on wood, the DAEM has been applied to the experimental results found in the TGA. This model assumes that a complex fuel as wood is a mixture of components, each of which decomposes following a first-order reaction. The complex

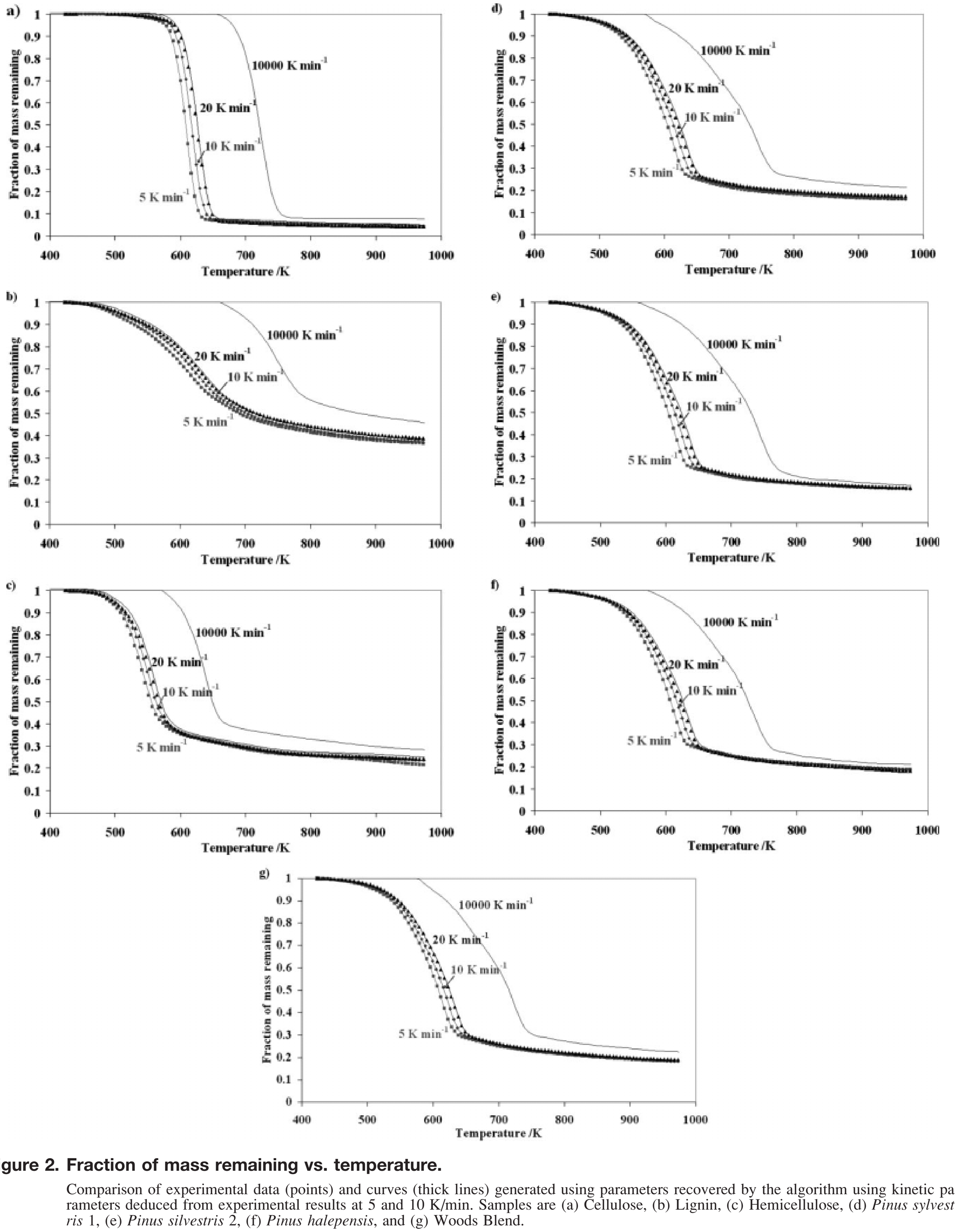

Figure 2. Fraction of mass remaining vs. temperature.

Comparison of experimental data (points) and curves (thick lines) generated using parameters recovered by the algorithm using kinetic parameters deduced from experimental results at 5 and 10 K/min. Samples are (a) Cellulose, (b) Lignin, (c) Hemicellulose, (d) *Pinus sylvestris* 1, (e) *Pinus silvestris* 2, (f) *Pinus halepensis*, and (g) Woods Blend.

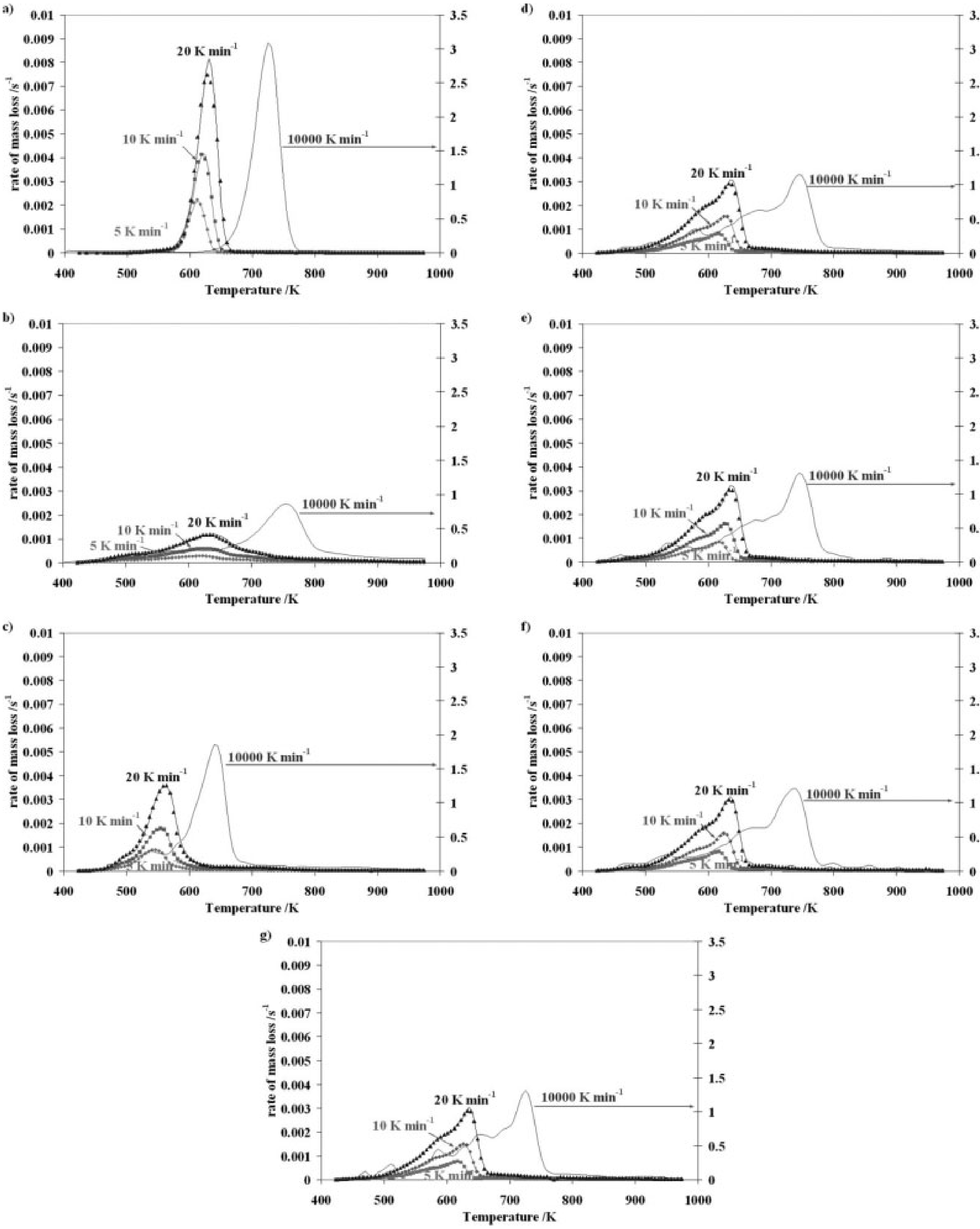

Figure 3. Rate of mass loss vs. temperature.

Comparison of experimental data (points) and curves (thick lines) generated using the parameters recovered by the algorithm using kinetic parameters deduced from the experimental results at 5 and 10 K/min. Samples are (a) Cellulose, (b) Lignin, (c) Hemicellulose, (d) *Pinus sylvestris* 1, (e) *Pinus sylvestris* 2, (f) *Pinus halepensis*, and (g) Woods Blend.

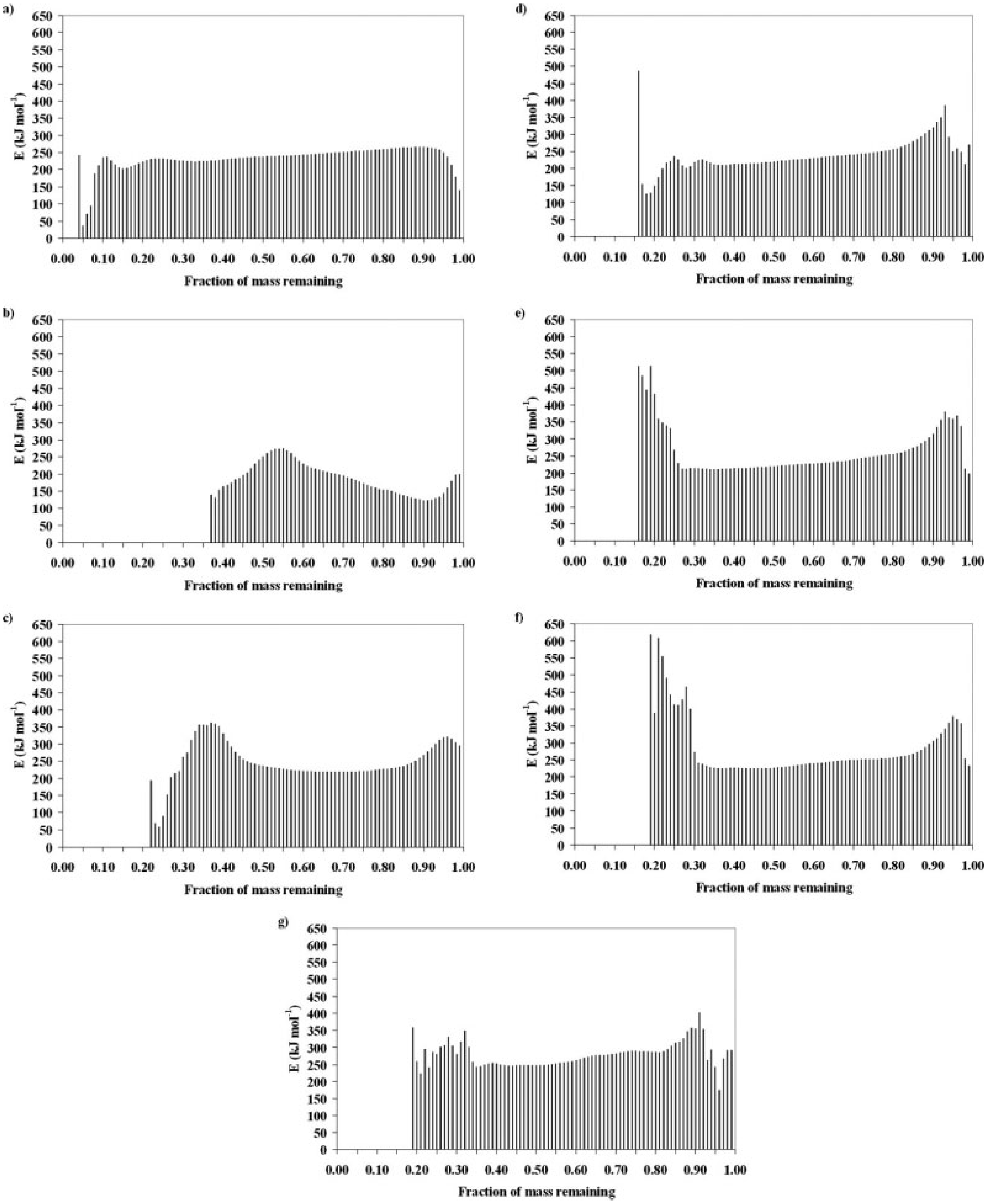

Figure 4. Activation energy vs. fraction of mass remaining calculated from the experimental results at 5 and 10 K/min.

Samples are (a) Cellulose, (b) Lignin, (c) Hemicellulose, (d) *Pinus sylvestris* 1, (e) *Pinus sylvestris* 2, (f) *Pinus halepensis*, and (g) Woods Blend.

composition produces a wide variety of chemical groups and a continuous distribution of reactions during pyrolysis with characteristic activation energy.[19]

There are several approximations to the DAEM for pyrolysis of coal.[20] In this work the algorithm recently developed by Scott et al.[19] has been implemented in a Fortran

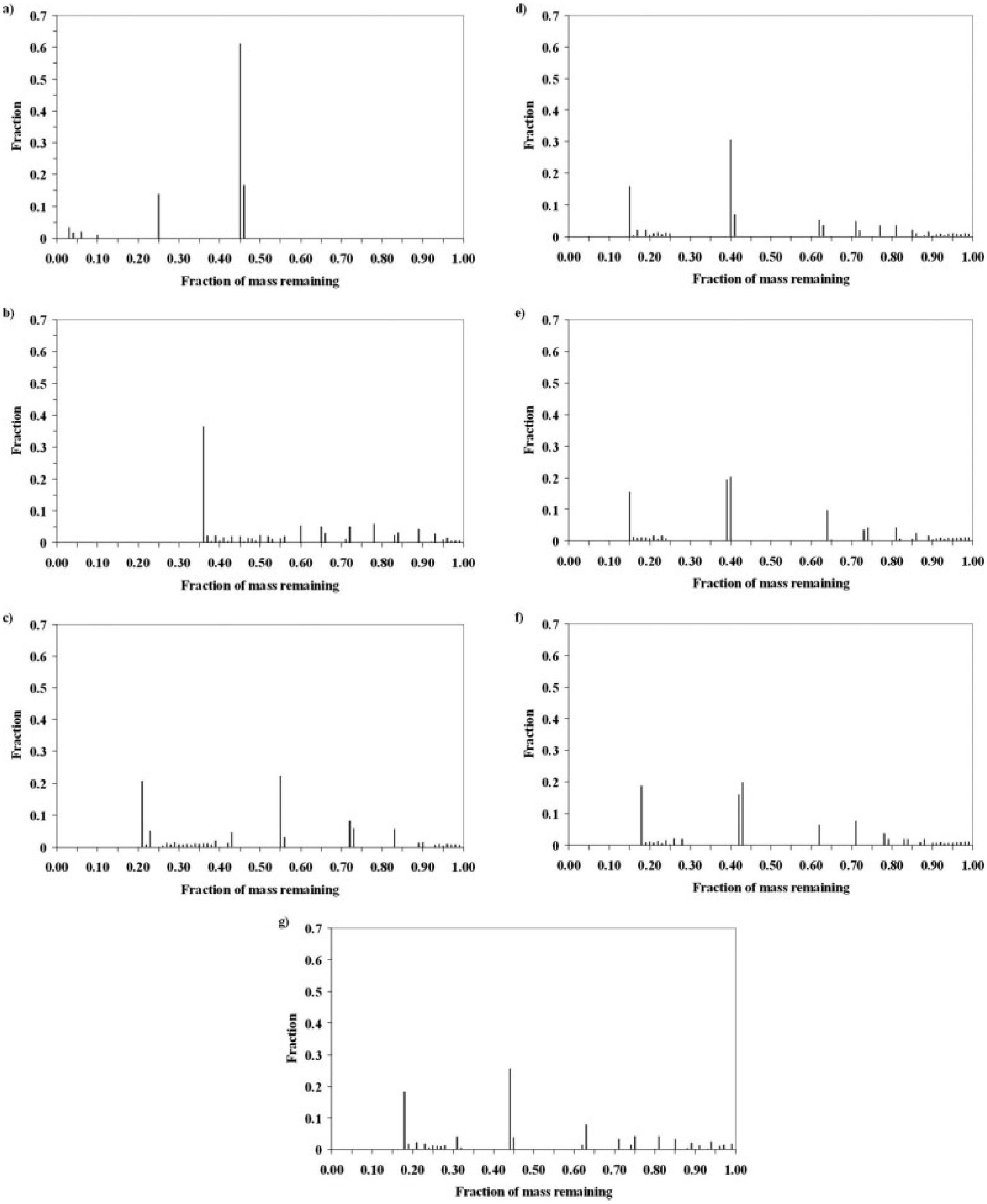

Figure 5. Fraction of sample vs. fraction of mass remaining calculated from the experimental results at 5 and 10 K/min.

Samples are (a) Cellulose, (b) Lignin, (c) Hemicellulose, (d) *Pinus sylvestris* 1, (e) *Pinus sylvestris* 2, (f) *Pinus halepensis*, and (g) Woods Blend.

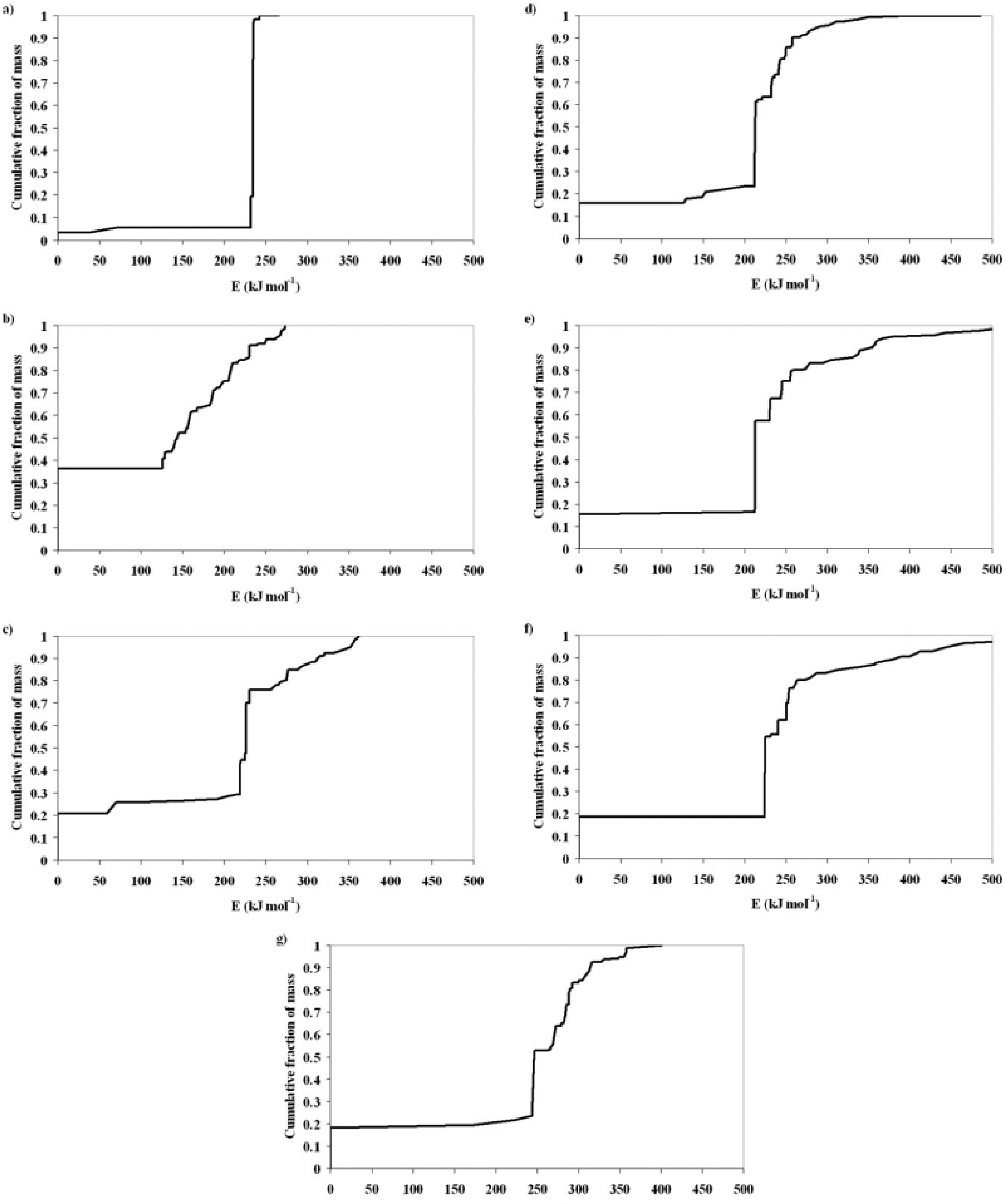

Figure 6. Cumulative fraction of mass vs. activation energy calculated from the experimental results at 5 and 10 K/min.

Samples are (a) Cellulose, (b) Lignin, (c) Hemicellulose, (d) *Pinus sylvestris* 1, (e) *Pinus sylvestris* 2, (f) *Pinus halepensis*, and (g) Woods Blend.

subroutine to solve this model with equations described elsewhere[21] adapted to take into account the inert part of the samples. This algorithm was developed to solve the problem of determining the kinetics of reactions for a material decomposing subject to many, parallel first-order reactions described by the following equation:

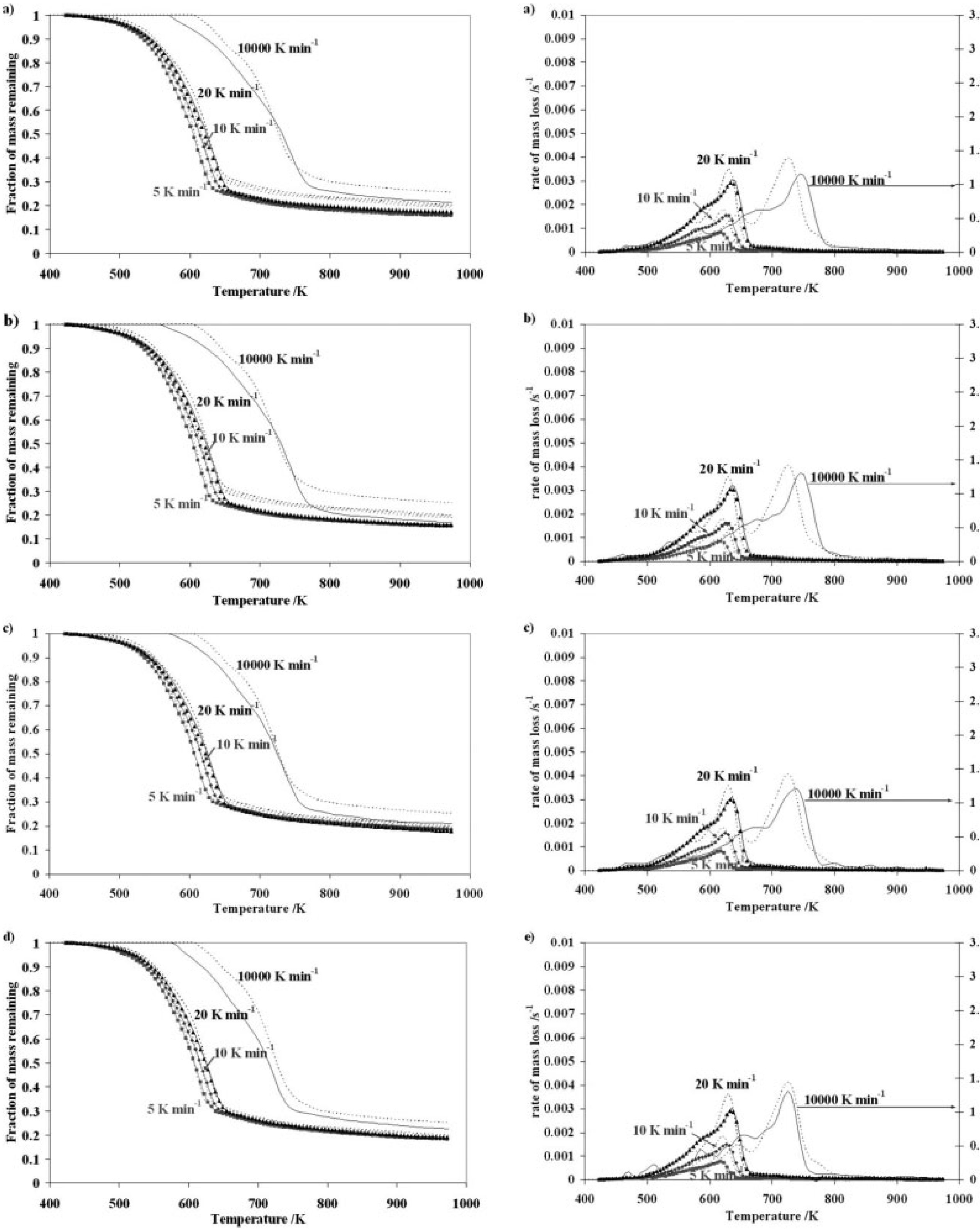

Figure 7. Comparison of the progression of experimental (points) fraction of mass remaining and rate of mass loss with curves calculated from data of the samples (thick lines) and from data of the constituents (dashed lines).

Samples are (a) *Pinus sylvestris* 1, (b) *Pinus sylvestris* 2, (c) *Pinus halepensis*, and (d) Woods Blend.

$$\frac{M(t)}{M} = w + \sum_i f_{i,0} \exp\left[-A_i \int_0^t \exp\left(\frac{-E_i}{RT(t)}\right) dt\right] \quad (2)$$

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 a pre-exponential factor A_i. Using experimentally measurements $M(t)$ at two different heating rates, the problem is to find $f_{i,0}$, A_i and E_i. This algorithm was applied to the results of thermogravimetric experiments of the pyrolysis of the four different kinds of wood, cellulose, lignin, and hemicellulose. To introduce the thermogravimetric experiments data into the model, Eq. 1 has been used. 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 to produce a robust test of how well the kinetics extracted by the algorithm reproduces the original data and extrapolate to different heating rates. For this last purpose, one more theoretical curve was produced for a heating rate of 10,000 K/min close to the conditions of flash pyrolysis processes. This application has been previously tested[19] theoretically with model curves generated at different heating rates, 20, 40, and 10,000 K/min and different number of parallel reactions. In this study the inversion algorithm evaluated E_i and A_i at 100 equally spaced intervals of conversion, corresponding to an unreacted fraction in the range 0.99–0.01.

Results of evolution of the remaining mass fraction and rate of mass loss vs. temperature for seven samples are compiled in Figures 2 and 3. For all 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.

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 behavior can be explained on the basis of heat transfer and medium diffusion. The perfect fit of the pyrolysis path is not only carried out depending on the temperature, but the model also produces a perfect fit with the inert fraction of mass remaining for all the samples, for homogeneous constituents cellulose, lignin, and hemicellulose and for heterogeneous wood samples in less than 5% error.

In the case of cellulose, when comparing experimental and predicted data there is a loss of accuracy for conversion higher than 0.96. This fact can be due to the sharp change in the slope of the curve for conversions above 0.96, that is, for small conversions the reaction turns from a very slow reaction into a very fast one. However, in spite of this inaccuracy, the fitting achieved by the model, not only for data obtained at 5 K/min and 10 K/min, but also for data obtained at 20 K/min is extremely good from this point to the end of the devolatilization, Figure 2 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, combustion or flash pyrolysis processes.

Table 2. Relations of Cellulose, Lignin, and Hemicellulose in 100% Analyzed by CIEMAT

Sample	Cellulose	Lignin	Hemicellulose
Pinus sylvestris 1	0.43	0.34	0.23
Pinus sylvestris 2	0.44	0.33	0.23
Pinus halepensis	0.44	0.34	0.22
Woods blend	0.45	0.34	0.21

In Figure 3 the results obtained by the model for rate of mass loss vs. temperature compared to experimental results are compiled. The axes are kept constant to facilitate the comparison. In the seven cases studied the model not only fits perfectly the data used at 5 and 10 K/min in both rate change with temperature and location of maximum devolatilization rate with temperature, but also predicts the pyrolysis behavior of samples when the heating rate is increased up to 20 K/min. Comparing the different samples, the model is able to deal with a wide range of reaction rate values, from the one of cellulose with a maximum of 0.004 s^{-1} to the maximum of lignin 0.0006 s^{-1} (heating rate 10 K/min), one order of magnitude lower. In addition, the model also placed correctly the peaks of reaction rate no matter the temperature. For example, hemicellulose has the maximum placed at 555 K and lignin at 625 K almost 100° difference.

The most relevant point of the DAEM is the capacity of analysing the devolatilization process in a distribution of reactions with characteristic activation energies and pre-exponential factors described by Eq. 2. In Figure 4 the distributions of activation energies for seven samples are shown related to the fraction of sample remaining. Regarding to the distribution of activation energies, different trends can be observed depending on the sample. Components: for cellulose the most part of the reactions are favored the same with a mean activation energy of 250 kJ/mol; for lignin there are two maxima of activation energy at the very beginning of the reaction (198 kJ/mol) and at 0.55 fraction of mass remaining (273 kJ/mol); hemicellulose has a similar behavior with two maxima at the beginning (320 kJ/mol) and at 0.35 fraction of mass remaining (361 kJ/mol). Depending on the values of activation energies, apart from the maximum, lignin has the lowest values followed by cellulose and finally hemicellulose. Therefore, reactions of lignin will be more favored than cellulose and than hemicellulose. Regarding to the wood samples, they also have two maxima, the first one at the beginning of the pyrolysis and the second one around the end of the reaction. According to the distributions of pre-exponential factors, the results obtained are in the same range of the results obtained previously by Scott et al.[21] for dried sewage sludge. Like in that case, the distribution of pre-exponential factors of each sample has a closely related behavior to its distribution of activation energies; therefore, the comparison of samples follow the same pattern for that parameter and this discussion has been omitted.

Comparing the fraction of mass allocated for every reaction ($f_{0,i}$ in Eq. 2) for the seven samples (Figure 5), one interesting point is that cellulose pyrolysis is described in more than a 75% by only two reactions placed around 0.45 of fraction of mass remaining. This fact explains the steep decrease of fraction of mass remaining around 615 K (Figure 2a, heating rate 5 K/min). Other samples, lignin, hemicellulose, and the wood

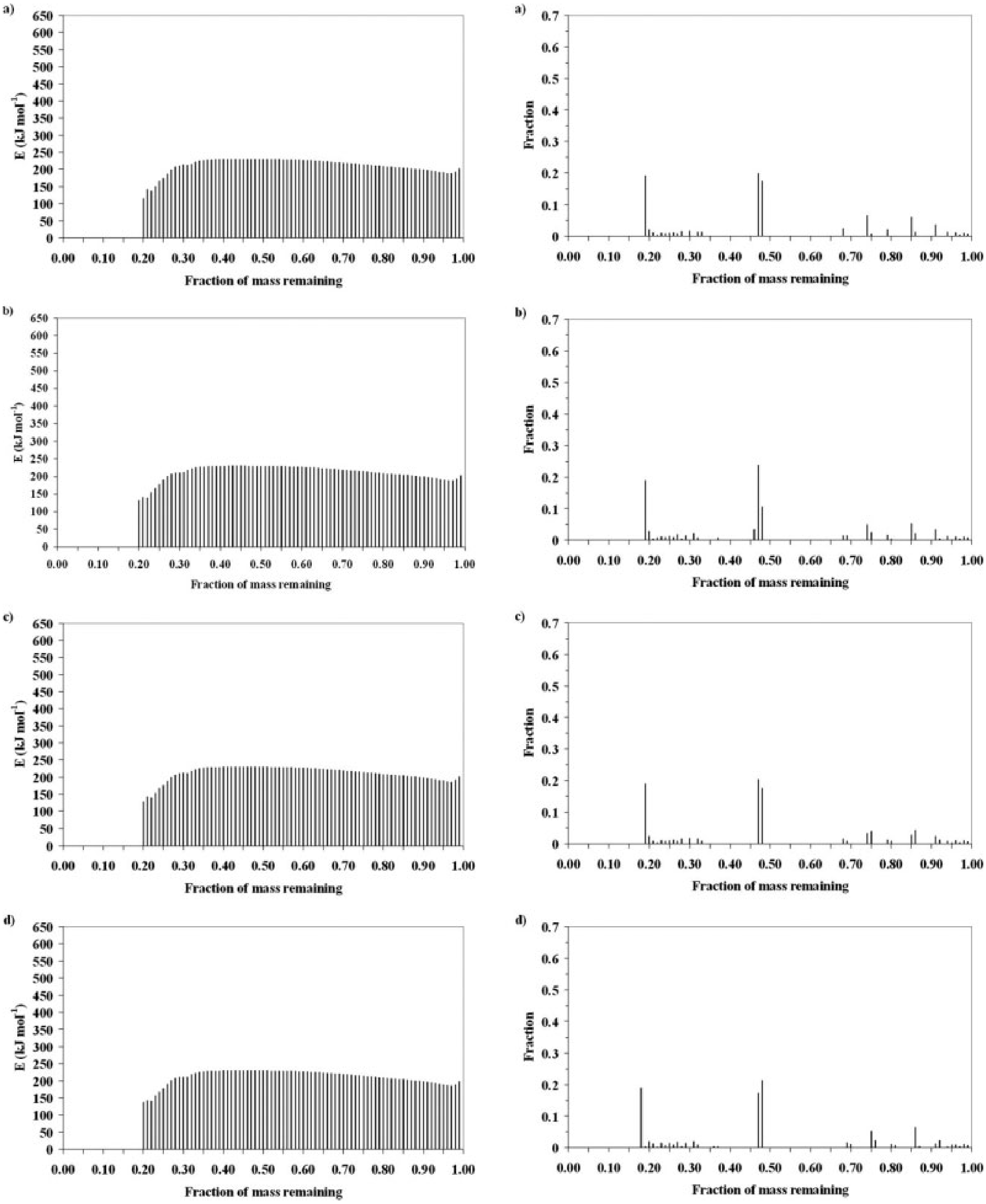

Figure 8. Activation energy and fraction of mass vs. fraction of mass remaining calculated from data of the constituents.

Samples are (a) *Pinus sylvestris* 1, (b) *Pinus sylvestris* 2, (c) *Pinus halepensis*, and (d) Woods Blend.

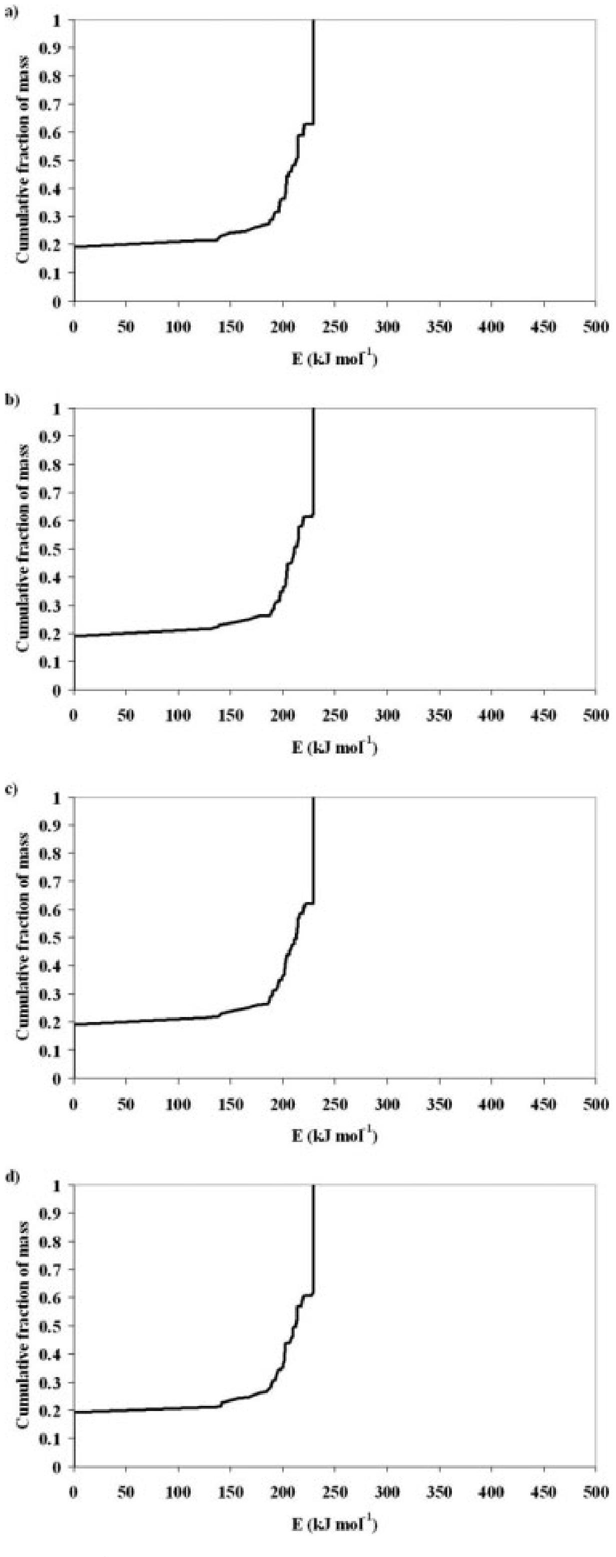

Figure 9. Cumulative fraction of mass vs. activation energy calculated from data of the constituents.

Samples are (a) *Pinus sylvestris* 1, (b) *Pinus sylvestris* 2, (c) *Pinus halepensis*, and (d) Woods Blend.

samples, have an important fraction of mass allocated in the last fraction of mass related to the fraction of inert mass. Apart from that inert mass, while lignin has a homogeneous distribution of mass throughout the reactions defined, hemicellulose decomposes in an extent of 22% by the reaction placed at 0.55 of fraction of mass remaining. The distribution of fraction of mass allocated for samples of wood is more focused in a couple of reactions placed at 0.4 in the case of *Pinus sylvestris* 1 and 2, at 0.42 for *Pinus halepensis* and at 0.45 in the case of woods blend. These fractions of mass would be related to the influence of cellulose in the sample and the shift of the maxima to the hemicellulose influence.

Figure 6 compiles the description of the cumulative fraction of mass with activation energy. Regarding to the three main components of biomass, different behaviors can be observed again. For cellulose a steep increase is observed at 230 kJ/mol, lignin has a homogeneous distribution of activation energies depending on the mass fractions and hemicellulose shows again an increase, not as steep as in the case of cellulose, around activation energies of 220–230 kJ/mol. Studying the results obtained for wood samples, they have most of the mass allocated in reactions with activation energy around 225 kJ/mol (related to cellulose), from 0.4 for *Pinus sylvestris* 2 which would have a higher influence of cellulose, to 0.3 of wood blend, with a lower influence of cellulose.

To sum up, the model describes different properties of the devolatilization of wood and its constituents that can be used to know the influence of these compounds in the final behavior of the wood sample.

Wood analysis

To put into production a process based on a biomass treatment, a wide range of biomass origins should be taken into account. This biomass would have in cellulose, lignin, and hemicellulose its main components but in different proportions. To be able of predicting the behavior of biomass from the behavior of its main components will reduce to a minimum the needs of study of different samples and will increase process sustainability.

In this work, the equation proposed previously by this group[22] to deal with feed mixtures has been developed to take into account the inert part of the different components and increase the number of components in the blend.

$$\frac{M(t)}{M} = \sum_n CF_n \times \left(w_n + \sum_i f_{n,i,0} \exp\left[-A_{n,i} \int_0^t \exp\left(\frac{-E_{n,i}}{RT(t)} \right) dt \right] \right) \quad (3)$$

where CF_n are the fractions of n components of the feed. To use the model with biomass n will be three for cellulose, lignin, and hemicellulose.

In Figure 7 there is a comparison of the experimental, fitted, and calculated data from constituents for the

Table 3. Relations of Cellulose, Lignin, and Hemicellulose for Rice Straw, Rice Husk, and Corncob

Sample	Cellulose	Lignin	Hemicellulose
Rice straw	0.36	0.25	0.39
Rice husk	0.35	0.30	0.35
Corncob	0.52	0.16	0.32

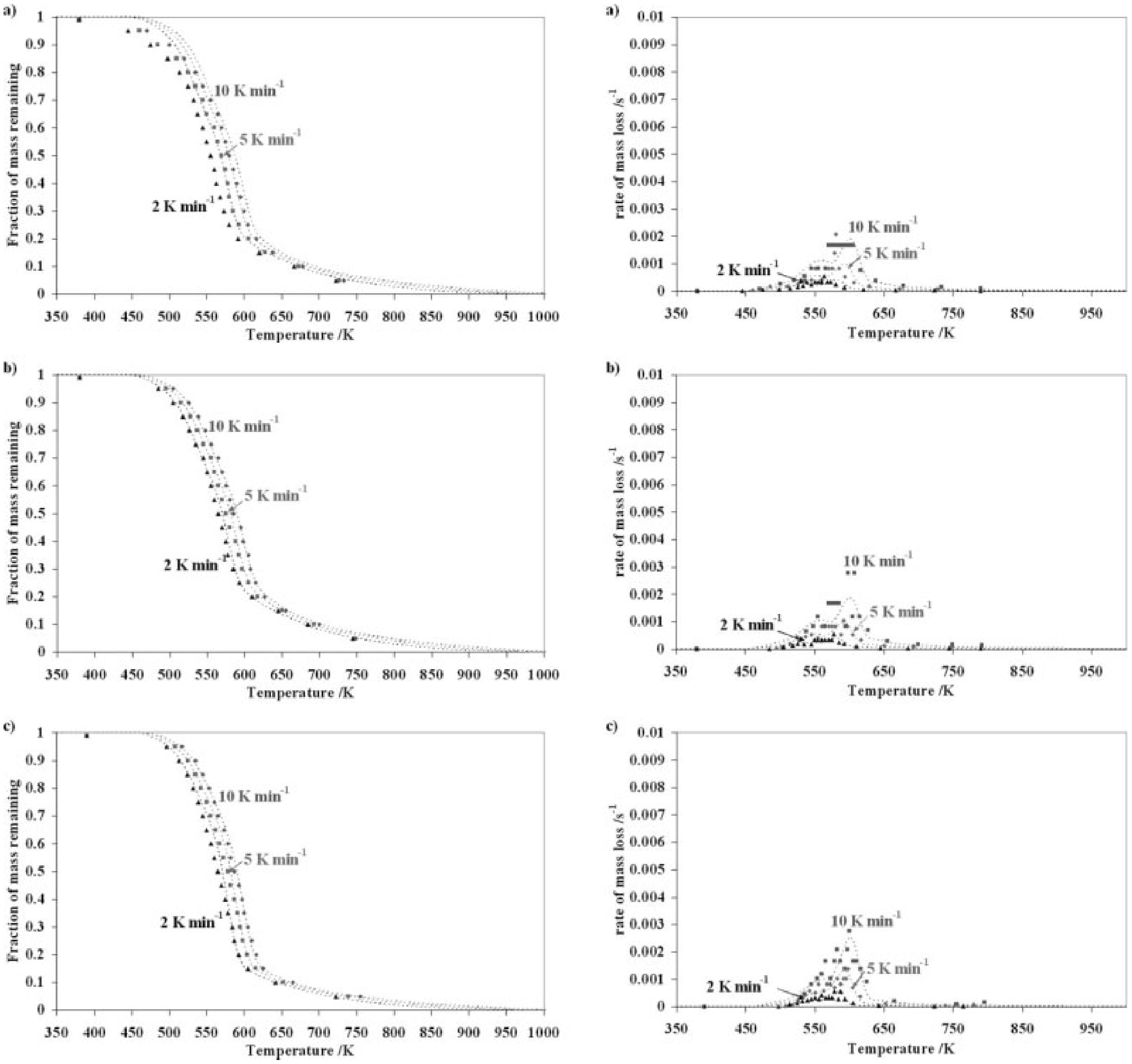

Figure 10. Comparison of the progression of experimental (points) fraction of mass remaining and rate of mass loss from literature with curves calculated from data of constituents (dashed lines).

Samples are (a) rice straw, (b) rice husk, (c) corncob.

devolatilization of four wood samples. The data calculated have been obtained using values of fractions of cellulose, lignin, and hemicellulose provided by an external laboratory CIEMAT and normalized to 100. The analytical procedure for the determination of structural carbohydrates and lignin in biomass was carried out following the standards of the National Renewable Energy Laboratory (NREL). Therefore, carbohydrates were analysed by acid hydrolysis to determine the monomeric sugars in the solution, while lignin was determined as the insoluble solid after the acid attack. These values are compiled in Table 2.

In Figure 7 there is a very good fit between experiments and theoretically calculated data at three heating rates focused into two points: the relation of fraction of mass remaining with temperature and the prediction of the fraction of inert mass. These results allow thinking that the interactions between constituents during pyrolysis are very scarce,[4] so an additive model as the one proposed is very useful to predict the behavior of these samples from the composition analysis.

Regarding to the evolution of mass loss rate with temperature compared to the experimental results (see Figure 7), the model produces very good data. The results calculated by the model clearly distinguish the influence of cellulose and hemicellulose with a first knee at lower temperatures (related to hemicellulose) than the main peak (related to cellulose) in all cases. This fact could be explained by the weak interaction between constituents in the biomass samples as described earlier. Despite this weak interaction, the model predicts a

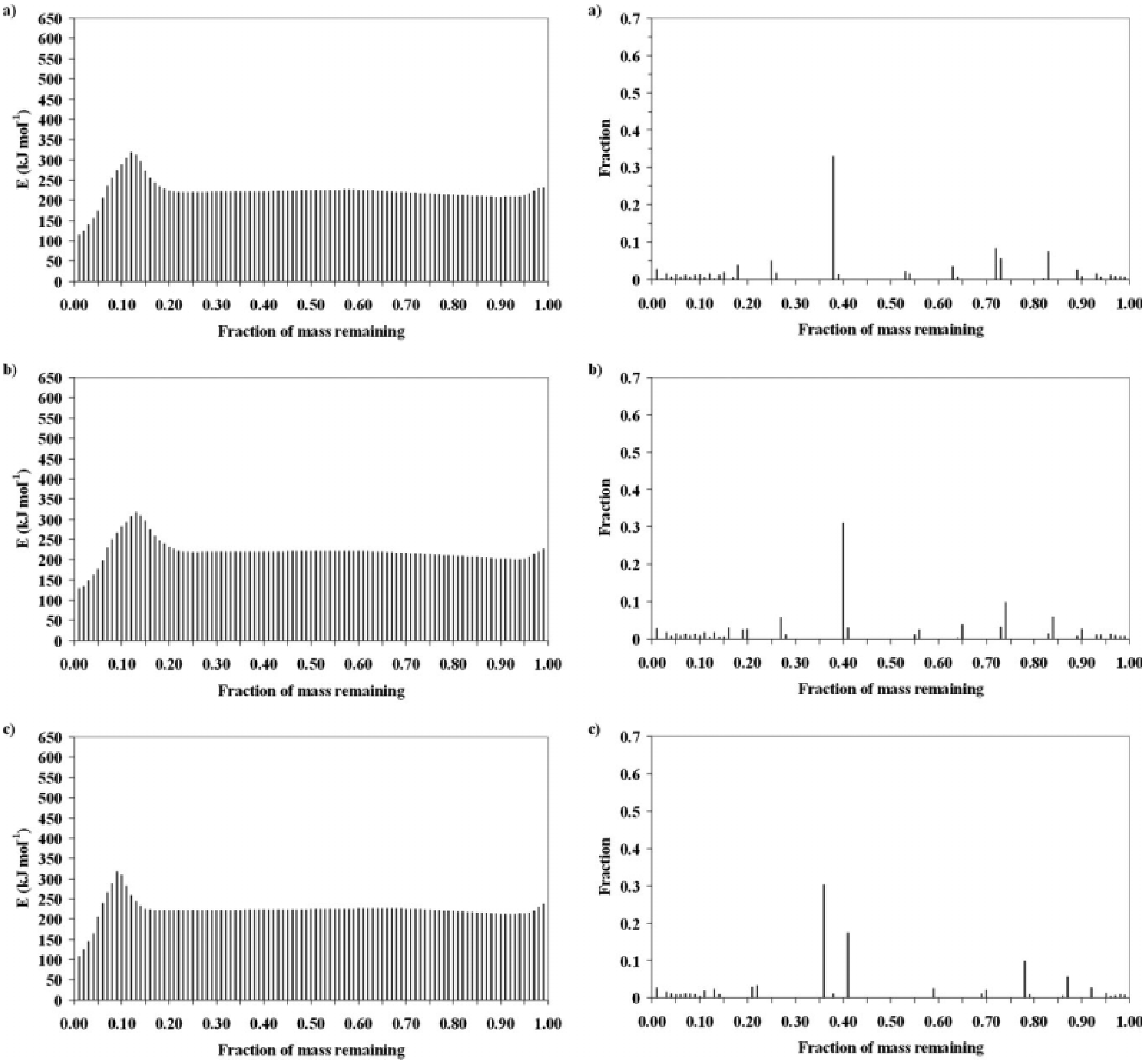

Figure 11. Activation energy and fraction of mass vs. fraction of mass remaining calculated from data of the constituents.

Samples are (a) rice straw, (b) rice husk, (c) corncob.

reaction rate maximum 20% higher than the experimental one. However, the error in the temperature prediction is lower than 1% which gives to this model a conservative characteristic. Therefore, this additive model of principal constituents is successfully describing wood pyrolysis both fraction of mass remaining and reaction rate vs. temperature.

The predicted results for four wood samples (from its components assuming no interaction between them) has been analysed with the DAEM and the parameters obtained have been plotted in Figures 8 and 9. From the comparison between these results and the results obtained from the DAEM applied to experimental results (Figures 4, 5, and 6), the theoretical behavior of the sample results in a homogenization of the activation energies to lower values. Regarding to the fraction of mass allocated in the 100 different reactions studied, in addition to the fraction of inert mass (initial bar), the model distinguishes one main reaction for all the samples placed in a fraction slightly higher. Finally, the cumulative fraction of mass depending on activation energy is sharper and at lower activation energies in this theoretical case due to the more homogeneous activation energies with lower values.

Biomass analysis

To complete the viability of applying this model to biomass, there are some points to take into account, (i) different kinds of biomass samples, (ii) calculation of pyrolysis behavior at different heating rates, (iii) use of data obtained in different equipments. To fulfill these points we used data published by Worasuwannarak et al.[3,23] for rice straw, rice husk,

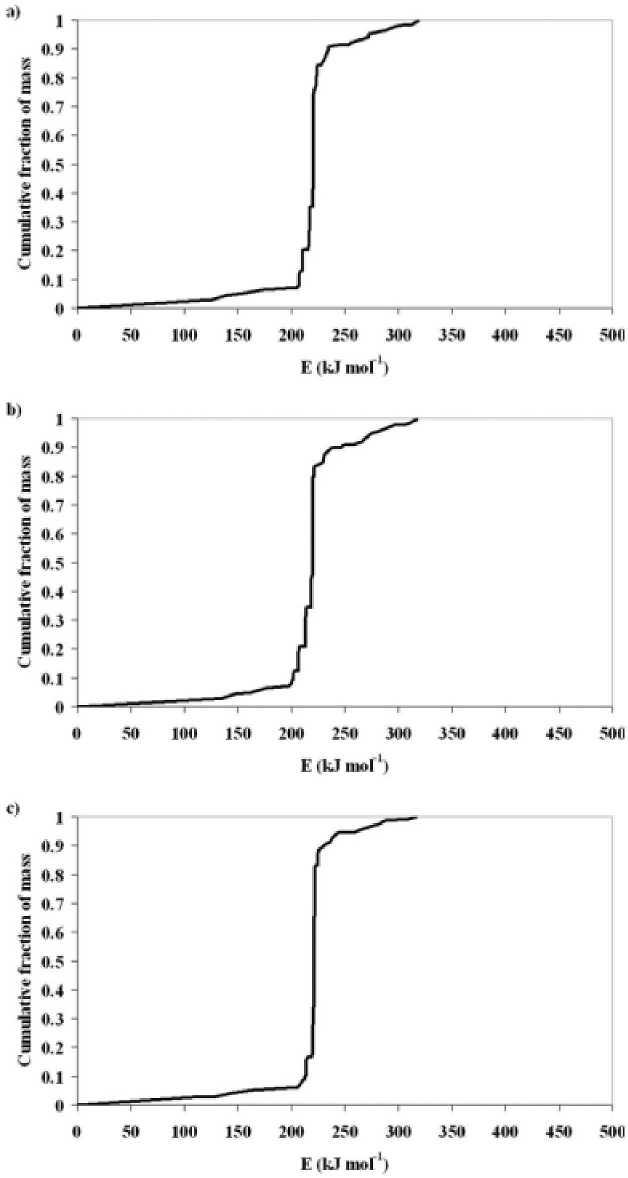

Figure 12. Cumulative fraction of mass vs. activation energy calculated from data of the constituents.

Samples are (a) rice straw, (b) rice husk, (c) corncob.

and corncob. In these studies they used data from other researchers to get the composition of these samples related to cellulose, lignin, and hemicellulose colleted in Table 3. Comparing Tables 2 and 3 we can observe the different nature of the samples studied. Wood samples are much more lignocellulosic than rice straw which has an increase in hemicellulose or corncob with a lower content of lignin.

In Figure 10 the fitting results for these three samples at heating rates, 2 K/min, 5 K/min, and 10 K/min are shown. Conversion is calculated excluding the inert part of the samples hence the model will be checked in other input conditions, from 1 to 0 fraction of mass remaining. Regarding to the evolution of this fraction of mass depending on the temperature, for rice husk and corncob samples the difference between experimental and calculated data is lower than 2% for the whole range of conversion studied. Only for rice straw at the very beginning and at the end of the pyrolysis (more than 0.75 and less than 0.1 of fraction of mass remaining) the difference between experimental and calculated data is higher than this value of 2% but lower than 10%. It is worthy pointing out the fact that for all samples the model is able to keep the relation between data at 2, 5, and 10 K/min. In this case the data predicted are at a heating rate of 2 K/min compared to the 20 K/min used for wood samples. According to the evolution of rate of mass loss with temperature, the number of experimental points is scarce in this study but it still shows the first knee related to hemicellulose content and the maximum related to cellulose. For the calculated data, the model clearly distinguishes these two points and places them in the range of temperatures limited by the experimental data. The values of the maxima are lower than the experimental ones but, the lack of points could amplify mathematically this effect.

The DAEM study of the properties activation energy, fraction of mass allocated and cumulative fraction of mass (Figures 11 and 12), show on one hand an increase in the values of activation energy at the beginning of the reaction to keep an almost constant value of around 220 kJ/mol. On the other hand there is only one main fraction of mass allocated close to 0.40 of fraction of mass remaining related to cellulose like in the case of wood samples. Finally, the previous properties are reflected in a distribution of cumulative fraction of mass centred in activation energy of 220 kJ/mol.

Data for pyrolysis of three biomass samples from literature have also been studied with DAEM. From the comparison of the results, it can be concluded that the model can perfectly explain biomass behavior in pyrolysis from the behavior of its components cellulose, lignin, and hemicellulose. It can also be concluded that exists a slight interaction between constituents that not allow differentiate the influence of constituents as clear as for an additive behavior. However, the model places a higher maximum for reaction rate in a very close temperature to the experimental one, so this model based on the three main constituents of biomass produces a conservative approximation to the biomass samples pyrolysis.

Conclusions

An algorithm of DAEM developed by Scott et al.[19] has been applied to study biomass devolatilization. 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 good comparison of experimental and calculated data allows the use of this model to generate also good approximations of the temperature ranges where the reaction will take place at the high heating rates of flash pyrolysis, gasification or combustion processes. The model describes as well the influence of the activation energies and fraction of mass allocated to every reaction.

In addition, the model implemented previously by Navarro et al.[22] to predict the behavior of coal and petcoke blends, has been developed to include the influence of the inert part of solids and work with wood samples and their three main constituents cellulose, lignin, and hemicellulose. As a result of the comparison of predictions and experimental data, the DAEM can be used to produce a very good approximation to the wood sample pyrolysis from its main constituents with a good prediction both in fraction of mass and reaction rate variation with temperature.

Finally, the model has been tested against data from literature for rice straw, rice husk, and corncob to check its applicability to different kind of biomass, heating rates, conditions of input data and different equipment. To put into production a process based on a biomass treatment, a wide range of biomass origins should be taken into account. To be able of predicting the behavior of biomass from the behavior of its main components will reduce to a minimum the needs of study of different samples and will increase process sustainability. As introduced before, this model will help optimizing pyrolysis performance of the different biomass components (cellulose, hemicellulose, and lignin) and can be used as a tool to control working conditions in future integrated biomass systems. From the very good results obtained both for fraction of mass remaining and rate of mass loss, the model has been proved to be a very good choice to study flexibility of biomass feed to operational systems.

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Notation

X = fraction of mass remaining
$M(t)$ = mass of the sample at time t, kg
M_0 = initial mass of the sample, kg
m = mass of volatile matter, kg
n = number of constituents in the sample
i = number of reactions describing the process
CF_n = fraction of constituent n
E_i = specific activation energy, kJ/kg
$f_{i,0}$ = fraction of M_0 which decomposes with a specific activation energy, dimensionless
A_i = pre-exponential factor, s^{-1}
t = time, s
T = temperature, K
R = ideal gas constant, kJ/mol·K
TGA = thermogravimetric analyser
DAEM = distributed activation energy model

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