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b) Authors reference and address:

M.V. Navarro*, J.M. López, A. Veses, M.S. Callén, T. García

Department of Energy and Environment, Instituto de Carboquímica (ICB-
CSIC), C/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain

Corresponding author: Dr. María Victoria Navarro

Department of Energy and Environment, Instituto de Carboquímica (ICB-
CSIC), C/Miguel Luesma Castán 4, 50018 Zaragoza, Spain

Phone: +34 976 733977, Fax: +34 976 733318

e-mail: navarro@icb.csic.es

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HIGHLIGHTS

- The Distributed Activation Energy Model was applied to co-pyrolysis
- Mixtures of lignocellulosic biomass and plastic wastes were studied
- Different proportions of components and heating rates were successfully simulated
- Deviations of simulations from experiments were ascribed to interactions of solids
- Interactions depend on the nature and proportion of plastics and the heating rate

Kinetic study for the co-pyrolysis of lignocellulosic biomass and plastics using the distributed activation energy model

M.V. Navarro*, J.M. López, A. Veses, M.S. Callén, T. García

Department of Energy and Environment, Instituto de Carboquímica (ICB-CSIC),

C/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain

ABSTRACT

The characteristics of bio-oil produced from biomass pyrolysis can be improved by co-feeding waste materials. In this work, co-pyrolysis of lignocellulosic biomass with six different waste plastics (waste tyre (WT), polylactic acid (PLA), polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP) and high density polyethylene (HDPE)) were conducted in a thermogravimetric analyser to study thermal decomposition of the mixtures. The distributed activation energy model (DAEM) was applied to pure feedstocks at 5 and 10 °C/min heating rates to fit the kinetic parameters. The model was used to simulate the co-pyrolysis of biomass/plastic mixtures assuming additive effect of components at different weight proportions and heating rates. Profiles of the fraction of mass remaining for mixtures at 100 °C/min were reproduced with a remarkable agreement. Discrepancies between the experimental and calculated profiles were considered as a measure of the extent of interactions occurring in the co-pyrolysis. Projections of the behaviour of mixtures under flash pyrolysis conditions were performed to study important aspects of the process, such as radical interactions and optimum working temperature.

Keywords: Co-pyrolysis, kinetics, DAEM, biomass, plastics

Corresponding author. Tel: +34 976733977; fax: +34 976733318.

E-mail address: navarro@icb.csic.es (María Victoria Navarro)

1. Introduction

The pyrolysis of lignocellulosic biomass provides an opportunity to obtain energy from an abundant, clean and renewable source [1, 2], while significantly reducing the negative impact of petrochemical processes on climate change. The pyrolysis process is considered a beneficial option in waste treatment, largely due to the liquid biofuels and bio-chemical products generated and energy recovery achieved when compared to other methods [3]. The use of lignocellulosic biomass contributes to the sustainable management of a regional or local raw material such as forestry debris, to job creation, and to the application of subproducts with no added value. It is in this context that the development of small-scale production units capable of processing a few tonnes of biomass per day is attracting great interest. These could efficiently produce a bio-oil of a higher energy density compared to that of the starting biomass, which would significantly reduce the costs associated with the handling and transportation of biofuel.

The main challenge faced by the scientific community is that of improving the quality of those bio-oils obtained from biomass by means of conventional pyrolysis processes. Despite bio-oil being environmentally friendly, its fuel characteristics are lower than those of fossil fuels because of its high oxygen content, low calorific value, corrosion problems and instability [4]. Many works have been undertaken to achieve this goal by means of upgrading techniques. Among these, numerous studies have focused on the co-pyrolysis of biomass with different materials [1, 2, 4-9]. In relation to the co-pyrolysis of biomass and plastic wastes, this approach has demonstrated that it is possible to obtain bio-oils with improved quality, while synergetic effects have even been found in improved oil stability, yield to liquids, water content and heating value compared to those results found for the pyrolysis of the separate components [4]. These

synergetic effects are linked to the promotion of interactions between radicals released from both substances during the devolatilisation process [6]. Onal et al. [10] mentioned that several radical reactions during co-pyrolysis can be produced as follows: initiation, formation of secondary radicals and termination by isoproportionation or recombination of radicals. For instance, Chattopadhyay et al. indicated that initially during the co-pyrolysis of paper biomass and plastics, cellulose sets off radical formation, resulting in the initiation of polymer chain scission [6]. In another example, results obtained from the co-pyrolysis of different mixtures of lignocellulosic biomass and waste tyres [11] showed positive synergetic effects in a more stable pyrolysis oil that avoids phase separation and with increased both bio-oil yield and various bio-fuel chemical and physical properties such as acidity, viscosity and oxygen content.

It has been pointed out that synergetic effects in co-pyrolysis of biomass and plastics blends can only be observed in pyrolysis of certain biomass/polymer mixtures [12]. Therefore, for the purpose of accelerating the study of different biomass/plastic mixtures, it would be of great interest to have a kinetic model of the co-pyrolysis process in order to identify those plastics that can enhance the quality of bio-oil at relevant heating rates for pyrolysis processes, because they release radicals at the same time as some components of the biomass do [4]. Knowledge of the thermal behaviour and reactivity of these mixtures of biomass with plastics is very important as well for the effective design and operation of the thermal conversion units, given that solid devolatilisation is always a fundamental step [13]. The thermal behaviour depends of the type of co-pyrolysed mixture and the blending ratio of each material [8, 14, 15] as well as reaction conditions like heating rate, final temperature and reaction time.

Several studies on co-pyrolysis have been developed to examine the thermal behaviour and decomposition kinetics of organic and plastic blends using

thermogravimetric analysis. Interactions between biomass and plastics have been studied by comparison of experimental and theoretical mass loss calculated assuming additive effect of pure materials [13, 16-26]. The kinetic parameters of pure components and their mixtures have also been compared to study interactions between biomass and plastics. The kinetic parameters were calculated either by dividing the mixture into main degradation regions for each material [13, 20-28] or by applying the isoconversional method [19, 29, 30]. Narobe et al. [30] concluded with the isoconversional method that the activation energy (E_a) parameter did not have a constant value throughout the whole process of thermal decomposition. To the contrary, its values varied widely with conversion as a sign of a complex process that cannot be explained by a single reaction that could be considered as a rate-determining step. To the best of our knowledge, only two studies have modelled the co-pyrolysis kinetics of biomass and plastics [5, 31]. The pyrolysis kinetic model used by Oyedun et al. [5] is based on a pseudo-component kinetic model for bamboo and PS feedstocks that represent groups of similar reactive species that undergo a particular mass loss process at the same rate in a given time [32]. The pyrolysis kinetic model used by Burra et al. [31] is a first-order distributed activation energy model (DAEM) with 5 pseudo-components.

The DAEM is considered an accurate and versatile approach to reproduce complex pyrolysis processes [33, 34]. The DAEM assumes that pyrolysis occurs through numerous independent, parallel first-order reactions, each with its own frequency factor and activation energy [35]. The DAEM has been used to describe the pyrolysis kinetics of lignocellulosic biomass [36], and Varhegyi et al. [37] pointed out that the DAEM is the best method available for mathematically representing the physical and chemical heterogeneity of biomass during a devolatilisation process. The application of this model has also been previously studied for polymers with a fast

decomposition [36, 38-41] and blends of coal with petcoke [42], wastes [43] and biomass [44].

The present study applied the DAEM in order to simulate for the first time, to our knowledge, the behaviour of different biomass/plastic mixtures under flash pyrolysis conditions. Six different waste plastics were evaluated as potential promoters during the flash pyrolysis of lignocellulosic biomass obtained from pine forestry residues. First, data from the thermogravimetric analysis of pure feedstocks were used to obtain the kinetic parameters of the model. By using these data, the model was applied to study important aspects of the co-pyrolysis process at high heating rates, such as the possibility of radical interactions and optimum pyrolysis temperature.

2. Experimental

2.1 Materials and sample preparation

Pine woodchips (PINE-15 mm nominal size) and six waste plastics (waste tyre (WT), polylactic acid (PLA), polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP) and high-density polyethylene (HDPE) were used for the experiments. The PINE sample consisted of Aleppo pine (*Pinus halepensis*), containing bark, from forestry debris. It was dried, crushed and sieved to a particle size of less than 250 μm prior to the experiments. The WT sample (5 mm nominal size) consisted of rubber crumb from waste tyres after removal of the steel thread and the textile netting. The biopolymer PLA, PP and HDPE samples came in granulated form. The PS and PET samples were obtained from used packaging. All the WT and plastic samples were subjected to cryogenic crushing and sieved to a particle size smaller than 250 μm . The moisture, ash and volatiles contents of the samples were determined according to the ISO-589-1981, ISO-1171-1976 and ISO-5326-1974 standards, respectively. In

accordance with these standards, the measurements were within a confidence interval of $\pm 0.2\%$, $\pm 0.2\%$ and $\pm 3\%$, respectively. Ultimate analyses were carried out in a Thermo Flash 1112 analyser device with confidence interval lower than $\pm 0.3\%$ in the measurements. The higher heating value was measured in an IKA C-2000 calorimeter and determined according to UNE 164001EX for the biomass, and ISO-1929-76 for the plastic samples, with differences in the measurements lower than 0.12 MJ/kg. Table 1 shows the feedstock characterisation.

2.2 Experimental techniques

Thermogravimetric analyses were performed in a Netzsch Libra F1 Thermobalance. All the tests in this study were run at a constant nitrogen flow of 50 mLn/min in a reactor with a 13 mm internal diameter. The sensitivity of this apparatus was 0.1 μ g. The samples were placed in an alumina crucible forming a small fixed bed with an initial mass of approximately 9 mg. Sets of experiments at different heating rates of 5, 10 and 100 $^{\circ}\text{C}/\text{min}$ and a final temperature of 700 $^{\circ}\text{C}$ were performed for every sample.

The fraction of mass remaining (X) was calculated according to equation (1):

$$X_{\text{exp}} = \frac{M(t)}{M_0} \quad (1)$$

where M_0 is the initial sample weight at 150 $^{\circ}\text{C}$ and $M(t)$ is the sample weight at any time.

3. Results and discussion

The main characteristics of the PINE wood and six plastic samples are listed in Table 1. Proximate analysis shows each sample comprising mainly combustible content

(fixed carbon and volatile matter) and a small proportion of moisture and ash content. All materials had a high C-content, an intermediate H-content, and a very low N-content. O-content was very low in the WT sample, compared to the absence of this element in PS, PP and HDPE, and the high content of PINE, PLA and PET. Only a low sulphur content was detected in WT. The higher heating values, HHV, of the input materials varied between 19 MJ/kg for the PINE and PLA samples, and 46 MJ/kg for the petrochemical plastics PP and HDPE.

3.1. Kinetic study for pyrolysis of pure solids

Figure 1 shows the fraction of mass remaining and the rate of mass loss curves for PINE and WT at two different heating rates, 5 and 10 °C/min. The shape of the curves did not change with variations in the heating rate, but the mass loss temperatures showed an increase at higher heating rates for both samples. This shift to higher temperatures was due to the decomposition kinetics at different heating rates. The TG curves showed a wide decomposition of both samples starting at approximately 200 °C, and the mass loss continues until 500 °C was reached. It can be observed that working temperatures lower than 500 °C could lead to the incomplete pyrolysis of the samples, depending on the reaction time.

The composition of biomass mainly consists of cellulose, lignin and hemicellulose in different proportions, and thermal degradation of the individual components has previously been employed to extrapolate the overall degradation of the original biomass [45]. The biomass used in this study was a sample of *Pinus halepensis* with an approximate chemical composition of these main components as follows: 44% cellulose, 34% lignin and 22% hemicellulose. These analyses were performed according to the National Renewable Energy Laboratory standards and normalized to 100. Wood

decomposition can be described to take place in three main steps: the slow decomposition of lignin, which lasts at a heating rate of 5 °C/min from low temperatures up to 500 °C, followed by the rapid decomposition of hemicellulose up to 350 °C, identified with the shoulder of the PINE sample centred at 325 °C in the curve of rate of mass loss. Finally, the also rapid decomposition of cellulose takes place from around 275 °C up to 375 °C, and this can be explained by the peak at 350 °C in that sample. Thus, the hemicellulose portion of biomass devolatilises at lower temperatures than cellulose, which devolatilises at lower temperatures than part of the lignin portion of biomass. This sequential devolatilisation of the main components of biomass has been previously suggested in the literature as related to the increasing activation energies of hemicellulose, cellulose and lignin [46]. Most of the volatile matter is released from the biomass structure at temperatures between 200 °C and 375 °C. Therefore, this temperature region is the most significant to examine since it is where the release of radical and gaseous products and char formation take place [47]. At the heating rate of 10 °C/min, the shoulder, identified as hemicellulose decomposition, was centred at 337 °C and the peak denoted as cellulose decomposition was observed at 360 °C in the rate of mass loss curve. As the heating rate increased, the significant temperatures shifted toward higher values, as observed for the curves of the fraction of mass remaining.

The WT sample comprising tyre rubber was a blend of additives [48], natural rubber (NR) and synthetic rubber: styrene-butadiene copolymer (SBR) and butadiene rubber (BR) as well as carbon black and fillers. Several authors [49-51] agree that additives decompose first at around 270 °C, with a heating rate of 5 °C/min that is corroborated with a first shoulder found in the rate of mass loss curve of the WT sample. NR decomposition took place at around 370 °C, identified by the highest peak

of the WT sample studied, while SBR and BR decomposed at higher temperatures, around 400 °C and 470 °C, respectively, producing a plateau between a first peak at 370 °C and a second peak observed in the WT sample at 460 °C. At this heating rate, most of the volatile matter of the WT sample was released from the structure at temperatures between 280 °C and 480 °C, the most significant temperature region. At the heating rate of 10 °C/min, maximum decomposition rates took place at 381 °C and 466 °C in the rate of mass loss curve, corroborating the shift toward higher values of significant temperatures.

The experimental data for the fraction of mass remaining versus temperature and rate of mass loss for PLA, PS, PET, PP and HDPE samples are compiled in Figure 2. It can be observed that the curves obtained for plastics shifted to higher temperatures with the increased heating rate, with unaltered shapes as reported previously for PINE and WT samples. However, compared to these samples it can also be observed that plastics decomposed at higher temperatures, in agreement with previous publications [17-19, 23, 28]. For example, PLA started decomposing at a heating rate of 5 °C/min at approximately 300 °C, while PS, PET and PP did so at 350 °C and HDPE at 400 °C, with one main peak of rate of mass loss at 361, 416, 427, 451 and 476 °C, respectively. Compared to PINE and WT samples as well, most of the transformation of these samples occurred in a relatively narrow temperature range, around 100 °C compared to 300 °C for the PINE and WT samples. This narrow temperature range for devolatilisation implies that plastic pyrolysis is produced by a narrow range of reactions accounted for by smaller variety in bond types. This is expected because these synthetic polymers have a relatively simple monomeric composition. Almost all synthetic polymers present C-H bonds of primary, secondary and tertiary C atoms, and C-C bonds that produce the probability distribution of bond selection for radical formation or

breakage [31]. PLA and PET with oxygen in their monomers can also present intramolecular transesterification [52] and scission of ester functional groups [31], respectively. The presence in PET and PS of aromatic rings on their structures can also cause differences on their thermal behaviour [53]. In addition, most of the polyolefin materials produced negligible solid residue compared to PINE and WT, which presented a high percentage of final fractions of mass remaining, 0.2 and 0.38, respectively. This fact is related to the low content of fixed carbon joined to a high content of volatiles in these samples. Only the PET sample presented a value for the residual mass-fraction of 0.17, in line with the higher fixed carbon value obtained for this sample in the proximate analysis (Table 1). Both of these points, in addition to the narrower temperature ranges of devolatilisation and higher proportion of volatiles in the samples, produced higher rates of mass loss in these samples compared to PINE and WT. At the heating rate of 10 °C/min, the maximum decomposition rates took place at 371, 425, 438, 464 and 483 °C for PLA, PS, PET, PP and HDPE, respectively. Compared with data obtained at the heating rate of 5 °C/min, these values corroborate the displacement toward higher temperatures of around 10 °C, from 7 °C displacement for HDPE and 13 °C for PP.

The DAEM was applied to study the devolatilisation kinetics of the different single materials. This model assumes that each solid is a mixture of components that decomposes during pyrolysis into a variety of chemical groups following a distribution of first-order reactions with characteristic activation energies [54]. There are several developments of the DAEM depending on the approach proposed to solve the double integral generated by the distributed activation energy (DAE) problem, the form of the DAE applied, the number of data sets used, the conditions for measuring devolatilisation, etc. The algorithm developed by Scott et al. [54] was used in this work

to describe the devolatilisation of the samples with an approach to solve the DAE problem in that there is assumed to be only a finite number of reactions but large enough to approximate a continuous distribution of activation energies with no predefined form. To achieve this, the approach uses two data sets at different, but constant heating rates to describe the profile of the fraction of mass remaining by the basic equation (2):

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

where, w is the residual mass-fraction, $f_{i,0}$, is the mass-fraction of M_0 that decomposes with an activation energy E_i (kJ/mol) and pre-exponential factor A_i (s^{-1}), t is time (s), T is temperature (K) and R is the ideal gas constant (kJ/mol·K). The algorithm is intended to solve the problem of determining the kinetics for a material using test curves at low heating rates. A measure of the deviation between the experimental and the calculated curves with the fitted set of parameter values has been calculated for all the tests by the correlation coefficient R^2 and the deviation percentage $Dev\%$ with the following equation 3 [55]:

$$Dev\% = 100 \times \frac{\sqrt{\frac{\sum_1^n (X_{exp} - X_{theo})^2}{n}}}{X_{max}} \quad (3)$$

where X_{max} is the maximum experimental fraction of mass remaining. A lower value of $Dev\%$ in equation 3 indicates a better quality of simulation. In addition, a measure of discrepancies between experimental and calculated points was obtained by percentage difference of temperature and differences of fraction of mass remaining ΔX with equation 4 [22]:

$$\Delta X = (X_{exp} - X_{theo}) \times 100 \quad (4)$$

The results of applying the algorithm described by Scott et al. [54] at heating rates of 5 and 10 °C/min for PINE and WT samples are shown in Figure 3. This figure shows for both samples the distributions of a) activation energy, b) pre-exponential Arrhenius factor and c) mass-fraction assigned at each value of fractional mass remaining. In this case, we postulated 100 first-order reactions related to the fractional mass remaining, which was unity at the start of pyrolysis and would decrease to the residual mass-fraction during the reaction. Wood and tyre rubber had wide distributions of mass-fraction, f , allocated all over the fractions of mass remaining (See Figure 3.c). The distribution of f for the PINE sample was concentrated at around the 0.4 fraction of mass remaining, which was related to the influence of its cellulose component, as previously reported in literature [45]. The wide distribution of lower mass-fractions was associated with the lignin and hemicellulose parts of the sample [45], the other two main components of lignocellulosic biomass. With regard to WT, the reaction close to 0.35 fraction of mass remaining with the highest allocated f of 0.36 could be associated with the carbon black content of the sample [48]. The fraction of mass remaining up to 0.6 could be linked to volatile content in NR, while the reactions between 0.60 and 0.82 of the fraction of mass remaining could be associated with the SBR and BR components.

The results of applying the DAEM algorithm to the measurements at heating rates of 5 and 10 °C/min for other polymer samples PLA, PS, PET, PP and HDPE are also compiled in Table 2. These samples presented a lower residual mass-fraction and narrower distributions than those of PINE and WT. All of them were described to an extent higher than 75% by only one reaction, which was increased to an extent of 90% in the cases of PLA and PS.

The accuracy of fit was studied in Figure 4, where a notable agreement is observed between the experimental and calculated data at the two lowest heating rates tested, 5 and 10 °C/min. The applicability of the model to simulate higher heating rates was also assessed in this figure with a very good agreement between the calculated and experimental data at 100 °C/min. It was observed that the model with the fitted kinetic parameters accurately predicted the shift to higher temperatures of the devolatilisation curves at all the heating rates. The model simulated the entire range of experimental fractions of mass remaining with R^2 higher than 0.999 for all tests. The value of $Dev\%$ was lower than 2.25 for all tests, which was within acceptable ranges ($Dev\% < 4$ is generally acceptable for fitting [55]). Moreover, the model simulated the temperatures required to reach the entire range of fraction of mass remaining to within $\pm 2\%$ of the experimental values, and ΔX was calculated lower than $\pm 8\%$ in all the tests carried out.

This good comparison allowed results to be projected at higher heating rates. Figure 5 shows the results corresponding to 1000 °C/min, which is a heating rate closer to those found in flash pyrolysis processes. The results of all the samples were compared by rate of mass loss (dx/dt), which allows the observation of the main decomposition temperatures with higher values of dx/dt for all the samples. The interaction of radicals from the different samples is favoured when the dx/dt curves of the solids overlap. It is observed in Figure 5 that the major overlap with the curve generated for the PINE sample was obtained with the devolatilisation of the PLA biopolymer, which points to its renewable plant origin. This overlap occurs in the middle region of PINE devolatilisation, where the devolatilisation of cellulose should be taking place. Thus, major interaction between the devolatilisation of polylactic acid and cellulose molecules can be expected during the co-pyrolysis of both materials. An overlap can also be observed between the PINE and WT curves, mostly in the region of

cellulose and lignin from the PINE sample and additives and natural rubber from the WT sample [48]. Finally, an overlap of devolatilisation curves is observed with PS in the latter part of the region of cellulose and lignin devolatilisation. The other plastics produced from fossil sources – PET, PP and HDPE –barely commence their devolatilisation at the temperatures required for full conversion of the PINE sample at a heating rate of 1000 °C/min. Therefore, no major interaction of radicals can be expected during their co-pyrolysis processes. It can also be concluded from Figure 5 that the complete conversion in the flash pyrolysis process of biomass and any of the polymers studied will be reached at a temperature of around 600 °C.

3.2. Kinetic study for the co-pyrolysis of mixtures

The results obtained for pure solids were introduced into the implemented model previously described [42], suitable for feed mixtures comprising two components. In this development, coefficients accounting for the fraction of mass of each pure component were introduced in order to calculate the evolution of the total fraction of mass remaining with temperature in the following equation 5:

$$X_{theo} = aw_a + \sum_i af_{a,i,0} \exp \left[-A_{a,i} \int_0^t \exp \left(\frac{-E_{a,i}}{RT(t)} \right) dt \right] + \\ + bw_b + \sum_i bf_{b,i,0} \exp \left[-A_{b,i} \int_0^t \exp \left(\frac{-E_{b,i}}{RT(t)} \right) dt \right] \quad (5)$$

where, a and b are the fractions of components a and b in the feed mixture. The different parameters are also identified by the subscripts a or b depending on the mixture component. Equation 5 considers an additive effect of pure components at low heating rates to calculate the devolatilisation of the mixture at different proportions and heating rates. The accuracy of this assertion was verified in this work with mixtures of PINE and plastics in different proportions of interest for bio-oil production.

Figure 6 shows the results obtained for mixtures of PINE with all the polymers studied at different proportions and a heating rate of 5 °C/min. The simulation results obtained for the PINE/WT mixture showed highly comparable results to those obtained experimentally. The increase in the proportion of WT did not modify the remarkable fit found between the experimental and the simulated results. Therefore, the model perfectly reproduced the devolatilisation process of the mixture PINE/WT, supporting the additive behaviour of the components with regard to the fraction of mass remaining at a low heating rate, with ΔX lower than $\pm 2\%$. The thermal behaviour of the PINE/PET and PINE/HDPE mixtures was also reproduced with a high accuracy by the model at this low heating rate (ΔX lower than $\pm 2\%$). However, some subtle discrepancies could be observed in other mixtures studied. With regard to the results for mixtures of PINE and PLA given in Figure 6, the small differences observed between the experimental and the simulated data (less than 2% in temperature and ΔX lower than $\pm 6\%$) meant that although it was possible to apply the model to the study of the mixture, the model predicted both a slightly higher fraction of mass remaining at temperatures between 275 °C and 370 °C and a lower value for the residual mass-fraction. These differences increased with the proportion of PLA in the mixture. This shift agrees with previous results observed by Tai and Chen [28] that adding rice straw to PLA effectively reduced the decomposition temperature of the pyrolysis reactions, while the higher amount for the residual mass-fraction could be explained by a promotion of radical interactions that increase the reactivity of the mixture and lead to the formation of char by retrogressive reactions. In the case of the PINE/PS mixture, a different trend was observed from that shown by the PINE/PLA mixture (Figure 6). The simulated fraction of mass remaining at the lower temperatures up to 400 °C compared very well with the experimental results, and the presence of polymer in the mixture did not significantly change the

decomposition curve of the wood. However, at temperatures between 380 °C and 450 °C, the experimental fraction was marginally higher than the simulated fraction, while the residual mass-fraction was correctly predicted by the DAEM. From the results given by the pure components (Figure 4), it can be seen that PS decomposition mainly takes place in this temperature range. Thus, the pyrolysis of the PINE/PS mixture at between 380 °C and 450 °C can be mainly attributed to the contribution from the devolatilisation of PS. This shift to higher temperatures in the presence of lignocellulosic biomass produced a difference between the experimental and theoretical mass loss, ΔX , of $\pm 7\%$ and a $Dev\%$ of 1.5. These results agree with previous conclusions reported by Jakab et al. [18] where an interaction was reported between components. At these temperatures the thermal decomposition of PS takes place by a depolymerisation mechanism with release of a high yield of monomer and small amounts of styrene oligomers formed by radical transfer and subsequent β -scission. This thermal decomposition of PS is hindered in the presence of char arising from the lignocellulosic material [18]. In the case of the PINE/PP mixture, the experimental fraction of mass remaining at temperatures above 430 °C was slightly higher than the simulated fraction (ΔX lower than $\pm 7\%$). This difference can also be mostly attributed to the contribution of plastic devolatilisation because the main stages of decomposition of the wood ends before the PP starts to degrade. It has been proposed that the pyrolysis pattern of PP is a free radical degradation mechanism of the polymer chain involving thermal initiation, propagation, intramolecular and intermolecular transfer and termination of radicals. Only the slow charring reaction of wood, mainly from the lignin constituent of the sample, still takes place within the temperature range of polymer decomposition [13, 17, 18]. The small effect of biomass on PP thermal decomposition has been reported to increase the decomposition temperature because of a delay in

biomass residue dehydration reaction due to hydrogen type interactions between solids and thermal stabilisation effect of biomass char [13], which concurs with this work. Zhou et al. [25] also found that the reaction of hydrogen transferring from a polyolefin chain to biomass-derived radicals would stabilise the primary products from biomass degradation. This would result in higher weight loss and lower yield of char.

Experiments at a higher heating rate of 100 °C/min were performed to study the application of the kinetic model to describe the thermal behaviour of the mixtures outside of the fitting conditions (see Figure 7). This approach ensures a more rigorous validation test for computed kinetic parameters, as suggested by S. Vyazovkin et al. [56]. The experimental results obtained from the PINE/WT and PINE/PET mixtures showed remarkably comparable results to those obtained by simulation for the tests performed. Neither the increase in the proportion of polymer nor the increase in the heating rate modified the remarkable fit observed at this high heating rate. Results from PINE with either PLA or PS at this high heating rate were in line with those previously obtained at the low heating rate. Thus, for PLA it was observed that the model predicted a higher fraction of mass remaining at temperatures from 300 °C to 420 °C and a lower final fraction of mass remaining (ΔX lower than $\pm 8\%$). For PS the model predicted a lower fraction of mass remaining at temperatures attributed to polymer decomposition. It must be pointed out that the difference between experimental and predicted results decreased with the increasing heating rate, which supports the reliability of the model for application at high heating rates (ΔX lower than $\pm 4\%$). In the cases of PP and HDPE different trends were observed compared to results at the lower heating rate, with increasing percentages of polymer in the mixtures. On the one hand, the thermal behaviour of the PINE/PP mixture at this higher heating rate was perfectly simulated by the kinetic model for the two percentages of polymer studied. On the other hand, the

mixture of PINE with HDPE required experimentally lower temperatures than that predicted by the model mainly at a fraction of mass remaining lower than 0.4 related to polymer decomposition (ΔX lower than $\pm 5\%$). The experimental final fraction of mass remaining obtained for mixtures of biomass with plastics PS, PET, PP and HDPE was slightly lower than those predicted, in agreement with Zhou et al. [25]. This result was also observed by J. Chattopadhyay et al. [6] in co-pyrolysis of paper biomass with PET, PP and HDPE. Initially, cellulose (the main component of paper and the PINE sample) starts radical formation during the co-pyrolysis reaction, resulting in the scission of the polymer chain. The hydrogen present in the plastic materials transfers from the polyolefin chain to the biomass-derived radicals, resulting in higher weight loss and lower yield of char [6]. Despite the differences between the experimental and modelled results, it should be highlighted that for all the tests performed with mixtures of PINE and WT, PLA, PS, HDPE, PP and PET at different heating rates and weight proportions, the model produced trends in remarkably good agreement with the experimental data. The model accurately reproduced the shape of the fraction of mass remaining profiles, the shift to higher temperatures with increasing heating rates and the residual mass-fraction with a regression coefficient R^2 higher than 0.99. The values of $Dev\%$ were less than 2.75 in all the cases, indicating a very high accuracy of the model simulations. The model also simulated the temperatures required to produce the entire range of conversion within 3% of the experimental values, and ΔX was less than $\pm 8\%$. This value of ΔX was highly accurate, in line with the results previously reported in co-pyrolysis processes, which ranged from $\pm 4\%$ to $\pm 34\%$, depending on the components, proportions and heating rates [5, 22, 24, 25]. The generated profiles also concurred remarkably, compared to those previously reported by Oyedun et al. [5], which

simulated a comparable trend to the experimental mass loss profiles and the profiles calculated, assuming the additional behaviour of components in the mixture.

The model demonstrated its ability to produce close projections at different proportions of PINE/Polymer of interest for bio-oil production at high heating rates. Thus, the calculated rates of mass loss in Figure 8 were compiled at a heating rate of 1000 °C/min for the 80/20 wt% biomass/plastic mixtures. It was observed that PLA greatly increased the rate of mass loss for the pure PINE. It can therefore be assumed that the devolatilisation of both materials took place simultaneously. Similarly, the rate of mass loss of the PINE/WT mixture was also mainly produced in the same temperature range as that of pure PINE. With regard to the plastics synthesised from fossil sources, only the devolatilisation of PS was cohabitant with the devolatilisation of PINE, but the final pyrolysis temperature should be increased (550 °C) to ensure the total decomposition of both components. The main decomposition temperatures of the PET, PP and HDPE identified in the second main degradation region of rate of mass loss lay outside of the temperature range of PINE pyrolysis. Therefore, the presence of radical interaction is mainly expected for three of the initially proposed plastics, PLA, WT and PS, which in turn, may lead to a bio-oil with improved properties. It can also be concluded from Figure 8 that the complete conversion in the flash co-pyrolysis process of the blends will be reached at a temperature slightly below 600 °C as determined from projections of single solids.

4. Conclusions

The distributed activation energy model, DAEM, has been successfully applied to the study of the co-pyrolysis of mixtures from data of pure components comprising lignocellulosic biomass and six different plastics (WT, PLA, PS, PET, PP and HDPE).

The model simulated the entire range of the experimental fraction of mass remaining of pure solids at fitted conditions and higher heating rates with a very high accuracy, indicated by $Dev\% < 2.25$ and $\Delta X < 8\%$. With regard to blend decomposition simulation, the DAEM accurately reproduced the shape of the fraction of mass remaining curves as well as the shift to higher temperatures with increasing heating rate and residual mass-fraction. For all the tests performed, the values obtained for $Dev\%$ and ΔX were lower than 2.75 and 8%, respectively. Outside of the fitting conditions, under high heating rate, the remarkable agreement between the experimental data and the simulated data by the DAEM allow the reliable application of the model to simulate decomposition of these solids and their mixtures under flash pyrolysis conditions. From the comparison of calculated and experimental data, no interaction was observed for the thermal decomposition of the mixture of PINE/WT, negligible interactions with PET, PP or HDPE, and only some slight interactions with PLA. The PINE/PS blend showed interactions at temperatures above 400 °C mainly related to hindered PS decomposition in the presence of char arising from the lignocellulosic material.

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REFERENCES

- [1] Zhang Q, Li Q, Zhang L, Yu Z, Jing X, Wang Z, Fang Y, Huang W. Experimental study on co-pyrolysis and gasification of biomass with deoiled asphalt. *Energy* 2017;134:301-310.
- [2] Choi D, Oh J-I, Baek K, Lee J, Kwon E.E. Compositional modification of products from Co-Pyrolysis of chicken manure and biomass by shifting carbon distribution from pyrolytic oil to syngas using CO₂. *Energy* 2018;153:530-538.
- [3] Xing S, Yuan H, Huhetaoli, Qi Y, Lv P, Yuan Z, Chen Y. Characterization of the decomposition behaviors of catalytic pyrolysis of wood using copper and potassium over thermogravimetric and Py-GC/MS analysis. *Energy* 2016;114:634-646.
- [4] Abnisa F, Daud WNA. A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. *Energy Convers Manag* 2014;87:71-85.
- [5] Oyedun OA, Gebreegziabher T, Ng DKS, Hui CW. Mixed-waste pyrolysis of biomass and plastics waste e A modelling approach to reduce energy usage. *Energy* 2014;75:127-135.
- [6] Chattopadhyay J, Pathak TS, Srivastava R, Singh AC. Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE (high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate)) and product analysis. *Energy* 2016;103:513-521.
- [7] Guo F, Li X, Wang Y, Liu Y, Li T, Guo C. Characterization of Zhundong lignite and biomass co-pyrolysis in a thermogravimetric analyzer and a fixed bed reactor. *Energy* 2107;141:2154-2163.
- [8] Hassan H, Lim JK, Hameed BH. Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil. *Bioresour Technol*, 2016;221:645-655.
- [9] Wong SL, Ngadi N, Abdullah TAT, Inuwa IM. Current state and future prospects of plastic waste as source of fuel: a review. *Renew Sust Energ Rev* 2015;50:1167-1180.
- [10] Onal E, Uzun BB, Putun AE. Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene. *Energy convers Manag* 2014;78:704-10.
- [11] Martínez JD, Veses A, Mastral AM, Murillo R, Navarro MV, Puy N, Artigues A, Bartroli J, García T. Co-pyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. *Fuel Proces Technol* 2014;119:263-271.
- [12] Dorado C, Mullen CA, Boateng AA. H-ZMS5 catalyzed co-pyrolysis of biomass and plastics. *ACS Sustainable Chem Eng* 2013;2:301-11.

- [13] Aboulkas A, El harfi K, El bouadili A, Nadifiyine M, Benchanaa M, Mokhlisse A. Pyrolysis kinetics of olive residue/plastic mixtures by non-isothermal thermogravimetry. *Fuel Process Technol* 2009;90:722-728.
- [14] Sharypov VI, Marin N, Beregovtsova NG, Baryshnikov SV, Kuznetsov BN, Cebolla VL, Weber JV. Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases. *J Anal Appl Pyrol* 2002;64:15–28.
- [15] Abnisa F, Wan Daud WMA, Ramalingam S, Azemi MNBM, Sahu JN. Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesis liquid fuel. *Fuel* 2013;108:311–318.
- [16] Ansah E, Wang L, Shahbazi A. Thermogravimetric and calorimetric characteristics during co-pyrolysis of municipal solid waste components. *Waste Manag* 2016;56:196–206.
- [17] Jakab E, Varhegyi G, Faix O. Thermal decomposition of polypropylene in the presence of wood-derived materials. *J Anal Appl Pyrol* 200;56:273-285.
- [18] Jakab E, Blazso M, Faix O. Thermal decomposition of mixtures of vinyl polymers and lignocellulosic materials. *J Anal Appl Pyrol* 2001;58-59:49-62.
- [19] Aboulkas A, El Harfi K, El Bouadili A. Non-isothermal kinetic studies on co-processing of olive residue and polypropylene. *Energy Convers Manag* 2008;49:3666-3671.
- [20] Oyedun AO, Tee CZ, Hanson S, Hui CW. Thermogravimetric analysis of the pyrolysis characteristics and kinetics of plastics and biomass blends. *Fuel Proces Technol* 2014;128:471–481.
- [21] Chattopadhyay J, Kim C, Kim R, Pak D. Thermogravimetric characteristics and kinetic study of biomass co-pyrolysis with plastics. *Korean J Chem Eng* 2008;25(5):1047-1053.
- [22] Xiong S, Zhuo J, Zhou H, Pang R, Yao Q. Study on the co-pyrolysis of high density polyethylene and potato blends using thermogravimetric analyzer and tubular furnace. *J Anal Appl Pyrol* 2015;112:66–73.
- [23] Zhang X, Lei H, Zhu L, Zhu X, Qian M, Yadavalli G, Wu J, Chen S. Thermal behavior and kinetic study for catalytic co-pyrolysis of biomass with plastics. *Bioresour Technol* 2016;220:233–238.
- [24] Rotliwala YC, Parikh PA. Thermal degradation of rice-bran with high density polyethylene: A kinetic study. *Korean J Chem Eng* 2011;28(3):788-792.

- [25] Zhou L, Wang Y, Huang Q, Cai J. Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis. *Fuel Proces Technol* 2006;87:963–969.
- [26] Han B, Chen Y, Wu Y, Hua D, Chen Z, Feng W, Yang M, Xie Q. Co-pyrolysis behaviors and kinetics of plastics–biomass blends through thermogravimetric analysis. *J Therm Anal Calorim* 2014;115:227–235.
- [27] Çepeliogullar O, Pütün AE. Thermal and kinetic behaviors of biomass and plastic wastes in co-pyrolysis, *Energy Convers Manag* 2013;75:263–270.
- [28] Tai HS, Chen CY. Kinetic study of copyrolysis of waste polyethylene terephthalate, polylactic acid and rice straw. *Env Eng Sci* 2016;33(9):671-680.
- [29] Suriapparao DV, Ojha DK, Ray T, Vinu R. Kinetic analysis of co-pyrolysis of cellulose and polypropylene. *J Therm Anal Calorim* 2014;117:1441–1451.
- [30] Narobe M, Golob J, Klinar D, Francetic V, Likozar B. Co-gasification of biomass and plastics: Pyrolysis kinetics studies, experiments on 100 kW dual fluidized bed pilot plant and development of thermodynamic equilibrium model and balances. *Bioresour Technol* 2014;162:21–29.
- [31] Burra KG, Gupta AK. Kinetics of synergistic effects in co-pyrolysis of biomass with plastic wastes. *Applied Energy* 2018;220:408-418.
- [32] Oyedun AO, Gebreegziabher T, Hui CW. Mechanism and modelling of bamboo pyrolysis. *Fuel Proces Technol* 2013;106:595-604.
- [33] Sobone T, Worasuwanarak N. Kinetic analyses of biomass pyrolysis using the distributed activation energy model. *Fuel* 2008;87:414-421.
- [34] Mani T, Murugan P, Mahinpey N. Determination of distributed energy model kinetic parameters using simulated annealing optimization method for nonisothermal pyrolysis of lignin. *Ind Eng Chem Res* 2008;48:1464-1467.
- [35] Wang S, Dai G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Prog Energy Comb Sci* 2017;62:33-86.
- [36] Cai J, Wu W, Liu R. An overview of distributed activation energy model and its application in the pyrolysis of lignocellulosic biomass. *Renew Sust Energy Rev* 2014;36:236–246.
- [37] Varhegyi G, Szabo P, Antal MJ Jr. Kinetics of charcoal devolatilization. *Energy Fuels* 2002;16:724-731.
- [38] Navarro MV, Martínez JD, Murillo R, García T, López JM, Callén MS, Mastral AM. Application of a particle model to pyrolysis. Comparison of different feedstock: Plastic, tyre, coal and biomass. *Fuel Proces Technol* 2012;103:1-8.

- [39] Meng A, Chen S, Long Y, Zhou H, Zhang Y, Li Q. Pyrolysis and gasification of typical components in wastes with macro-TGA. *Waste Manag* 2015;46:247–256.
- [40] Che T, Wu W, Wu J, Cai J, Wu J. Determination of the pseudocomponents and kinetic analysis of selected combustible solid wastes pyrolysis based on Weibull model. *J Therm Anal Calorim* 2016;126:1899-1909.
- [41] Liu S, Yu J, Bikane K, Chen T, Ma C, Wang B, Sun L. Rubber pyrolysis: Kinetic modeling and vulcanization effects. *Energy* 2018;155:215-225.
- [42] Navarro MV, Aranda A, García T, Murillo R, Mastral AM. Application of the distributed activation energy model to blends devolatilisation. *Chem Eng J* 2008;142:87-94.
- [43] Fang S, Yu Z, Ma X, Lin Y, Chen L, Liao Y. Analysis of catalytic pyrolysis of municipal solid waste and paper sludge using TG-FTIR, Py-GC/MS and DAEM (distributed activation energy model). *Energy* 2018;143:517-532.
- [44] Goldfarb JL, Ceylan S. Second-generation sustainability: Application of the distributed activation energy model to the pyrolysis of locally sourced biomass-coal blends for use in co-firing scenarios. *Fuel* 2015;160:297-308.
- [45] Navarro MV, Murillo R, Mastral AM, Puy N, Bartroli J. Application of the Distributed Activation Energy Model to Biomass and Biomass Constituents Devolatilization. *AIChE J* 2009;55:2700-2715.
- [46] Cai J, Wu W, Liua R, Huber GW. A distributed activation energy model for the pyrolysis of lignocellulosic biomass. *Green Chem* 2013;15:1331-1340.
- [47] Heydari M, Rahman M, Gupta R. Kinetic Study and Thermal Decomposition. Behavior of Lignite Coal. *Int J Chem Eng* 2015;481739:1-9.
- [48] Aylón E, Callén MS, López JM, Mastral AM, Murillo R, Navarro MV, Stelmach S. Assessment of tire devolatilization kinetics. *J Anal Appl Pyrol* 2005;74:259-264.
- [49] Murillo R, Aylón E, Navarro MV, Callén MS, Aranda A, Mastral AM. The application of thermal processes to valorise waste tyre. *Fuel Proces Technol* 2006;87:143–147.
- [50] Williams PT, Besler S. Pyrolysis-thermogravimetric analysis of tyres and tyre components. *Fuel* 1995;74(9):1277–1283.
- [51] Seidelt S, Müller-Hagedorn M, Bockhorn H. Description of tire pyrolysis by thermal degradation behaviour of main components. *J Anal Appl Pyrol* 2006;75:11–18.

- [52] Zou H, Yi C, Wang L, Liu H, Xu W. Thermal degradation of poly(lactic acid) measured by thermogravimetry coupled to Fourier transform infrared spectroscopy. *J Therm Anal Calorim* 2009;97:929–935.
- [53] Diaz Silvarrey LS, Phan AN. Kinetic study of municipal plastic waste. *Int. J. Hydrogen Energy* 2016;41:16352-16364.
- [54] Scott SA, Dennis JS, Davidson JF, Hayhurst AN. An algorithm for determining the kinetics of devolatilisation of complex solid fuels from thermogravimetric experiments. *Chem Eng Sci* 2006;61:2339-2348.
- [55] Zhang J, Chen T, Wu J, Wu J. A novel Gaussian-DAEM-reaction model for the pyrolysis of cellulose, hemicellulose and lignin. *RSC Adv* 2014;4:17513-17520.
- [56] Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda L.A, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta* 2011;520:1-19.

Table 1

Proximate, ultimate analyses (wt%) and calorific value (MJ/kg) of stabilised samples (as received).

	PINE	WT	PLA	PS	PET	PP	HDPE
Moisture	6.3	1.1	0.4	0.5	0.4	0.2	0.1
Ash	0.6	8.1	0.0	0.3	0.1	0.1	0.0
Volatiles	77.6	62.5	99.3	99.0	89.2	99.8	100.0
Fixed carbon*	15.5	28.2	0.3	0.2	10.3	0.0	0.0
Carbon	49.7	84.6	51.1	97.9	62.7	85.4	85.5
Hydrogen	6.6	7.7	5.8	8.3	4.4	14.5	14.5
Nitrogen	0.1	0.4	0.0	0.0	0.0	0.0	0.0
Sulphur	0.0	1.2	0.0	0.0	0.0	0.0	0.0
Oxygen	44.4	4.3	44.0	0.0	32.8	0.0	0.0
HHV	19.2	36.8	18.4	41.0	23.0	46.0	46.4
LHV	17.6	35.1	17.2	39.3	22.2	43.1	43.1

*by difference

HHV. Higher heating value

LHV. Lower heating value

Table 2

Pyrolysis kinetic parameters from the DAEM algorithm fitting of experimental results at 5 and 10 °C/min.
Values calculated at the main mass-fraction other than residual mass-fraction.

	E, kJ/mol	A, s ⁻¹	f
PINE	254.2	4.64·10+18	0.15
WT	302.8	1.40·10+22	0.06
PLA	235.8	1.63·10+17	0.93
PS	314.4	3.74·10+21	0.94
PET	275.8	1.80·10+18	0.81
PP	279.4	7.98·10+17	0.78
HDPE	361.6	1.22·10+23	0.75

Fig. 1. TG curves of a) PINE and b) WT samples at different heating rates. Inset: corresponding rate of mass loss curves.

Fig. 2. TG curves of PLA, PS, PET, PP and HDPE samples at different heating rates. Inset: corresponding rate of mass loss curves.

Fig. 3. Pyrolysis kinetic parameters from the DAEM algorithm fitting of experimental results at 5 °C/min and 10 °C/min. E_a , $\log A$ and mass-fraction allocated vs. fraction of mass remaining for PINE wood and WT samples.

Fig. 4. Fraction of mass remaining vs Temperature of pure solids. Comparison of experimental data (points) and curves generated (lines) with the DAEM algorithm at 5 °C/min, 10 °C/min and 100 °C/min.

Fig. 5. Rate of mass loss vs Temperature of pure solids. Comparison of curves generated at 1000 °C/min heating rate.

Fig. 6. Fraction of mass remaining vs Temperature biomass/plastic mixtures of different ratios. Comparison of experimental data (points) and curves generated (lines) with the DAEM algorithm at 5 °C/min.

Fig. 7. Fraction of mass remaining vs Temperature biomass/plastic mixtures of different component ratios. Comparison of experimental data (points) and curves generated (lines) with the DAEM algorithm at 100 °C/min.

Fig. 8. Rate of mass loss vs Temperature. Comparison of curves generated for biomass/plastic mixtures of 80:20 wt% at 1000 °C/min heating rate.