Kinetic Study of Thermal Degradation of a Lignin Nanoparticle-Reinforced Phenolic Foam

Juan C. Domínguez, Belén Del Saz-Orozco, María V. Alonso, Mercedes Oliet, Francisco Rodríguez

Abstract—In the present study, the kinetics of thermal degradation of a phenolic and lignin reinforced phenolic foams, and the lignin used as reinforcement were studied and the activation energies of their degradation processes were obtained by a DAEM model. The average values for five heating rates of the mean activation energies obtained were: 99.1, 128.2, and 144.0 kJ.mol^{-1} for the phenolic foam; 109.5, 113.3, and 153.0 kJ.mol^{-1} for the lignin reinforcement; and 82.1, 106.9, and 124.4 kJ.mol^{-1} for the lignin reinforced phenolic foam. The standard deviation ranges calculated for each sample were 1.27-8.85, 2.22-12.82, and 3.17-8.11 kJ.mol^{-1} for the phenolic foam, lignin and the reinforced foam, respectively. The DAEM model showed low mean square errors ($<1 \times 10^{-5}$), proving that is a suitable model to study the kinetics of thermal degradation of the foams and the reinforcement.

Keywords—Kinetics, lignin, phenolic foam, thermal degradation.

I. INTRODUCTION

PHENOLIC foams show high thermal stability in a broad range of temperature, excellent fire properties (low flammability, no dripping combustion and low smoke density) and low thermal conductivity. These materials are usually employed in insulating and structural applications where fire resistance is critical, such as in buildings and aircrafts. Therefore, the thermal degradation of phenolic foams is an important field to study for its final application. In the present work, the kinetics of thermal degradation of a lignin nanoparticle reinforced phenolic foam, and its main components, a phenolic foam (used as matrix) and lignin employed as reinforcement, were studied in order to compare their thermal stability and to determine if the reinforcement enhanced the final properties of the foam. The mean activation energies of the degradation processes were obtained by applying a DAEM model to the experimental data obtained using five different heating rates.

II. DESCRIPTION OF THE MODEL

A. Kinetic Models

Chemical reactions, such as the degradation process of a composite material, are commonly described by a single step kinetic equation where the influence of temperature and conversion are described by two independent functions [1]:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{1}$$

$$\alpha(t) = \frac{w_0 - w_t}{w_0 - w_f} \tag{2}$$

where α represents the conversion (defined as the ratio between the instant mass loss and the total mass loss); t is the time; $k(T)$ is the rate constant, which depends on temperature; w_0, and w_f, w_t are initial, final mass of the sample and its mass at a certain time, respectively; and $f(\alpha)$ is the process mechanism function. $k(T)$ is usually assumed to follow Arrhenius behavior, as described by (3):

$$k(T) = k_0 \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \tag{3}$$

where E_a is the activation energy of the process, T is the temperature at a fixed conversion, R is the universal gas constant, and k_0 is the pre-exponential factor.

B. DAEM Model

The modeling of degradation processes can be described by using a model that use a distribution of the activation energy of the process instead a constant value. These models are called distribution energy models (DAEM) and the original model was described by [2], and it is a quite interesting option to study the kinetics of thermal degradation processes that has been frequently used in the literature with coal, biomass and other thermally degradable materials. This model states that decomposition takes places through a number of independent, parallel, and nth order (commonly the reaction order is fixed to 1) reactions with different activation energies. These activation energies are usually described by a continuous distribution function [3], [4]. The model equation that expresses the DAEM model for non-isothermal process and assuming a constant reaction order of 1 is given by (4):

$$\alpha(T) = \int_0^\infty \left\{ 1 - \exp\left[-\frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E_a}{R \cdot T}\right) dT \right] \right\} f(E_a) dE_a \tag{4}$$

where β is the heating rate, and $f(E)$ is the activation energy distribution.

In the literature, four distribution functions are found for the DAEM model: the Gaussian distribution (also called normal distribution), the Weibull distribution, the Gamma distribution

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and the Logistic distribution [4], [5]. Probably, the most popular activation energy distribution is the Gaussian distribution, described by (5):

$$f\left(E_a\right)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{\left(E_a-E_{a_0}\right)^2}{2\sigma^2}\right] \quad (5)$$

The Gaussian distribution is defined by two parameters: the mean activation energy (E_{a0}) and the standard deviation (σ). One of the main properties of the Gaussian distribution, which in certain cases turns into a disadvantage when modeling reacting systems, is that is a symmetric function. When reactivity distributions tend to be asymmetric, the Weibull, Gamma and Logistic distributions are used instead [4].

The activation energy distribution can be also estimated by multi-DAEM models where the total distribution, $f(E)$, is calculated as a linear combination of single distributions. This combination is commonly employed when the DTG curves obtained for the degradation processes show more than one peak [5], [6]. The following equation is used for the total distribution function:

$$f\left(E_a\right)=\sum_{j=1}^{n}c_jf_j\left(E_a\right)\bigg/\sum_{j=1}^{n}c_j \quad (6)$$

where c_j represents the fraction of volatiles produced by the jth distribution function, and n is the number of functions. Multi-Gaussian DAEM models are also a useful option to describe asymmetric reactivity distributions instead of using other distribution functions as previously mentioned (depending on the number of Gaussian distributions linearly combined the number of parameters of the model might be reduced compared to the application of other type of function, i.e. the model could be more simple and therefore more suitable to be employed in the modeling of the degradation process).

III. EXPERIMENTAL PROCEDURE

Thermogravimetric analyses (TGA) of a 8.5 wt.% lignin nanoparticle reinforced phenolic foam (LRPF), a phenolic foam (PF) and the lignin used as reinforcement were performed in a Mettler-Toledo TGA/DSC1. Dynamic temperature runs were carried out from 30 to 900°C at 6, 8, 10, 12 and 14°C.min^{-1} heating rates under nitrogen atmosphere. The multi-Gaussian-DAEM model (3-Gaussian) was used to obtain the distribution of the activation energy of the degradation process of both foams and the reinforcement.

IV. RESULTS AND DISCUSSION

The study of thermal degradation and the determination and analysis of the stages of degradation of LRPF and PF foams and the lignin was performed using the thermograms (TG) obtained at the 5 heating rates and the calculated derivative of TG curves (DTG curves). In Figs. 1 (a), (b), thermograms and DTG curves, respectively, are shown for each of the studied materials at a 10 °C.min^{-1} heating rate.
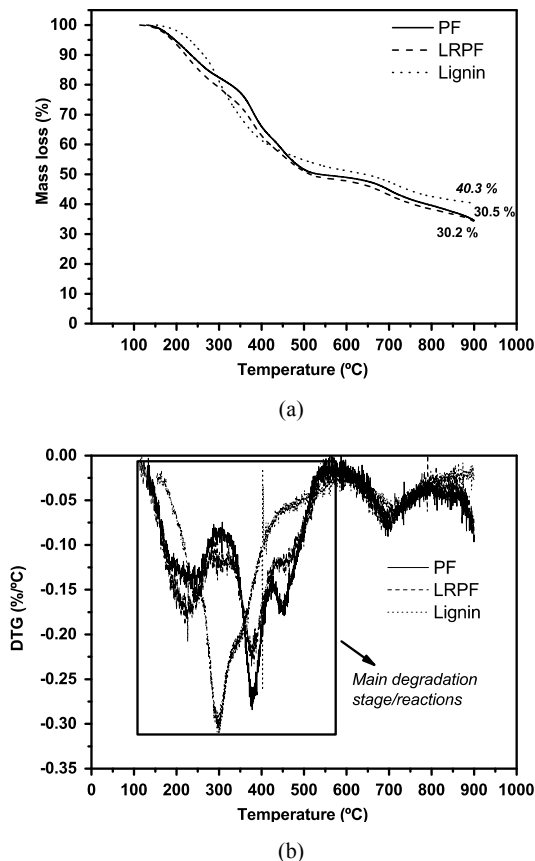

(a)

(b)

Fig. 1 TG (a) and DTG (b) curves for LRPF, PF and lignin

The main stages of degradation for the materials under study were determined, as shown in Fig. 1 (b). Conversion of the process was calculated from these experimental data using (2); conversion was plotted versus temperature, as shown in Fig. 2 for a heating rate of 10 C.min^{-1}.

The DAEM model was applied to the experimental conversions. A multi-DAEM model was chosen as the most suitable model to be applied since, from the DTG curves, three peaks, associated to three degradation reactions, were found for the main degradation stage of the materials. The chosen distribution function was the Gaussian function, widely employed in the modeling of thermal degradation processes of biomass. Therefore, a 3-Gaussian DAEM model was applied to the experimental data for LRPF, PF and lignin.

A least-squares minimization algorithm was used to estimate the parameters of the model, evaluating the model for 100 conversion values. Fig. 2 shows that the 3-Gaussian DAEM model reproduced very well the experimental data for the degradation process of all the materials. In Table I the kinetic parameters calculated for the model are exhibited. The mean square errors were calculated as a parameter to evaluate the quality of the fits and low values ($<1\times10^{-5}$) were for this parameter. The low mean square errors were in agreement the good fits shown in Fig. 2.
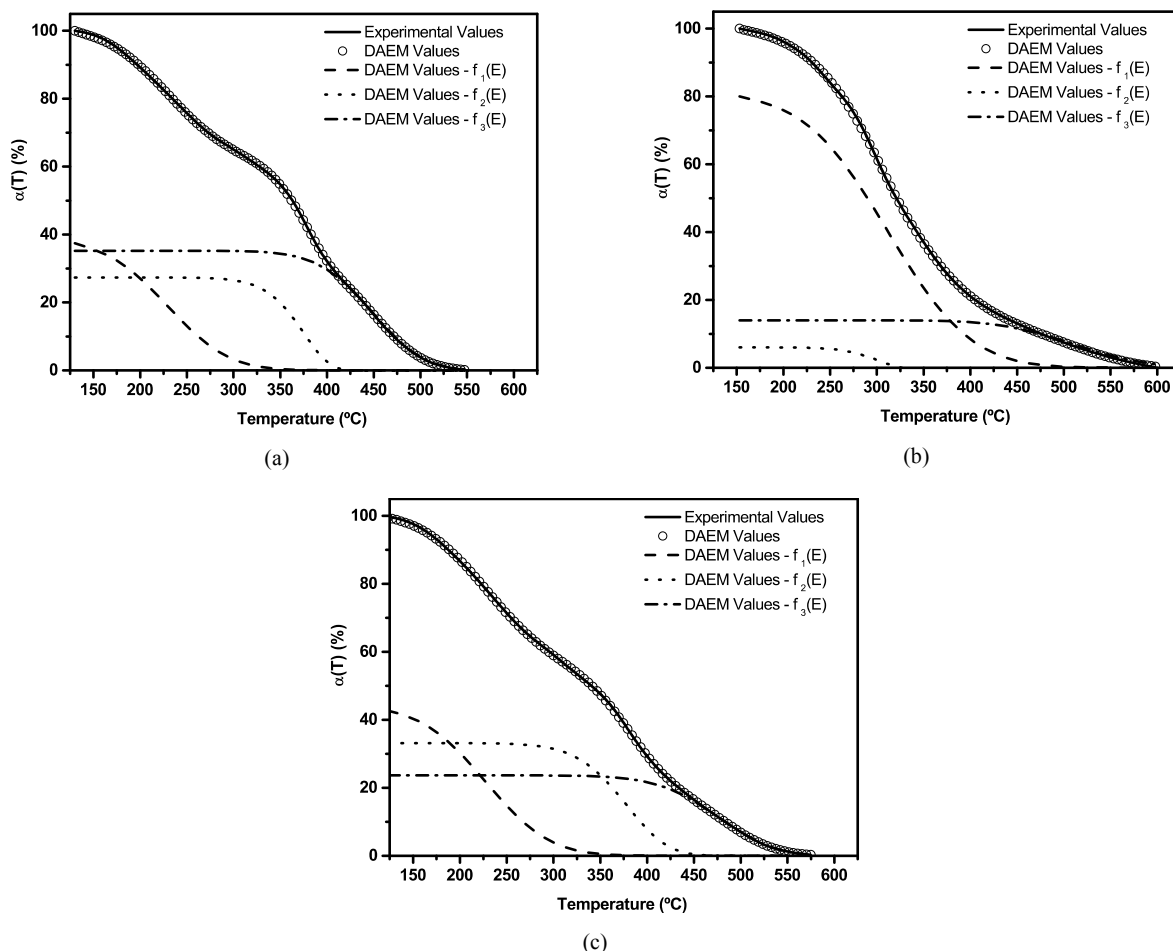
(a)

(b)

(c)

Fig. 2 DAEM predictions for conversion vs. temperature: (a) PF foam, (b) lignin reinforcement, and (c) LRPF foam

In Fig. 2, together with the conversions estimated using the DAEM model for the total $f(E)$ function calculated by (6), the conversion values corresponding to the individual contributions of each of the three distribution functions are exhibited. These values were calculated from the mean activation energies and the standard deviations and the c_j parameters of the DAEM model, shown all of them in Table I.

TABLE I
KINETIC PARAMETERS OF THE MATERIALS OBTAINED BY THE DAEM MODEL

Parameter	Lignin	PF	LRPF
$Ln(k_0)$	21.87	22.56	18.41
E_{a1} (kJ.mol^{-1})	113.3	99.1	82.1
E_{a2} (kJ.mol^{-1})	109.5	128.2	106.9
E_{a3} (kJ.mol^{-1})	153.0	144.0	124.4
σ_1 (kJ.mol^{-1})	12.82	8.85	8.11
σ_2 (kJ.mol^{-1})	2.22	1.27	3.17
σ_3 (kJ.mol^{-1})	9.79	6.76	5.89
c_1	0.795	0.365	0.436
c_2	0.067	0.276	0.319
c_3	0.137	0.359	0.244

The mean activation energies of the three Gaussian distribution of the DAEM model (113.3, 109.5, and 153.0 kJ.mol^{-1}) obtained for lignin were within the usual values found in literature for the thermal degradation of lignin under inert atmosphere: e.g. 101.0 kJ.mol^{-1} [7], 58.6-291.6 kJ.mol^{-1} [8], 135 kJ.mol^{-1} [9]. For the PF, the mean activation energies of its degradation process are in good agreement with activation energies found in the literature for other foams, such as polystyrene (113.2 kJ.mol^{-1} [10], and 116.4 kJ.mol^{-1} [11])).

The cumulative distribution functions (for each Gaussian distribution and for the 3-Gaussian model distribution, i.e. the total distribution of the model $f(E)$) and the total probability density functions for PF, LRPF and the lignin reinforcement are shown in Fig. 3.
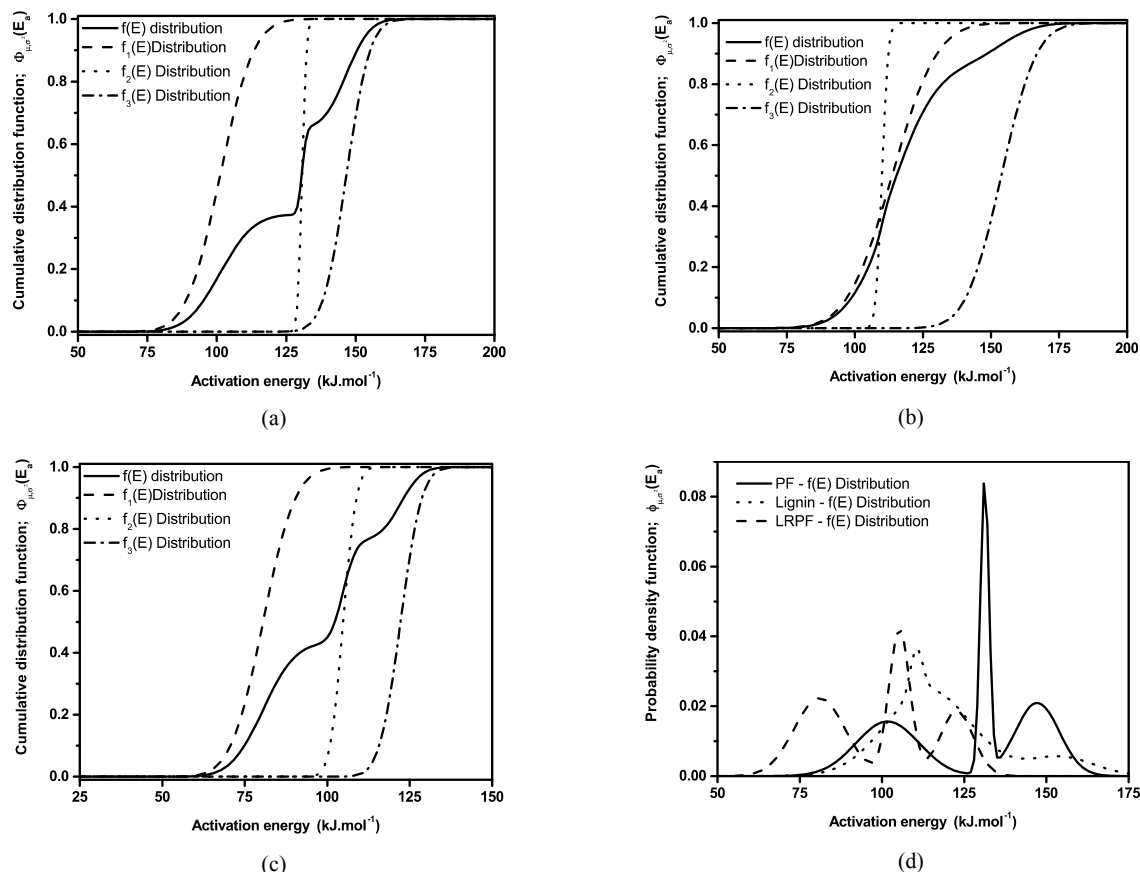
Fig. 3 DAEM cumulative distribution functions vs. activation energy: (a) PF foam, (b) lignin reinforcement, and (c) LRPF foam (d) DAEM probability density functions for PF, lignin and LRPF

The cumulative distributions of the activation energy for the PF and LRPF had a similar shape and with three clearly separated individual cumulative functions for each of the Gaussian distributions. Therefore, there was no overlapping between the distribution function, as becomes clear in Fig. 3 (d) where three individual peaks were found for the probability density functions of the activation energy for PF and LRPF. For the second individual cumulative function of LRPF, a broader distribution was found than the same cumulative function for the PF foam. This increase of the standard deviation of the distribution function can be probably related to the influence of the lignin reinforcement. For lignin, the first and the second distributions clearly overlapped, as it is shown in Fig. 3 (d), where only two peaks are found for the density function of the total distribution function, $f(E)$. This broad peak for density function of lignin overlapped with the second and third peaks obtained for the density function of the activation energies calculated for the LRPF foam, which supported the previously mentioned influence of lignin on the LRPF foam. Summarizing, the addition of lignin as reinforcement to the reference foam resulted in a broader density function for the activation energy of the kinetics of the thermal degradation process of LRPF, with peaks less sharp than those found for the PF.

V. CONCLUSION

The 3-Gaussian DAEM model is a suitable option to model the thermal degradation process of PF and LRPF foams. The model also showed good fits when used to describe the main degradation stage of lignin from *Pinus radiata*, as widely found in previous works for other biomass. The mean activation energies obtained by the model for the foams (99.1, 128.2, and 144.0 kJ.mol^{-1} for the PF and 82.1, 106.9, and 124.4 kJ.mol^{-1} for the LRPF) and the lignin reinforcement (109.5, 113.3, and 153.0 kJ.mol^{-1}) are in good agreement with the values found in the literature.

The kinetics of the degradation process of the LRPF is modified with respect to the PF foam due to the use of lignin as reinforcement of the foam, as its distribution function shifted to lower values for the activation energy of the process shows.

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