

# Estimation of Flame Retardancy Effect by Thermal Analysis Using Kinetic Parameters Obtained under Non-Isothermal Conditions in Air

VLASE, Gabriela<sup>a</sup> VLASE, Titus<sup>a</sup> DOCA, Nicolae<sup>a</sup> ILIA, Gheorghe<sup>\*,a,b</sup>

<sup>a</sup> Research Center for Thermal Analysis in Environmental Problems, West University of Timisoara, 16 Pestalozzi Str, 300115-Timisoara, Romania

<sup>b</sup> Institute of Chemistry Timisoara, 24, M. Viteazul Bvd., 300223-Timisoara, Romania

A series of compounds obtained from urea, phosphoric acid and inorganic salts of Zn, Ni and Ca, were tested in respect of their flame-retardancy behavior. The estimation criteria were the kinetic parameters obtained in air, under non-isothermal conditions, on a Perkin-Elmer Diamond device, at heating rates of 5, 10, 12 and 15 deg•min<sup>-1</sup>. The flame-retardancy effect was assigned to the significant endothermic decomposition at relatively low temperature (150—200 °C). The quantitative estimation of the thermal behavior was performed by comparison of the kinetic data obtained by Flynn-Wall-Ozawa, Friedman and NPK (Sempere-Nomen) methods. The kinetic homogeneity and a very good quality of the model are arguments in favour of the NPK method. The Ni containing material exhibited the best flame-retardancy behavior, *i.e.* higher activation energy and mass loss, respectively a single decomposition step with both physical and chemical processes. The results were validated by fire resistance tests.

**Keywords** non-isothermal kinetics, thermal decomposition, flame-retardant

## Introduction

The use of flame retardants (FR) is to reduce the combustibility of the materials, smoke and toxic fume production, therefore they become a pivotal part of developments and application of new materials.<sup>1</sup> Their application is wide, ranging and extending from electronic and electrical equipment to fibers, textiles, plastics and wood products. Many of today's consumer products contain flame retardants and with the predicted continued growth of electronics, communications (mobile phones, palm tops, *etc.*) their use is likely to continue to increase. FR provides fire safety by inhibiting the combustion process at a number of different possible stages from heating, to gaseous release to ignition. It has been shown that damage to property is significantly reduced, available escape time dramatically increased and quantities of toxic gases released are reduced when FR protected products are tested by fire safety authorities. In recent years concerns have been raised in regards to the environmental impact of some of the more commonly used FR. According to the European Flame Retardant Association (EFRA), flame retardants (FR) are additives that can be added to or applied as a treatment to organic materials such as plastics,<sup>2,3</sup> textiles and timber.<sup>5</sup> In essence, they are compounds which when integrated into or coated over the surface of a fiber or

material will provide a flame retardant barrier and so protect against fire.<sup>4</sup> There are three main families of flame-retardant chemicals:<sup>5-13</sup>

(1) The main inorganic flame retardants are aluminium hydroxide, magnesium hydroxide, ammonium polyphosphate and red phosphorus. This group represents about 50% by volume of the worldwide flame retardant production. Some of these chemicals are also used as flame retardant synergists, of which antimony trioxide is most important.

(2) Halogenated products are based primarily on chlorine and bromine. This group represents about 25% by volume of the worldwide production.

(3) Organophosphorus products are primarily phosphate esters which represent about 20% by volume of the worldwide production. Products containing phosphorus, chlorine and/or bromine are also important.

(4) In addition, nitrogen-based flame retardants are used for a limited number of polymers.

In this paper, a series of compounds obtained from urea, phosphoric acid and inorganic salts of Zn, Ni and Ca were tested in respect of their flame-retardancy behavior. The estimation criteria were the kinetic parameters obtained under non-isothermal conditions, in a dynamic air atmosphere. The results were validated by fire resistance tests.

\* E-mail: ilia@acad-icht-tm.edu.ro; gheilia@yahoo.com

Received October 4, 2008; revised April 14, 2009; accepted June 11, 2009.

## Experimental

The reagents, 85% phosphoric acid (Aldrich), commercial urea and reagent grade Zn, Ni and Ca salts were mixed with water in a mass ratio of  $m(\text{phosphoric acid}) : m(\text{urea}) : m(\text{salt}) : m(\text{water}) = 20 : 20 : 1 : 5$  and heated at 100 °C until a solid reaction mass was obtained. The reaction products present a characteristic IR absorption peak in 1250–1290  $\text{cm}^{-1}$ . The products were analyzed by determining the phosphorus content using a colorimetric method. Phosphate readily reacts with ammonium molibdate in the presence of suitable reducing agents to form a blue colored complex, the intensity of which is directly proportional to the concentration of phosphate in the solution. The phosphate content of an unknown sample can be obtained by first plotting the absorbance of a series of standard solutions against the corresponding concentrations, thus giving a calibration curve. The concentration of phosphate in the unknown sample is determined from the graph.

### Thermal analysis

A Perkin-Elmer Diamond device was used, with Al crucible, dynamic air atmosphere (100  $\text{mL} \cdot \text{min}^{-1}$ ) and heating rates of  $\beta = 5, 10, 12$  and 15  $\text{deg} \cdot \text{min}^{-1}$ .

### Burning tests

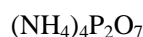
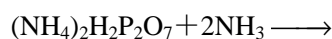
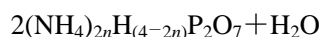
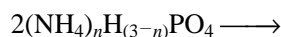
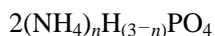
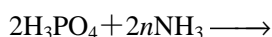
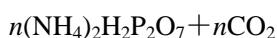
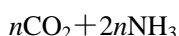
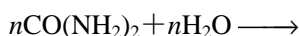
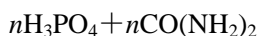
Small pieces of cotton fabrics (size 20 mm  $\times$  70 mm) and paper sheets (size 20 mm  $\times$  70 mm) were treated by soaking the material in flame retardant aqueous solutions with different concentrations, dried at 50 °C for 3 h and then used for tests.

The principle of used fireproofing test is measurement of flame persistence and surface damage using 45° flammability apparatus.

## Results and discussion

Our aim was obtaining condensed phosphates with short chains, soluble in water and suitable for treating cotton fabric and paper in order to improve the burning characteristics of these materials.

Urea phosphate is an addition compound, which behaves like a mixture of the two separate compounds. In the proposed system the following reactions occur:



During the process a part of ammonia was released. Based on phosphate determination the degree of condensation was 2 and the products consist predominantly of ammonium pyrophosphate. The metal is bonded in molecular chains. The products are soluble in water.

### Thermogravimetric data

The main characteristics of the synthesized compounds are systematized in Table 1. Typical thermoanalytical curves are presented in Figure 1.

**Table 1** The inorganic reagents and the thermal characteristics of the prepared samples

Sample <sup>a</sup>	Inorganic salt	Mass loss/%	Max of DTG/°C	Thermal effect and max of DTA/°C
FC	—	27.0	150	Endo 150
FC-Zn	Zn(SO <sub>4</sub> ) <sub>2</sub>	22.6	200	Endo 200
FC-Ca	CaCl <sub>2</sub>	27.0	170	Endo 170
FC-Ni	Ni(SO <sub>4</sub> ) <sub>2</sub>	34.3	200	Endo 200

<sup>a</sup> FC—the product obtained from phosphoric acid and urea only while the other ones are combination of the first with metal salts.

By a first inspection of these data, a relative homogeneous thermal behavior was observed, *i.e.* a mass loss around 27% (sample without cations). An endothermic effect at a relatively low temperature is a premise of an effective flame-retardant effect. In order to estimate quantitatively this effect, a kinetic study was done.

### Kinetic analysis

At the beginning, the integral method of Flynn-Wall<sup>14</sup> and Ozawa<sup>15</sup> (FWO) was used, in the form of Eq. (1).

$$\ln \beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \cdot \frac{E}{RT} \quad (1)$$

where

$$g(\alpha) = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} \quad (2)$$

In Eqs. (1) and (2)  $\alpha$  is the conversion,  $\beta$  the heating rate, and  $A, E$  are the Arrhenius kinetic parameters. According to the data in Figure 2, there is a significant and generally non-monotonous variation of the activation energy vs. conversion. Following a suggestion by

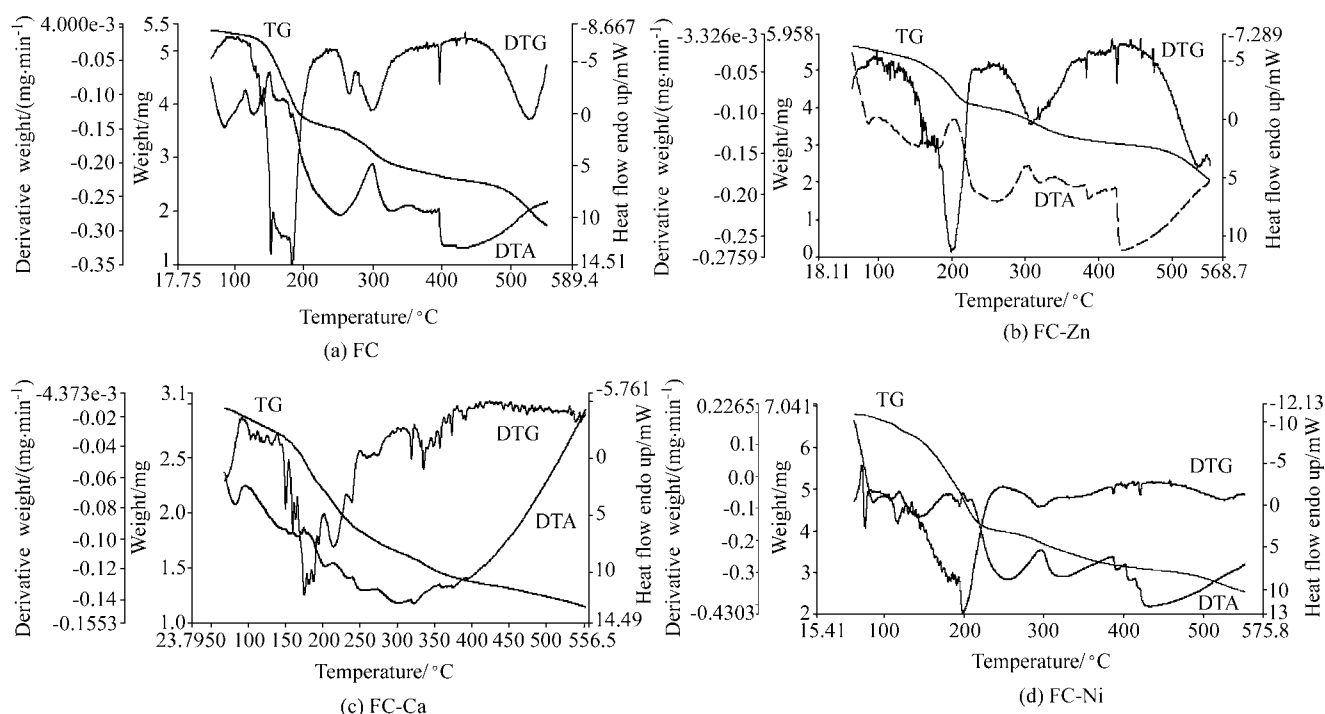


Figure 1 Thermoanalytical curves at 10 deg·min<sup>-1</sup>.

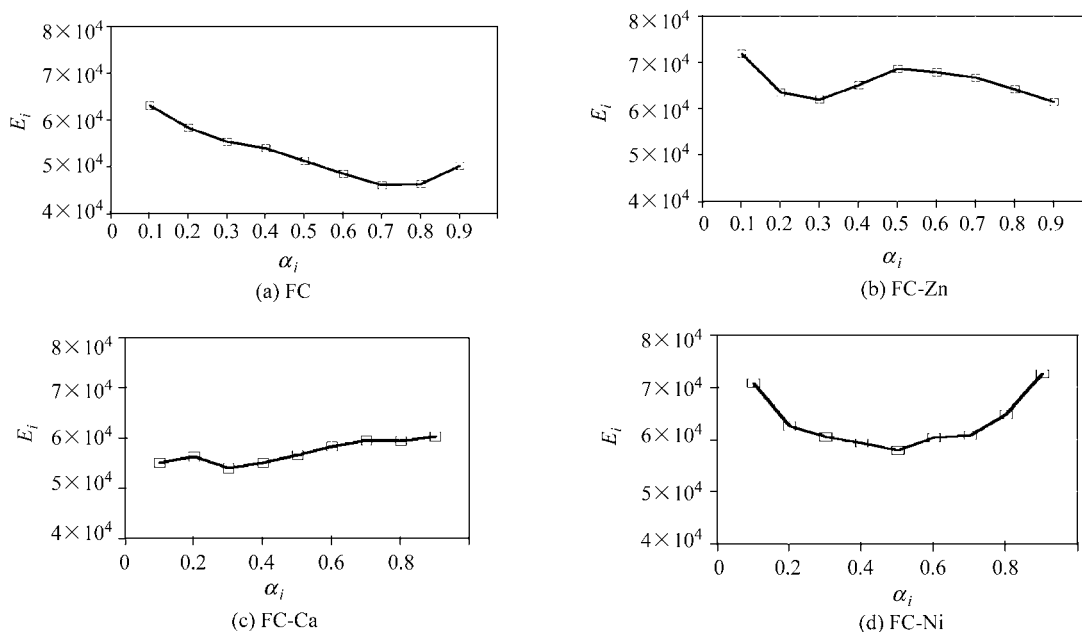


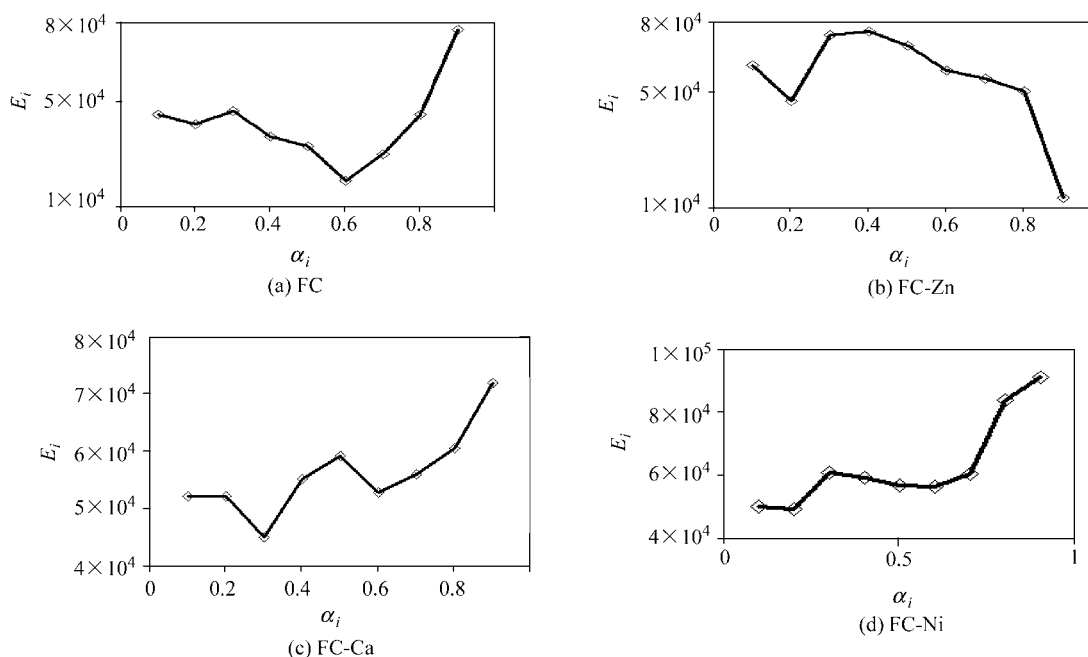
Figure 2 The variation of  $E$  vs. conversion degree by the FWO method.

Vyazovkin and Lesnikovich,<sup>16</sup> some supplementary remarks are possible: until  $\alpha=0.4-0.5$  a reversible process takes place, after which, a series of complex processes (parallel and/or successive reactions) occur.

Due to the irregular variation on  $E$  vs.  $\alpha$  and also for reasons of comparison, we continued the kinetic analysis with the Friedman's differential-isoconversional method,<sup>17</sup> using the equation:

$$\ln(\beta \cdot \frac{d\alpha}{dT})_{\alpha} = \ln[A \cdot f(\alpha)] - \frac{E}{RT} \quad (3)$$

The results are presented in Figure 3. Again a significant variation of  $E$  vs.  $\alpha$  was observed. This variation is not monotonous, so that data processing strategies based on a certain function  $E=f(\alpha)$  can not be used.



**Figure 3** The variation of  $E$  vs. conversion degree by the Friedman method.

The dependence on conversion of the activation energy is, however, a doubtless sign of a complex process.

Based on our previous results,<sup>18-20</sup> the kinetic analysis was continued with the Non Parametric Kinetics (NPK) method.<sup>21-23</sup>

By this method, the experimental points obtained at different heating rates  $\beta$ , are represented in a 3D space with the coordinates of  $(T_j, \alpha_i, r_{ij})$ , in accordance with the fundamental hypothesis that the reaction rate can be expressed as a product of two separable functions

$$r_{ij} = k(T_j) \cdot g(\alpha_i) \quad (4)$$

These points were interpolated by a proper algorithm and a continuous surface of the reaction rate was obtained.

This surface can be suitable discretized into an  $i \times j$  square matrix

$$M = \{r_{ij}\} \quad (5)$$

or, in accordance with Eq. (4)

$$M = \{g(\alpha_i) \cdot k(T_j)\} \quad (6)$$

The NPK method uses the Singular Value Decomposition (SVD) algorithm<sup>24</sup> to decompose the matrix  $M$ :

$$M = U(\text{diag } S)V^T \quad (7)$$

In this way, the influence of the conversion and temperature respectively, was separated since:

a vector  $u_1$  given by the first column of the matrix  $U$  was analyzed vs.  $\alpha$  to determine the conversion function  $g(\alpha)$ ; we suggested the Sestak-Berggren equation:<sup>25</sup>

$$g(\alpha) = \alpha^m (1 - \alpha)^n \quad (8)$$

a vector  $v_1$  given by the first column of the matrix  $V$  was searched for the temperature dependence  $f(T)$ ; a classical Arrhenius equation was suggested.

By applying the SVD algorithm, also a separation of two or more simultaneous steps of a complex process was possible. Indeed, if the observed reaction rate at  $\alpha_i$  and  $T_j$  is a result of two simultaneous reactions with the rates  $r_1$  and  $r_2$ , it means that

$$r_{ij} = r_1(ij) + r_2(ij) = g_1(\alpha_i) \cdot k_1(T_j) + g_2(\alpha_i) \cdot k_2(T_j) \quad (9)$$

and the corresponding matrix  $M$  became

$$M = U_1(\text{diag } S_1)V_1^T + U_2(\text{diag } S_2)V_2^T \quad (10)$$

In the same manner, two independent vectors  $u_1$  and  $u_2$  for the conversion function, respectively two independent vectors  $v_1$  and  $v_2$  for the temperature dependence should be obtained.

The contribution of each step to the total process was quantitatively expressed by the explained variance  $\lambda_i$ , so that  $\sum \lambda_i = 100\%$ .

The results of the NPK method are systematized in Table 2. The values of  $m$  and  $n$  are those obtained for correlation coefficients nearest to 1.00.

The data in Table 2 indicate a remarkable kinetic homogeneity at least for the first three samples, FC, FC-Zn and FC-Ca. Indeed: the decomposition takes place by two simultaneous process, both with a significant contribution; by the first process, the conversion

**Table 2** The kinetic parameters according to the modified NPK method

Sample	$\lambda_1/\%$	$E/(\text{kJ}\cdot\text{mol}^{-1})$	$A/\text{min}^{-1}$	$m$	$n$	$E=\Sigma\lambda_i E_i$
FC	80.7	29.1	$5.6\times 10^2$	1	4/3	34.2
	17.6	60.7	$3.0\times 10^6$	0	0.1	
FC-Zn	73.2	27.5	$3.4\times 10^2$	1	4/3	34.0
	25.1	55.4	$6.3\times 10^5$	0	0.1	
FC-Co	51.3	17.8	$2.8\times 10$	1	4/3	32.0
	43.2	52.9	$2.5\times 10^5$	0	0.1	
FC-Ni	93.0	50.5	$1.0\times 10^5$	1	0.6	47.8
	4.8	17.4	$1.9\times 10$	0	0.1	

function is the same,

$$g(\alpha)=\alpha(1-\alpha)^{4/3} \quad (11)$$

which means a complex process including physical and chemical phenomena; the second process, having a smaller significance, is also the same for the three samples, *i.e.*

$$g(\alpha)=(1-\alpha)^{0.1} \quad (12)$$

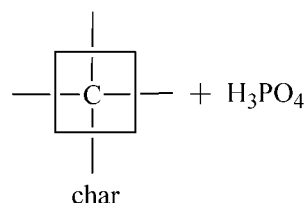
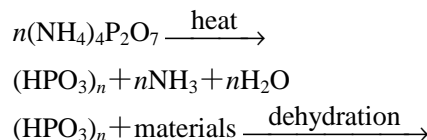
indicating a chemical transformation; the mean value of the activation energy,  $E$ , is also the same for the first three samples.

Generally, the introduction of Zn and Ca cations in the FR mixture does not affect the thermal behavior. By introduction of  $\text{Ni}^{2+}$  ion, the thermal behavior is significantly changed since: the mass loss increases; the thermodegradation takes place by a single significant step, described by  $g(\alpha)=\alpha(1-\alpha)^{0.6}$ ; the activation energy increases by 40%.

Taking into account the relative low values of the maxima of DTG and DTA curves and the value of activation energy, all these indicate a higher fire resistance and a good FR property. Ammonium pyrophosphates act as a flame retardant by a chemical effect in the condensed phase called "Intumescence".

When materials containing ammonium pyrophosphates are exposed to an accidental fire or heat, the flame retardant starts to decompose, commonly into polymeric phosphoric acid and ammonia. The polyphosphoric acid reacts with hydroxyl or other groups of

a synergist to a non stable phosphate ester. In the next step the dehydration of the phosphate ester follows. Carbon foam is built up on the surface against the heat source (charring). The carbon barrier acts as an insulation layer, preventing further decomposition of the material.



The results were validated by fire resistance tests. The burning tests are presented in Table 3.

The best results were obtained for the flame retardant containing Ni. Also the other products gave good results, which confirm that the thermal methods can give a good estimation for flame retardancy properties.

## Conclusion

A good flame retardancy effect of a certain compound is connected with an endothermic decomposition process. The higher the activation energy is, the efficient the flame retardant activity is. The decomposition of urea-phosphoric acid compound is a complex process, so a careful kinetic analysis is necessary for an accurate understanding of the thermal behavior. Only by NPK method a separation between the temperature, and the conversion part of the rate equation was possible, and at the same time to obtain the formal rate equation for the separate steps. The addition of Ni cation seems to increase the quality of flame retardancy properties of the urea-phosphoric acid compound.

**Table 3** The results obtained for burning test

Sample	15% aqueous flame retardant solution				5% aqueous flame retardant solution			
	Cotton		Paper		Cotton		Paper	
	Flame persistence/s	Burned surface/%	Flame persistence/s	Burned surface/%	Flame persistence/s	Burned surface/%	Flame persistence/s	Burned surface/%
FC	5–6	10	6–7	12	12	13	23	14
FC-Zn	3–4	7	4–6	9	14	10	14	11
FC-Co	2–3	2	2–4	6	10	9	10	9
FC-Ni	0 <sup>a</sup>	charring	0 <sup>a</sup>	charring	3	8	8	8

<sup>a</sup> Self extinguishing.

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(E0810041 Cheng, B.)