

# Thermal Stability and Pyrolysis Kinetics of Lignin-Phenol-Formaldehyde Resins

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Received 5 August 2010; accepted 29 April 2011

DOI 10.1002/app.34817

Published online 2 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A thermal stability and kinetic study from non-isothermal experiments of a commercial and a lignin-novolac resin mixed with two amounts of curing agent has been done employing thermogravimetric analysis technique. Three kinetic models have been tested: a single heating rate method, such as Coats-Redfern, employing several mechanistic functions and contrasted with Van Krevelen—it is the first time that this method has been employed in polymer degradation. Finally, the Ozawa method allowed the obtaining of the activation energy by the multiple-heating-rate without knowing the mechanism.

Results show that commercial mixtures of resins lose less weight than lignin-novolac resins. The calculated kinetic parameters showed that Coats-Redfern gives similar results to Van Krevelen, which means that these methods are adequate for novolac pyrolysis, and Ozawa shows activation energies in accordance with the last mentioned models. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3036–3045, 2012

**Key words:** novolac; TGA; ammonium lignosulphonate; Coats-Redfern; Van Krevelen; Ozawa

## INTRODUCTION

Phenolic resins are thermoset polymers obtained mainly by condensation of phenol and formaldehyde. There are two types of phenolic resins depending on the phenol (Ph) and formaldehyde (F) molar ratio. Novolac resins are synthesized in acid pH with molar ratio Ph/F > 1, and resol resins are prepared in basic pH with an excess of formaldehyde. Many researchers have substituted Ph by a phenol-like compound (lignin) in phenolic resins due to continuous increases in its cost and seeking the minimum possible amount of it within the resin. Ammonium lignosulphonate is the most suitable among many different types of lignosulphonate to substitute phenol because, apart from other reasons,<sup>1</sup> final properties of phenolic resins are better when ammonium lignosulphonate is used instead of calcium and sodium lignosulphonate.<sup>2</sup>

Phenolic resins are widely employed as adhesives for wood industry, house insulation, and textile felts for car industry. Among these industrial applications, textile-felts are not very known and this work is focused on this employment of resins. These phenolic resin-bonded textile felts can be considered as fiber-reinforced plastic with high fiber loading. The

fibers employed are textile scraps recycled from the textile industry.<sup>3</sup>

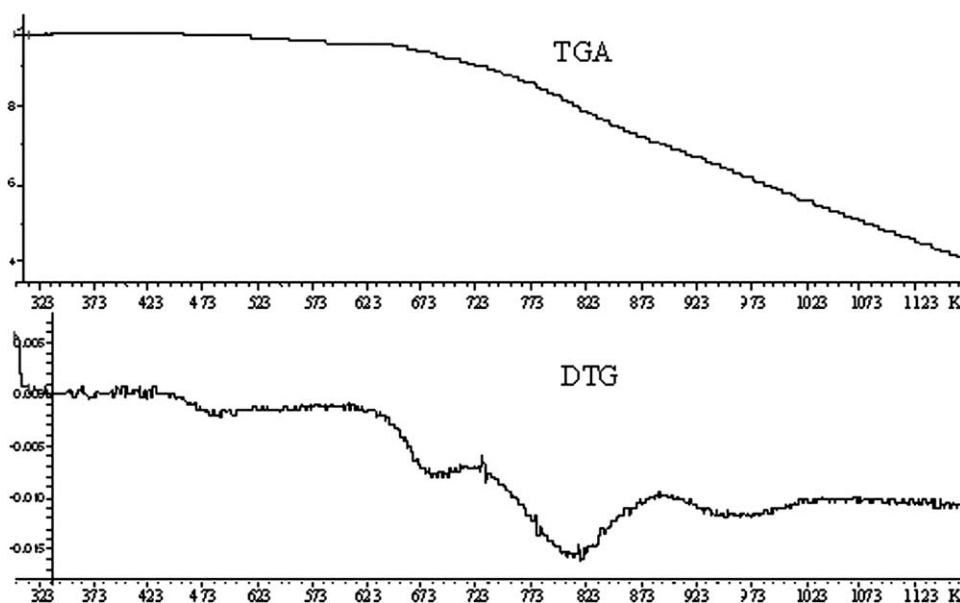
The polymer's thermal stability is a very important aspect of thermoset characterization. It is also important to know the thermal behavior of a novolac resin to focus on the application, so that it can be used as fire resistant<sup>4</sup> or to obtain active carbon.<sup>5</sup> Simple reaction of phenolic resins at high temperatures in absence of oxygen generates a carbonous structure or polymeric carbon that is usually employed as refractory material if it is mixed with dolomite or magnesium.<sup>3</sup> If thermal behavior needs to be improved, phenolic resins can be mixed with fire retardants.<sup>3</sup> So, thermal stability is very important but not mandatory.

When a polymer is heated, the changes in the sample's weight can be evaluated through temperature change (dynamic method) or by means of time at a constant temperature (isothermal method). In dynamic methods, rises in temperature agree with a heating program preset.

Kinetic information of thermal degradation is obtained by dynamic methods applying thermogravimetric analysis (TGA). Conversion can be defined by the loss of weight of the resin, so any of the two possibilities (dynamic or isothermal) that relate conversion with temperature or time could apply these data to a kinetic model to describe the thermal degradation of the material.

The main purpose of this work is to study the differences in the kinetic of the thermal degradations

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**Figure 1** TGA and DTG thermograms (313.2–1173.2 K; 10 K min<sup>-1</sup>) of PF previously cured with 9% HMTA.

between a lignin-novolac resin and the commercial reference. We also focused on the amount of curing agent and its influence on thermal behavior. Three different kinetic methods have been applied: Coats-Redfern (C-R), as a complete kinetic way to obtain the three parameters of reaction; Ozawa, as a known dynamic model that gives the activation energies without obtaining the pre-exponential factor; and Van Krevelen (V-K), that it has been tested and has been firstly applied to phenolic thermal stability.

## EXPERIMENTAL

### Materials

The lignin-novolac resin was synthesized in laboratory using ammonium liginosulphonate substituting directly phenol by lignin (LN). The operating conditions were reported in a previous work.<sup>1</sup> Commercial novolac resin (PF) was supplied by Hexion Speciality Chemicals SA, Guipúzcoa, Spain.

Hexamethylenetetramine (HMTA) was used as curing agent and mixed in a grinder with the prepolymer at a specific ratio. Two amounts (9 and 15 wt %) of HMTA are added to prepolymers being the lower amount the industry proportion.<sup>1</sup> These amounts of curing agent were employed to study the influence of this compound in the thermal stability and in the activation energy of the degradation process. The process to obtain the cured resins is alike to industrial process at 453.15 K.<sup>3</sup>

### Thermogravimetric analysis

TGA runs were done using a Mettler-Toledo TGA with alumina pans under nitrogen atmosphere. Res-

ins were cured in 70  $\mu$ L crucibles at the temperature mentioned above, then rapidly cooled. After the curing process, experiments were carried out at three heating rates: 5, 10, and 15 K min<sup>-1</sup> from ambient temperature to 1173.15 K<sup>6-12</sup> to study thermal degradation.

The data runs were fitted to C-R, V-K, and Ozawa methods. In this work, we employed a heating rate of 10 K min<sup>-1</sup> in C-R and V-K methods that allowed calculating activation energy. However, Ozawa method employs the three heating rates mentioned above.

### Kinetic methods

All kinetic models in this article use the basic equation:

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

where  $r$  is the reaction rate and  $k$  is the rate constant. To obtain the kinetic parameters of pyrolysis, conversion needs to be defined as:

$$\alpha = \frac{w_i - w}{w_i - w_f} \quad (2)$$

where  $w$  represents the weight of the sample at arbitrary time,  $w_i$  and  $w_f$  are initial and final weight of the sample, respectively, at a fixed time.

### Coats-Redfern method

Substituting  $k(T)$  by Arrhenius' expression in eq. (1):

TABLE I  
Kinetic Models

Mechanism	Symbol	$f(\alpha)$	$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha$
Two-dimensional growth of nuclei (Avrami equation)	A <sub>2</sub>	$2 \cdot (1 - \alpha) \cdot [-\text{Ln}(1 - \alpha)]^{1/2}$	$[-\text{Ln}(1 - \alpha)]^{1/2}$
Three-dimensional growth of nuclei (Avrami equation)	A <sub>3</sub>	$3 \cdot (1 - \alpha) \cdot [-\text{Ln}(1 - \alpha)]^{2/3}$	$[-\text{Ln}(1 - \alpha)]^{1/3}$
Three-dimensional growth of nuclei [Avrami eq. (3)]	A <sub>4</sub>	$4 \cdot (1 - \alpha) \cdot [-\text{Ln}(1 - \alpha)]^{1/4}$	$[-\text{Ln}(1 - \alpha)]^{1/4}$
Zero order	R <sub>1</sub>	1	$\alpha$
Phase boundary-controlled reaction (contracting area)	R <sub>2</sub>	$2 \cdot (1 - \alpha)^{1/2}$	$[1 - (1 - \alpha)^{1/2}]$
Phase boundary-controlled reaction (contracting volume)	R <sub>3</sub>	$3 \cdot (1 - \alpha)^{2/3}$	$[1 - (1 - \alpha)^{1/3}]$
One-dimensional diffusion (Jander equation)	D <sub>1</sub>	$1/2\alpha$	$\alpha^2$
Two-dimensional diffusion (Ginstling-Brounshtein)	D <sub>2</sub>	$1/[-\text{Ln}(1 - \alpha)]$	$(1 - \alpha) \cdot \text{Ln}(1 - \alpha) + \alpha$
Three-dimensional diffusion (Jander equation)	D <sub>3</sub>	$3 \cdot (1 - \alpha)^{2/3} / [2 \cdot [1 - (1 - \alpha)^{1/3}]]$	$[1 - (1 - \alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling-Brounshtein)	D <sub>4</sub>	$\frac{3}{2 \cdot [(1 - \alpha)^{-1/3} - 1]}$	$(1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3}$
First-order reaction	F <sub>1</sub>	$(1 - \alpha)$	$-\text{Ln}(1 - \alpha)$
Second-order reaction	F <sub>2</sub>	$(1 - \alpha)^2$	$\frac{1}{(1 - \alpha)} - 1$
Third-order reaction	F <sub>3</sub>	$(1 - \alpha)^3$	$(1/2)[(1 - \alpha)^{-2} - 1]$

$$\frac{d\alpha}{dt} = k_0 \cdot e^{(-Ea/R \cdot T)} \cdot f(\alpha) \quad (3)$$

The evolution of the conversion degree of the resin at any time can be found as the product of its variation with respect to temperature and the heating rate  $\beta$ , which can be expressed as:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \cdot \frac{dT}{dt} = \frac{d\alpha}{dT} \cdot \beta \quad (4)$$

Equations (3) and (4) may be combined as follows:

$$\frac{d\alpha}{dt} = \beta \cdot \left( \frac{d\alpha}{dT} \right) = f(\alpha) \cdot k_0 \cdot e^{-Ea/R \cdot T} \quad (5)$$

Rearranging eq. (5) and integrating from  $T_0$ , initial temperature which corresponds to  $\alpha_0$ , to  $T_p$  peak temperature of curve DTG (Fig. 1), which corresponds to  $\alpha_p$ , the expression remains as follows:

$$\int_{\alpha_p}^{\alpha_0} \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int_{T_0}^{T_p} e^{-Ea/R \cdot T} \cdot dT \approx \frac{k_0 \cdot Ea}{\beta \cdot R} \cdot p(x) \quad (6)$$

where  $p(x)$  is the named  $p$ -function defined by Doyle.<sup>13</sup> When the  $p$ -function is substituted by the C-R's approximation,<sup>14</sup> it is obtained the following expression known as the C-R's method:

$$\text{Ln} \left( \frac{g(\alpha)}{T^2} \right) = \text{Ln} \left( \frac{k_0 \cdot R}{\beta \cdot Ea} \right) - \frac{Ea}{R \cdot T} \quad (7)$$

where  $g(\alpha)$  is a function (Table I) that depends on the kinetic model applied.<sup>15-18</sup> The C-R method is one of the most popular model-fitting methods. The representation of  $\text{Ln}(g(\alpha)T^{-2})$  versus  $T^{-1}$  with the substitution of a  $g(\alpha)$  function allows the activation energy and the pre-exponential factor of resin degradation kinetics to be obtained from the slope value of the line and the origin ordinate, respectively.

### Van Krevelen model

This model was employed for the first time to study carbon pyrolysis.<sup>19</sup> It is based on the following approximation of the exponential function:

$$e^{-Ea/R \cdot T} = \left( e^{-T_p/T} \right)^{Ea/R \cdot T_p} \approx \left( b \cdot \frac{T}{T_p} \right)^{Ea/R \cdot T_p} \quad (8)$$

where  $b = 0.368$  in range  $0.9 T_p < T < 1.1 T_p$ .

Substituting eq. (8) into (5) and re-arranging:

$$\frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \cdot \left( \frac{b}{T_p} \right)^{Ea/R \cdot T_p} \cdot T^{Ea/R \cdot T_p} \cdot dT \quad (9)$$

Taking integrals, the following can be obtained:

$$\text{Ln} g(\alpha) = \text{Ln} B + \left( \frac{Ea}{R \cdot T_p} + 1 \right) \cdot \text{Ln} T \quad (10)$$

where,

$$\text{Ln} B = \text{Ln} \left[ \frac{k_0}{\beta} \cdot \left( \frac{b}{T_p} \right)^{Ea/R \cdot T_p} \cdot \frac{1}{(Ea/R \cdot T_p) + 1} \right] \quad (11)$$

When  $\text{Ln} g(\alpha)$  versus  $\text{Ln} T$  is drawn, activation energy can be obtained. The functions employed in this work were the same as the ones used in C-R in Table I.

### Ozawa method

Ozawa method<sup>20</sup> establishes a simple relationship between the activation energy  $E_a$  and the heating rate  $\beta$  as a function of peak temperature  $T_p$ . This  $T_p$  value is the temperature at which the TGA thermogram shows the maximum reaction rate. Ozawa method allows determination of the activation energy  $E_a$  and the pre-exponential factor using the deduced following expression<sup>21,22</sup>:

TABLE II  
Mass Loss Percentage During Thermal Degradation

Resin	Mass loss (%)			
	573.2 K	773.2 K	973.2 K	1173.2 K
LN 9% HMTA	18.43 ± 0.93	37.80 ± 1.98	55.15 ± 2.12	78.36 ± 3.01
LN 15% HMTA	12.97 ± 0.65	25.86 ± 1.29	54.59 ± 2.79	81.68 ± 3.08
PF 9% HMTA	1.68 ± 0.09	12.84 ± 0.64	37.66 ± 1.83	58.84 ± 2.92
PF 15% HMTA	1.44 ± 0.07	10.98 ± 0.55	38.00 ± 1.97	64.79 ± 3.23

$$\log \beta = A - 0.4567 \cdot \frac{Ea}{R \cdot T_p} \quad (12)$$

where,

$$A = \log \frac{k_0 \cdot Ea}{g(\alpha) \cdot R} \quad (13)$$

and the function  $g(\alpha)$  is defined as:

$$g(\alpha) = \int_{\alpha_0}^{\alpha_p} \frac{1}{f(\alpha)} d\alpha \quad (14)$$

where  $\alpha$  is the degree of conversion,  $\alpha_0$  represents the initial conversion degree of resin,  $\alpha_p$  is the conversion degree at peak temperature, and  $f(\alpha)$  is a function of conversion. Thus, activation energy can be obtained from the slope value of  $\log \beta$  versus  $T_p^{-1}$ . However, this method does not give information about the reaction order for resin degradation.

## RESULTS AND DISCUSSION

### Thermal stability

Assays were done at 10 K min<sup>-1</sup> to study thermal stability.<sup>6,7,10,23</sup> Table II shows mass losses at four temperatures. It can be checked that the smaller the loss of weight is at a certain temperature, the more stable the resin is.<sup>7,8,23-27</sup> High pyrolysis temperature implies that low volatile products are more present.<sup>26</sup>

Comparing the amount of HMTA, resins less stable are those that have a curing agent amount of 9 wt % at low temperatures. LN resins lose more mass (%) at lower temperatures as HMTA amount decreases. This implies that those resins with 9 wt % HMTA are more crosslinked than 15 wt % HMTA resins. It is also agreed that at higher temperatures, LN with 15 wt % HMTA has more loss of weight.<sup>7</sup> In contrast, PF resins lose similar weight at lower temperatures, which means that they have a similar crosslinked net but show differences at higher temperatures. At lower temperatures, commercial resins have just lost 10% of their initial weight, showing a

great thermal stability. This may happen because commercial resins form new products that are more stable.<sup>27</sup> The fact that pyrolyzed products present xanthenes and methyl derivatives is characteristic of degradation of phenolic resins that have been subject to curing process.<sup>26</sup> If novolac resins are cured with low amount of curing agent, besides xantene and methyl derivatives, bis(hydroxyphenyl)methane isomer is formed from pyrolysis fraction of noncured resin. This explains the presence of linear chains in novolac resins.<sup>26</sup>

Lignin is a natural compound that begins to burn at lower temperatures producing a char of about 40%.<sup>28,29</sup> As it can be seen in Table II, the final difference between LN and PF resins is over 20%. The amount of lignin incorporated was 30%, so the difference of char produced must be the amount of lignin that does not react (~ 10%) in lignin-novolac formulation.

At temperature of 973 K, resins have similar weight loss regardless of the curing agent amount, and from this temperature up to the end of the process resins cured using 15 wt % HMTA have more weight loss. Curing agent favors loss of weight and decreases stability at temperatures over 973 K. If we attend to weight loss, PF resin cured with 9 wt % HMTA is the most stable, and on the contrary, LN cured with 15 wt % HMTA is the most unstable.

### Kinetic methods

The methods employed to tackle the kinetic study are different in their mathematic approach. This selection has been done to show how reliable the model used is, and to provide the more reliable value when two results give the same value from different kinetic methods.

Figure 2 shows the rate of weight loss for all resins assayed. With this type of graph, it is easy to appreciate how difficult it is to set when a reaction ends and the next reaction begins. It is also necessary to make clear the fact that when a polymer presents high degradation speed this does not imply necessarily that this polymer loses high amount of weight as a consequence of this reaction. That is, as degradation speed is the derivate of weight loss

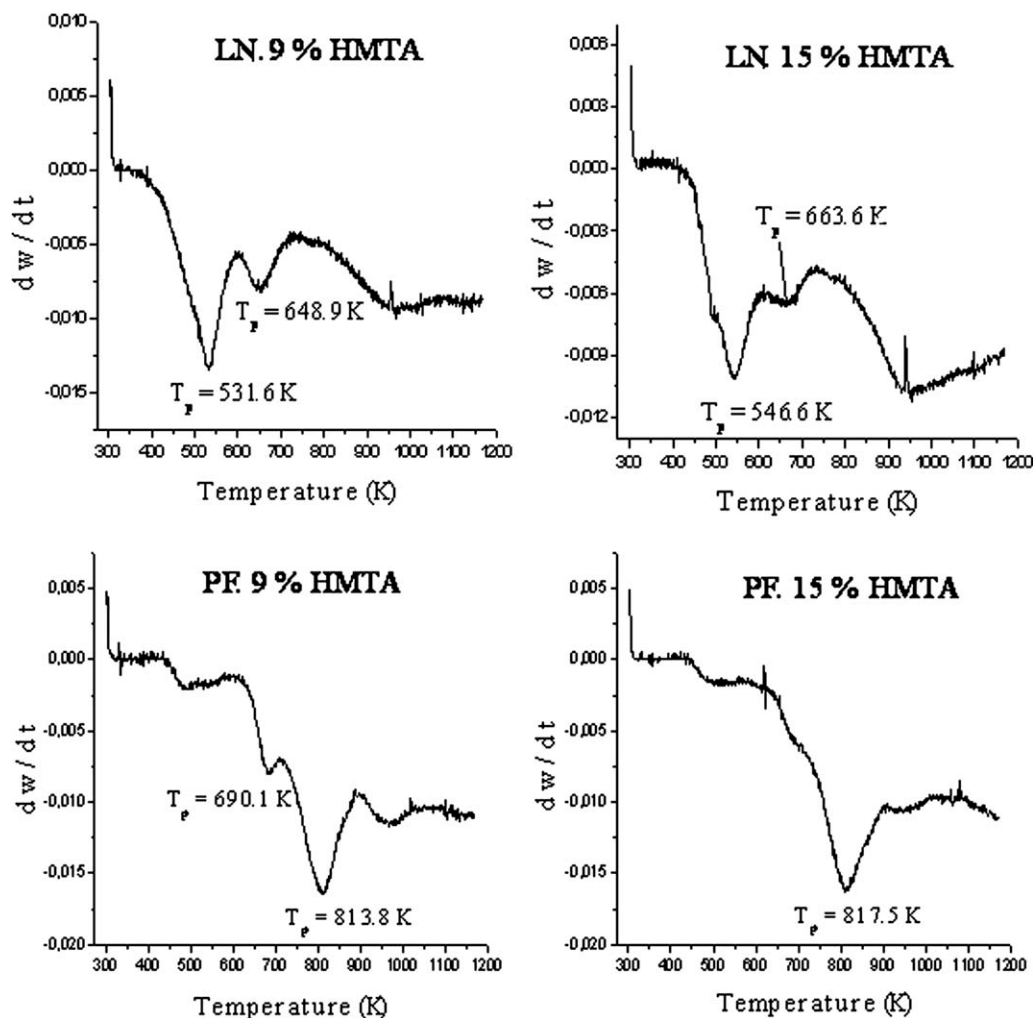


Figure 2 Evolution of weight losses rate of resins assayed during pyrolysis.

versus time, it can be that a resin has high speed of degradation regarding a specific reaction but does not lose much weight during this phase.

All peaks marked in Figure 2 could be fitted by a kinetic method. In some cases, peaks are not well defined or the method uses whole curve data, which gives us strange results in the present study. To clarify the kinetic study, we have divided the main reactions into two sections, one is "lower temperatures" (LT) and the other one "higher temperatures" (HT). We have also chosen the clearer reaction at each sec-

tion (this does not mean there are other reactions but, or they do not fit properly or the results are inconsistent). Some resins do not have a well-defined peak at one of these sections (PF) or they can have more than one reaction with more than one peak (LN resins). Table III shows the peaks of reactions and the reactions subject to the present study that have been selected.

#### Coats-Redfern method

In the present method (C-R) all conversions have been applied to the functions in eq. (7) (Table I) to determine which  $g(\alpha)$  fit best to experimental data. Table IV shows activation energy, Arrhenius pre-exponential factor, and correlation coefficient ( $R$ ) of the two sections for all resins. Conversion  $g(\alpha)$  of second-order ( $F_2$ ) and third-order ( $F_3$ ) do not fit well according to the experimental data. As it can be observed in Tables IV and V, the proposed model fits better for the commercial resins rather than lignin-novolac data. This can be explained by

TABLE III  
Temperatures Considered to Calculated  
Pyrolysis Kinetics

Resin	$T_p$ (K)	
	LT	HT
LN 9% HMTA	531.7	648.9
LN 15% HMTA	546.6	663.6
PF 9% HMTA	—	813.8
PF 15% HMTA	—	817.5

TABLE IV  
Activation Energies and Pre-exponential Factors of LN and PF Resins Pyrolysis Employing C-R Method

$g(\alpha)$	Parameter	Resin					
		LN + %HMTA				PF + %HMTA	
		9		15		9	15
		LT	HT	LT	HT	LT	HT
A <sub>2</sub>	$E_a$ (kJ mol <sup>-1</sup> )	25.7	87.8	33.8	31.2	85.8	54.2
	$k_0$ (min <sup>-1</sup> )	3.7E + 1	1.8E + 6	2.4E + 2	2.4E + 1	5.5E + 4	2.8E + 2
A <sub>3</sub>	$R$	0.975	0.953	0.965	0.938	0.963	0.965
	$E_a$	14.4	54.9	19.7	17.2	52.8	31.8
A <sub>4</sub>	$k_0$	1.6E + 0	2.9E + 3	6.3E + 0	1.1E + 0	2.5E + 2	6.2E + 0
	$R$	0.964	0.947	0.954	0.913	0.957	0.955
R <sub>1</sub>	$E_a$	8.8	38.4	12.7	10.2	36.3	20.6
	$k_0$	0.3E + 0	1.1E + 2	0.9E + 0	1.8E - 1	1.5E + 1	0.8E + 0
R <sub>2</sub>	$R$	0.945	0.940	0.938	0.869	0.949	0.941
	$E_a$	47.3	127.3	60.5	47.7	135.8	91.6
R <sub>3</sub>	$k_0$	5.0E + 3	1.7E + 9	9.2E + 4	4.1E + 2	8.3E + 7	6.7E + 4
	$R$	0.949	0.888	0.934	0.872	0.918	0.932
D <sub>1</sub>	$E_a$	52.6	153.0	67.4	58.6	157.3	104.8
	$k_0$	1.2E + 5	1.4E + 11	3.0E + 5	2.4E + 3	1.5E + 9	3.5E + 5
D <sub>2</sub>	$R$	0.968	0.929	0.956	0.921	0.947	0.956
	$E_a$	54.7	163.7	70.1	63.1	166.0	110.0
D <sub>3</sub>	$k_0$	1.5E + 4	7.5E + 11	4.2E + 5	4.3E + 3	4.4E + 9	5.8E + 5
	$R$	0.974	0.941	0.963	0.935	0.956	0.963
D <sub>4</sub>	$E_a$	102.6	265.5	129.4	106.0	284.7	196.1
	$k_0$	1.7E + 9	1.2E + 20	4.7E + 11	2.0E + 7	4.1E + 17	3.9E + 11
F <sub>1</sub>	$R$	0.957	0.896	0.943	0.894	0.925	0.940
	$E_a$	109.2	298.2	138.1	119.2	311.5	212.4
F <sub>2</sub>	$k_0$	5.5E + 9	3.5E + 22	2.4E + 12	1.7E + 8	1.7E + 19	3.2E + 12
	$R$	0.967	0.918	0.954	0.918	0.941	0.954
F <sub>3</sub>	$E_a$	117.5	338.4	148.6	136.9	345.0	233.0
	$k_0$	1.3E + 10	1.9E + 25	8.7E + 12	1.6E + 9	9.1E + 20	2.4E + 13
F <sub>4</sub>	$R$	0.982	0.944	0.973	0.945	0.959	0.967
	$E_a$	111.7	308.9	141.1	124.6	321.2	218.6
F <sub>5</sub>	$k_0$	2.5E + 9	6.4E + 22	1.2E + 12	1.2E + 8	1.8E + 19	2.1E + 12
	$R$	0.971	0.928	0.959	0.928	0.948	0.959
F <sub>6</sub>	$E_a$	59.4	186.6	76.0	73.0	184.6	121.2
	$k_0$	1.8E + 5	2.0E + 14	6.3E + 6	1.1E + 5	2.9E + 11	1.2E + 7
F <sub>7</sub>	$R$	0.978	0.958	0.967	0.955	0.968	0.972
	$E_a$	21.8	135.6	28.9	53.7	106.4	59.5
F <sub>8</sub>	$k_0$	5.3E + 1	6.2E + 10	2.7E + 2	1.0E + 4	6.0E + 6	2.6E + 3
	$R$	0.694	0.887	0.736	0.831	0.828	0.769
F <sub>9</sub>	$E_a$	51.6	282.0	66.2	118.1	225.9	131.8
	$k_0$	4.5E + 5	1.6E + 23	9.0E + 6	1.1E + 10	2.7E + 15	9.2E + 8
F <sub>10</sub>	$R$	0.750	0.894	0.778	0.854	0.843	0.799

analyzing Figure 2 where PF resins show a clearer curve than lignin-novolac resins, which show many peaks that avoid better correlation coefficients.

The fact that some data fit well to some mechanisms is a necessary condition but it is not the unique. It is usual that, with a similar fitted value, two or more models can give very different activation energies.<sup>30</sup> This is clearly observed in LT section of LN resin formed with 9 wt % HTMA. It is probed that R<sub>3</sub> and D<sub>3</sub>, where data are fitted equally ( $R = 0.972$ ), activation energies obtained are very far between them, one is double than the other. Therefore, in the present case, the mechanism chosen has to be contrasted with other kinetic method.

As it can be observed in Table IV, there are notable differences among activation energies of reactions inside a resin, and also within same reactions of different resins. Comparing models, the most suitable mechanism is first-order (F<sub>1</sub>), and three-dimensional diffusion (D<sub>3</sub>). In general, reaction data fit well to nucleation and growth mechanisms (A<sub>2</sub>, A<sub>3</sub> y A<sub>4</sub>), but give lower activation energies compared to the rest of models assayed.

Table V gives the opportunity to compare the pre-exponential factor calculated for two  $E_a$  almost equal. The LN 9% and PF 15% HMTA have quite similar activation energies (186.6 and 184.6 kJ mol<sup>-1</sup>, respectively) and different pre-exponential factors,

TABLE V  
Extract of Table V Best Results (C-R Method)

Resin	$g(\alpha)/E_a$ (kJ mol <sup>-1</sup> )/ $k_0$ (min <sup>-1</sup> )					
	LT			HT		
LN 9% HMTA	D <sub>3</sub>	117.5	1.3E + 10	F <sub>1</sub>	186.6	2.0E + 14
LN 15% HMTA	D <sub>3</sub>	148.6	8.7E + 12	F <sub>1</sub>	73.0	1.1E + 5
PF 9% HMTA	-	-	-	F <sub>1</sub>	184.6	2.9E + 11
PF 15% HMTA	-	-	-	F <sub>1</sub>	121.2	1.2E + 7

what it induces that the higher pre-exponential factor would lead to a higher degradation speed. Substituting the model (D<sub>3</sub> or F<sub>1</sub>) in eq. (1) proportion-

ates the speed for the same  $\alpha$  values. Model D<sub>3</sub> implies that for the same  $\alpha$  values that F<sub>1</sub>, it will have higher speed. So, the speed of the reaction

TABLE VI  
Activation Energy and Origin Ordinate Values of LN and PF Resins Employing V-K Method

$g(\alpha)$	Parameter	Resin					
		LN + %HMTA				PF + %HMTA	
		9		15		9	15
		LT	HT	LT	HT	LT	HT
A <sub>2</sub>	$E_a$ (kJ mol <sup>-1</sup> )	32.2	81.0	40.7	37.5	94.8	55.7
	$B$	-22.7	-45.2	-27.2	-22.0	-43.9	-26.8
	$R$	0.980	0.960	0.972	0.961	0.969	0.972
A <sub>3</sub>	$E_a$	20.0	52.2	25.6	23.1	61.0	34.9
	$B$	-15.1	-30.1	-18.2	-14.7	-29.2	-17.9
	$R$	0.980	0.960	0.972	0.961	0.969	0.972
A <sub>4</sub>	$E_a$	13.9	37.8	18.1	16.0	44.0	24.5
	$B$	-11.3	-22.6	-13.6	-11.0	-21.9	-13.4
	$R$	0.980	0.960	0.972	0.961	0.969	0.972
R <sub>1</sub>	$E_a$	55.2	115.1	68.9	54.0	145.6	90.9
	$B$	-37.2	-63.2	-44.4	-30.7	-66.0	-42.2
	$R$	0.950	0.896	0.938	0.900	0.925	0.938
R <sub>2</sub>	$E_a$	61.2	137.6	76.4	65.4	167.9	103.0
	$B$	-41.0	-75.2	-49.2	12.9	-75.9	-47.6
	$R$	0.967	0.932	0.957	0.935	0.950	0.958
R <sub>3</sub>	$E_a$	63.6	147.0	79.5	70.1	176.9	107.8
	$B$	-42.7	-80.2	-51.1	-39.3	-79.9	-49.8
	$R$	0.972	0.943	0.963	0.945	0.958	0.964
D <sub>1</sub>	$E_a$	114.8	235.7	142.3	113.5	403.9	188.6
	$B$	-74.3	-126.5	-88.8	-61.4	-177.5	-84.4
	$R$	0.950	0.896	0.938	0.900	0.929	0.938
D <sub>2</sub>	$E_a$	122.3	264.2	152.0	127.3	326.1	203.5
	$B$	-79.1	-141.5	-94.8	-68.6	-144.3	-91.0
	$R$	0.961	0.918	0.950	0.921	0.940	0.950
D <sub>3</sub>	$E_a$	131.5	299.5	163.5	145.8	360.6	222.4
	$B$	-85.3	-160.5	-102.2	-78.5	-159.8	-99.6
	$R$	0.972	0.943	0.963	0.945	0.958	0.964
D <sub>4</sub>	$E_a$	125.0	273.7	155.2	132.9	335.8	209.2
	$B$	-81.4	-147.1	-97.4	-72.1	-149.2	-94.0
	$R$	0.965	0.927	0.954	0.930	0.947	0.955
F <sub>1</sub>	$E_a$	68.9	167.5	86.0	80.5	196.4	118.2
	$B$	-45.4	-90.3	-54.5	-44.0	-87.7	-53.7
	$R$	0.980	0.960	0.972	0.962	0.969	0.972
F <sub>2</sub>	$E_a$	29.3	125.1	37.1	62.0	117.8	60.3
	$B$	-20.2	-67.6	-24.5	-33.9	-53.2	-28.2
	$R$	0.818	0.904	0.831	0.885	0.864	0.830
F <sub>3</sub>	$E_a$	63.0	255.6	78.7	129.6	307.7	127.3
	$B$	-40.5	-135.1	-48.9	-67.9	-132.0	-56.4
	$R$	0.818	0.904	0.831	0.885	0.846	0.830

$B$ , Van-Krevelen origin ordinate [eq. (11)].

TABLE VII  
Extract of Table VII Best Results (V-K Method)

Resin	$g(\alpha)/E_a$ (kJ mol <sup>-1</sup> )			
	LT		HT	
LN 9% HMTA	D <sub>3</sub>	131.5	F <sub>1</sub>	167.5
LN 15% HMTA	D <sub>3</sub>	163.5	F <sub>1</sub>	80.5
PF 9% HMTA	–	–	F <sub>1</sub>	196.4
PF 15% HMTA	–	–	F <sub>1</sub>	118.2

substituting in eq. (1) for the activation energy correspondent to each value implies that the LT region increases the instability in LN resins.

### Van Krevelen method

The V-K method has been studied before in carbon pyrolysis and in organic compounds, but has never been applied before to phenolic resins. However, this model is attractive because it comes from another mathematical deduction completely different from C-R, what induces to give more credibility to results that can be obtained in case of coincidence. As it happens with C-R model, a conversional function is supposed (Table I) to get kinetic parameters and all conversional degrees have been employed at this stage. This is detrimental to the fit of the data to kinetic models (Table VI). In this case, however, the equation employed does not come from approximate deductions, as it happens in C-R.

Table VII shows activation energies obtained by applying the mechanism that fits best the experimental data of reactions developed during pyrolysis by V-K model. It can be observed that the presented mechanisms are the same as Coast-Redfern. Thus, F<sub>1</sub> and D<sub>3</sub> describe best pyrolysis kinetics in general. The lowest activation energy has been obtained in LN resin (with 15 wt % HMTA), as it happened with C-R. Moreover, A<sub>2</sub>, A<sub>3</sub>, and A<sub>4</sub> mechanisms fit (Table VI), giving similar adjustments as it happens with the C-R method (Table IV), but different activation energies have been obtained from those shown in Table V.

Activation energies calculated with V-K (Table VII) are very close to those obtained by applying C-R (Table V). This points out the agreement of both models, in spite of the fact that both equations are obtained through different ways. Model F<sub>2</sub> and F<sub>3</sub> are those that worse describe pyrolysis reactions in all cases. One important thing is that a good fit in model of V-K is also a necessary condition. As commented above, very different activation energies are obtained with similar fit degrees. Thus, mechanism chosen must be equal, in C-R and V-K method, to decide it as the correct mechanism. In some cases, the fits are better than the ones obtained with C-R,

but those sensibly inferior values were obtained through other mechanisms, such as F<sub>1</sub>.

### Ozawa method

Ozawa method gives a single value for the activation energy for the overall process, it does not need to suppose a mechanism and employs more than one heating rate to calculate activation energy; this induces to think that their results are in agreement with other methods. This does not mean that activation energies will be more real using this model. As it is shown in Table VIII, activation energy to HT step of LN resin is higher compared to other bibliography data. However, activation energies can be assimilated to pyrolysis of a phenolic resin mixed with silica and ceramic hybrids in the rest of the reactions assayed, obtaining values of 200–280 kJ mol<sup>-1</sup>.<sup>9</sup>

### Overall

Activation energies obtained by these models are within the range of polymer degradation in general, although it could seem that their values are very high. For instance, resol phenolic degradation has activation energies within the 30–170 kJ mol<sup>-1</sup> range.<sup>10,22</sup> The range is wide due to differences among resins studied. This can be also compared with phenolic resins in abstraction, where activation energies in its degradation is 250–292 kJ mol<sup>-1</sup>.<sup>29</sup> The fact is that the activation energies of any degradation process of a polymer depend mainly on the material subject to study and the present work has found no reference in the bibliography thereto. In any case, it is reasonable to suppose that activation energies obtained in this work are not distant from the real values. They are quite similar between them and have been determined by different models. Actually, reached values are in range corresponding to pyrolysis of resol resins that also have phenolic base.

Besides, it is shown that as temperature of reaction goes higher the activation energy needed also rises.<sup>6</sup> It is not convenient set a relation between a resin with higher amount of activation energy and the fact that it is more stable at a set temperature,

TABLE VIII  
Pyrolysis Reaction's Activation Energy of the Resins  
Obtained by Ozawa Model

Resin	$E_a$ (kJ mol <sup>-1</sup> )	
	LT	HT
LN 9% HMTA	154.3	172.2
LN 15% HMTA	172.9	32.9
PF 9% HMTA	–	191.3
PF 15% HMTA	–	270.3



because, as it has been shown, it is not enough to study only this kinetic parameter, since weight loss has to be considered as well.

The models that suppose a conversional function  $g(\alpha)$ , that is, the C-R and V-K models, give information about the complexity of reactions involved in the degradation process. Besides, they allow testing that higher amount of HMTA in curing process produces a change in the model fitted to experimental data. These two models show quite similar results, despite the fact that different suppositions and approximations between them were used to obtain them. As it has been commented on section Thermal Stability, there seems to be a reaction for LN resins at lower temperatures than PF resins. The activation energy and the model proposed for this LT reaction ( $D_3$ ) may be due to the degradation of lignin and lignin-derivates compounds. And the other mechanism ( $F_1$ ) fits to the degradation of the phenolic bonds present in both resin types. The increase of  $E_a$  values as HMTA increases for LN resins at LT, might be due to the effect of the curing agent for the crosslinking of lignin. This  $E_a$  is the contrary as HMTA increases at HT, what it may be explained by the loss of weight. There is more weight lose for high HMTA and in HT. This may be attributed to the HMTA unfavoured the stability of the links between phenolic and curing agent (observed at higher temperatures) but, on the other hand, it favors the stability of the bonds between lignin and phenolic compounds. Also, higher  $E_a$  goes with lower weight loses. The differences found in models for both V-K and C-R methods can come from the lignin present in the modified resins. The  $D_3$  model corresponds to a three-dimensional diffusion, so it may explain that the lignin is being degrading in a three-dimensional advance of reaction. The HT section presents a  $F_1$  model meaning that the commercial and the part of the phenolic resin without lignin follow a first-order reaction.

The proposed mechanisms, in C-R and V-K models, to fit these reactions data are the most common employed in pyrolysis studies. Therefore, resol pyrolysis of resins with additives fits better to  $F_1$  model.<sup>10</sup> As it has been pointed out before, experimental data fit well to Avrami's mechanism ( $A_2$ ,  $A_3$  y  $A_4$ ), but activation energies are lower. This circumstance does not happen in other resins, like porfirine<sup>23</sup> or polyester-epoxy.<sup>12</sup> Resins employed in abrasion have higher activation energies (250–292 kJ mol<sup>-1</sup>),<sup>29</sup> and similar values are obtained with resol resins, 30–170 kJ mol<sup>-1</sup>,<sup>10,24,30</sup> that vary very much depending on their composition.

## CONCLUSION

According to the results presented in this article, it can be concluded that lignin-novolac resins seem to

be less stable at lower temperatures than PF resins. This fact could be explained due to the degree of crosslinking. At higher temperatures, all resins assayed lose similar mass showing a similar behavior.

To approach kinetics, three kinetic models have been employed. As it has been shown, C-R and V-K methods offer the chance of classifying reactions attending to the mechanism they follow. They are very similar in their results, what gives more reliability regarding the activation energies and mechanism proposed. Ozawa model is different from the others, because it gives the activation energy of the whole process without knowing the mechanism, but it gives activation energy values in range with the last two models explained. This means that the results obtained by the three methods are very reliable.

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