

## DISCRETE DAEM MODEL FOR THE STUDY OF THE KINETICS OF THE THERMAL DEGRADATION OF A LIGNIN NANOPARTICLE-REINFORCED PHENOLIC FOAM

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### Abstract

In the present work, the kinetics of thermal degradation of phenolic (PF) and lignin nanoparticle-reinforced phenolic (LRPF) foams, and of the lignin used as reinforcement (LR), were studied and the activation energies of their degradation processes were obtained through a discrete distributed DAEM model. The model was validated through comparison of the predicted values with the data obtained at a 8 °C min<sup>-1</sup> heating ramp; 6 and 12 °C min<sup>-1</sup> ramps were used to obtain the kinetic parameters by the model. The effect of the reinforcement on the kinetics of LRPF was studied by comparing it with the results obtained for the PF. The activation energies, for reactions with a non-zero mass fraction allocated to them, obtained for the PF were in the range between 79.9 and 177.6 kJ mol<sup>-1</sup>, for the LRPF, the activation energy ranges from 91 to 187 kJ mol<sup>-1</sup>. For the LR, the activation energy values were in a narrower range than for the foams: 150 – 187 kJ mol<sup>-1</sup>. According to these ranges, it was stated that the degradation process of the LRPF was modified due to the use LR: the range of activation energy for LRPF was comprised between the ranges for PF and LR.

### 1. Introduction

Phenolic foams are widely used for insulating applications in buildings due to their high thermal stability in a broad range of temperature, excellent fire properties and low thermal conductivity. The addition of a reinforcement to these foams that could enhance their thermal behavior is therefore a relevant issue, especially if the reinforcement is a natural and environmentally friendly product, such as lignin.

In a previous work, a study on the kinetics of thermal degradation of phenolic foams (unmodified and reinforced with wood flour) using a continuous DAEM model (Gaussian distribution) was reported [1]. Moreover, we recently studied the thermal stability of a cellulose fiber-reinforced phenolic foam [2]. However, to our knowledge, the effect of lignin nanoparticles used as reinforcement on the thermal stability of a phenolic foam has not been previously reported.

In the present work, the kinetics of the 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 obtain discrete activation energy distributions of their degradation processes by applying the discrete distributed activation energy model (DAEM) developed by Scott, et al. (2006) [3]. This model, as far as we know, has not been used previously to study the kinetics of the thermal degradation of a foam. After determining the activation energies and the fractions allocated to each degradation reaction, curves for the cumulative fraction of mass vs. the

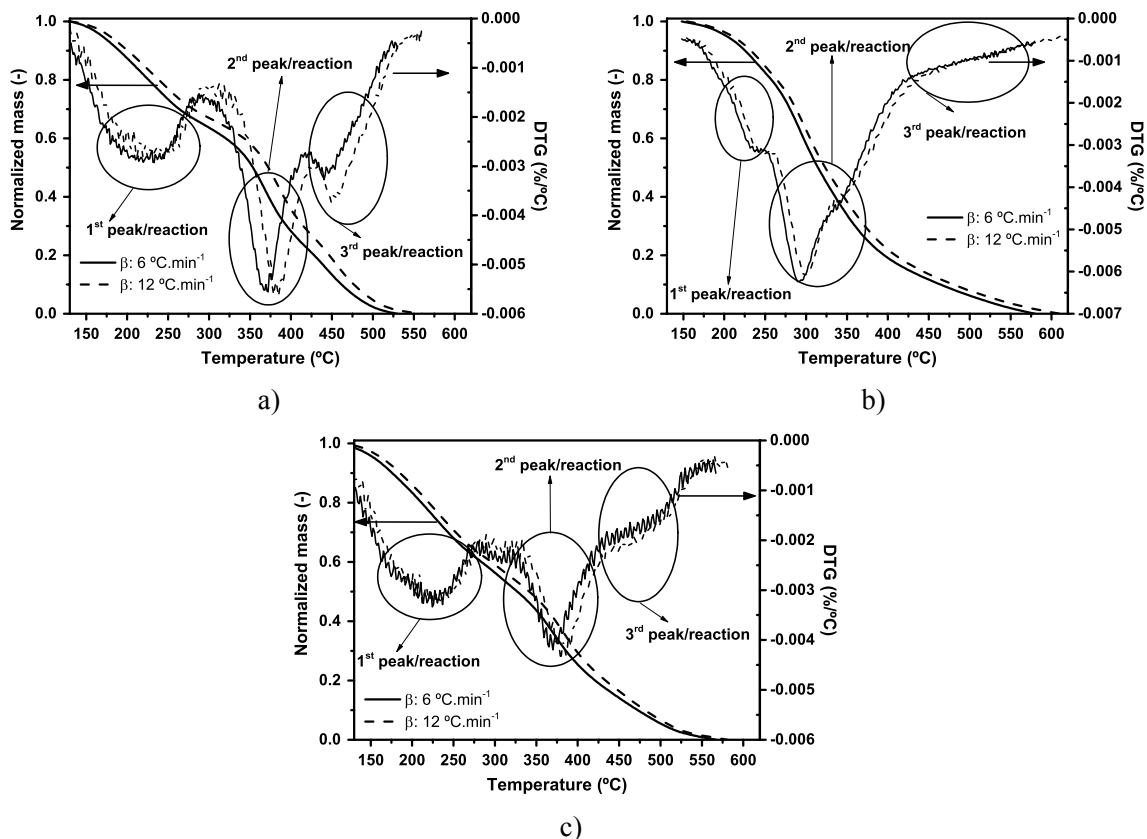
activation energy were obtained for both foams and the reinforcement, and used to study the effect of the LR on the thermal degradation of LRPF by comparison with the PF.

## 2. Material and methods

Thermogravimetric analyses (TGA) of an 8.5 wt.% lignin-reinforced phenolic foam (LRPF), a phenolic foam (PF) and lignin used as reinforcement (LR) were performed in a Mettler-Toledo TGA/DSC 1e. The foams were both manufactured according a previous work [4]. The size of the samples was  $5 \pm 0.3$  mg in the case of the foams (LRPF and PF), and  $10 \pm 0.3$  mg in the case of lignin samples. Foams were cut in small cubic samples and milled in a MM301 Retsch ball mill during 2.5 min at 30 Hz. Dynamic temperature runs were carried out from 30 to 900 °C using heating rates of 6 and 12 °C min<sup>-1</sup> for the estimation of the activation energy distributions and an 8 °C min<sup>-1</sup> heating rate for the validation of the model. All the experiments were carried out under nitrogen atmosphere with a flow rate of 20 mL min<sup>-1</sup>. At least three replicates were analyzed.

## 3. Results and discussion

The study of the kinetics of the main degradation stages for both foams (PF and LRPF) and the reinforcement (LR) was performed using the thermograms (TG) obtained at 6 and 12 °C min<sup>-1</sup>, and the corresponding curves (DTG). In Figures 1a-c, thermograms and differential thermogravimetric curves are shown for each of the studied materials.

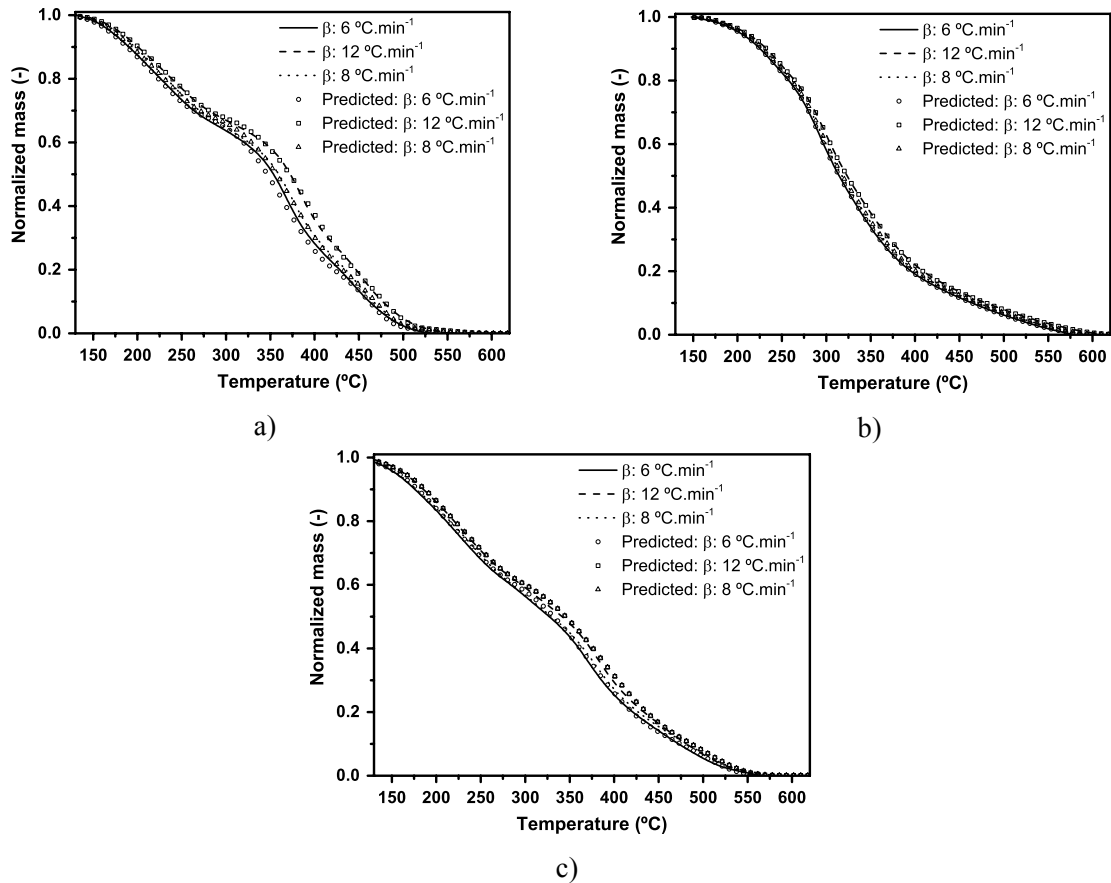


**Figure 1.** TGA measurements, thermograms and DTG curves, for: a) phenolic foam, b) lignin reinforcement and c) lignin reinforced foam.

From Figure 1.a-c, three different degradation stages were determined for WRPF and PF foams and LR reinforcement; notice that moisture release stage have been removed from all the thermograms, and initial temperature is ca. 130 °C. The stages for both foams can be attributed to different degradation processes. The first degradation stage occurred at temperatures below 250 °C for both foams, which is due to the volatilization of molecules of low molecular weight occluded in the structure of the foams, such as water, monomeric phenol and formaldehyde [5]. The second and third stages took place between 250 and 500 °C. During this stages, the most important mass loss occurred, which can be attributed to the release of formaldehyde and water molecules, as a result of bond breaking (mostly methylene ether) [5]. The last stage of thermal degradation of foams generally is found to be comprised between 500 and 900 °C due to the decomposition of the carbonaceous material into decomposition products such as water, carbon monoxide, carbon dioxide, methane and phenol [5]; only the beginning of this stage is included in the thermograms showed in Figure 1.

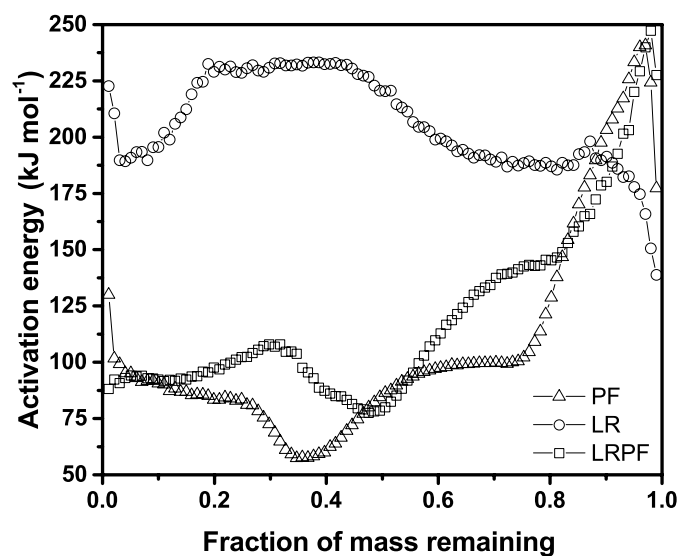
Lignin nanoparticles showed a wide temperature range for their degradation process. Slow pyrolysis was given at the heating rates used (typically for heating rates from 5 to 20 °C min<sup>-1</sup>), according to Janković (2014) [6]. The first degradation peak, at temperatures below 300 °C, is due to dehydration reactions. As the results of these reactions, the molecular weight of lignin is reduced. The second type of primary pyrolysis reactions, which can be linked to the second degradation stage found in Figure 1b., are fragmentation reactions. These reactions take place at temperatures above 300 °C. Anhydro-glucose compounds and other light combustible volatiles are produced during fragmentation [6]. The third peak of the DTG curve can be related to the production of tars, chars and volatile products of low molecular weight, such as CO, CO<sub>2</sub>, acetol, furfural, etc. [6].

The discrete DAEM model was applied on the raw data obtained 6 and 12 °C min<sup>-1</sup> heating rates to obtain the distribution of activation energy of the thermal degradation processes for PF, LR, and LRPF; kinetic parameters were evaluated at 100 equally spaced intervals of conversion [7]. Thermograms obtained at 8 °C min<sup>-1</sup> for all the samples were used to validate the model. The quality of the predictions was good according to the values of R<sup>2</sup> calculated for the predictions of the model at the validation heating ramp, 8 °C min<sup>-1</sup>: 0.997, 0.996, and 0.984 for PF, LR and LRPF, respectively; therefore, the discrete DAEM model showed to be suitable to predict the thermal degradation of all of the foams and the lignin reinforcement under study. Experimental and predicted values are shown in Figure 2.



**Figure 2.** TGA measurements and values predicted by the discrete distributed DAEM model vs. temperature for: a) phenolic foam, b) lignin reinforcement and c) lignin reinforced foam.

The activation energy distributions, plotted as a function of the fraction of mass remaining, determined by applying the discrete DAEM model for PF, LR and LRPF are shown in Figure 3.

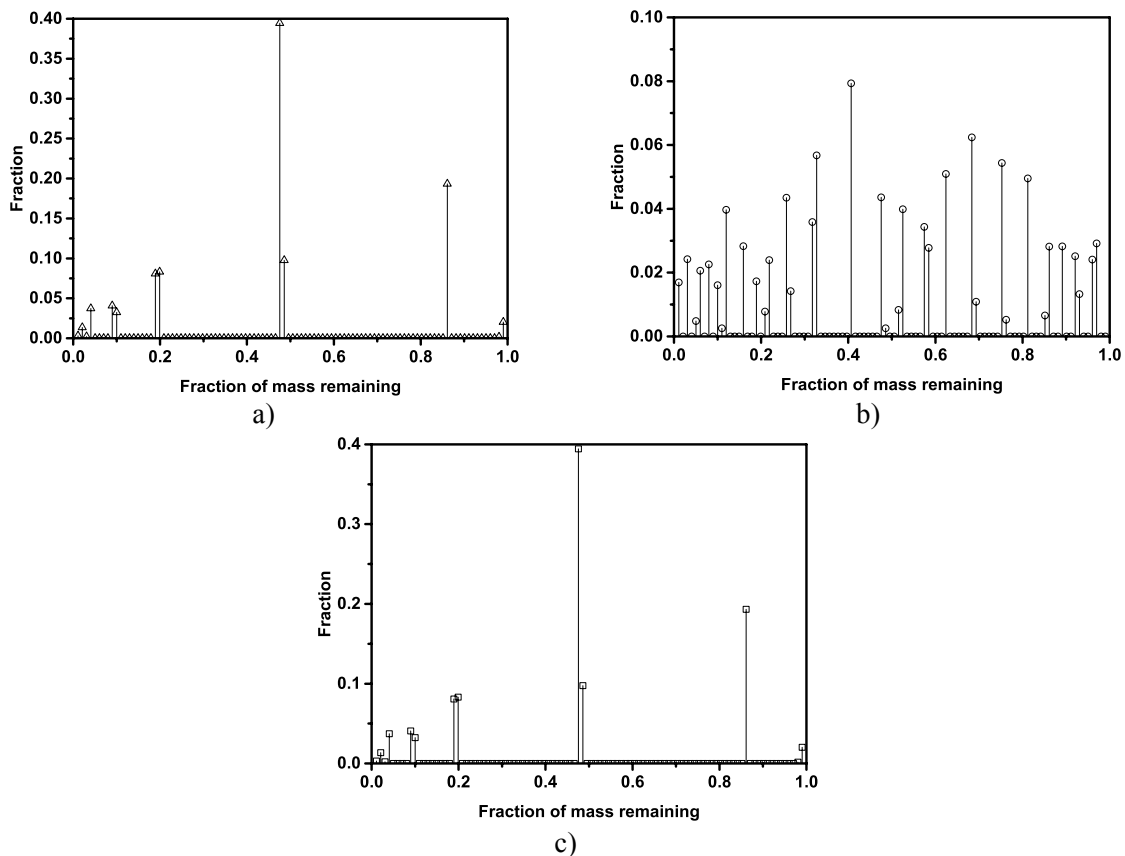


**Figure 3.** Activation energy vs fraction of mass remaining for the phenolic foam (PF), lignin reinforcement (LR), and lignin-reinforced foam (LRPF).

The activation energy for PF ranged from 57 to 241 kJ mol<sup>-1</sup>; for LR the range of activation energy of the degradation process was comprised between 139 to 233 kJ mol<sup>-1</sup>; finally, the reinforced foam showed an activation energy range from 77 to 247 kJ mol<sup>-1</sup>, which is more or less contained in the ranges determined for PF and LR. However, for a meaningful assessment of the importance of each discrete value of the activation energy, the fraction of mass allocated for every reaction have to be determined. These values are shown in Figure 4 for PF, LR, and LRPF.

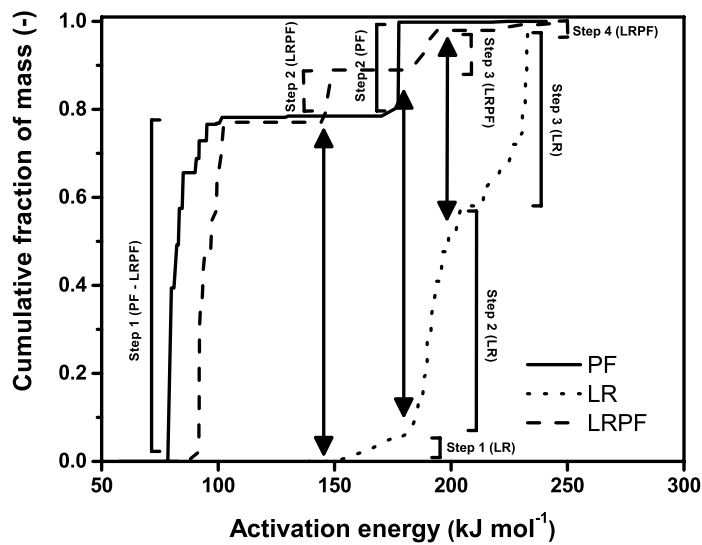
In Figure 4, it is clear that for both foams, PF and LRPF, just a few of the initially 100 reactions, fixed for the application of the DAEM model, have some mass fraction allocated to them; the fraction calculated for many of the reactions turned to be zero. A similar behavior was found by Scott, et al. (2006) [3] and Scott, et al. (2006) [8] when the model was developed and applied to complex solid fuels and dried sewage sludge.

In the case of LR, a higher number of reactions than for the foams became significant, i.e. non-zero mass fraction was allocated to them. This can be attributed to the high complexity and heterogeneity of lignin; moreover, lignin is a bio-compound with a broad molecular weight distribution that somehow can be linked to the different fractions linked to each reaction.



**Figure 4.** Fraction of sample vs. fraction of mass remaining for: a) phenolic foam, b) lignin reinforcement, and c) lignin reinforced foam.

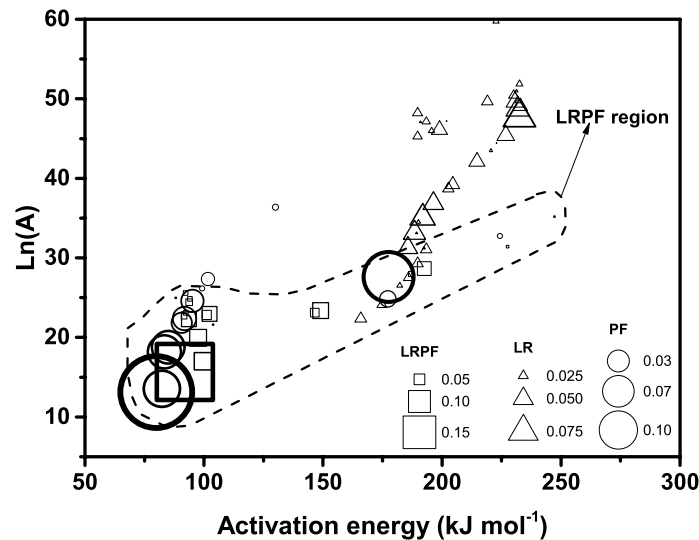
By applying the fractions allocated to each reaction to the activation energy determined for that reaction, the cumulative fraction of mass can be calculated. The resulting cumulative fraction of mass for PF, LR, and LRPF plotted vs. the activation energy are shown in Figure 5.



**Figure 5.** DAEM predictions for PF, LR and LRPF: discrete cumulative distribution functions vs. activation energy.

Two steps were found for the PF: a first step where  $E_a$  ranges from 79.9 to 95.1 kJ mol<sup>-1</sup> (0.766 fraction of the normalized mass), and an almost constant step for the remaining mass fraction with an  $E_a$  of 177.6 kJ mol<sup>-1</sup>. The range of values of  $E_a$  for first step, linked to the first degradation stage, is in agreement with the values found for when a 2-Gaussian DAEM model was applied to the first degradation of stage of the same foam (ca. 80 – 110 kJ mol<sup>-1</sup>) [1]. The first step for LRPF, which is almost parallel to the first step found for PF, was determined for an  $E_a$  range slightly higher than for PF (91 – 102.3 kJ mol<sup>-1</sup>); a second step coincided with the first step for LR (ca. 150 kJ mol<sup>-1</sup>), and so on for the third (ca. kJ mol<sup>-1</sup>) and fourth (ca. 187 kJ mol<sup>-1</sup>) steps found for the LRPF that mostly presented the same activation energies than the second and third steps of the cumulative distribution determined for the LR, respectively.

Finally, the value of the natural logarithm of the pre-exponential factors ( $A$ ) calculated for each reaction vs. their linked activation energies for PF, LR, and LRPF are plotted in Figure 6. For a better assessment of the mass fraction allocated to each pair of kinetic parameters, the area of each data point in Figure 6 is proportional to this value.



**Figure 6.** Logarithm of the pre-exponential factor vs. activation energy for: a) phenolic foam, b) lignin reinforcement, and c) lignin reinforced foam. The area of each data point is proportional to the mass allocated to the reaction; also linked to an edge thickness.

In Figure 6, an overlapping of the LRPF points (LRPF region) with the PF and LR data can be observed, and it is in agreement with the activation energy ranges for PF, LR and LRPF previously mentioned. A more or less linear trend of increasing  $\text{Ln}(A)$  with  $E_a$  is shown in Figure 6 for all the samples under study. This trend can be related to a compensation effect, which was already reported by Scott, et al. (2006) [8] when applying the same model, and often found when a continuous DAEM model is applied [9]. For continuous distribution DAEM models, this effect is usually avoided by fixing a constant value for the pre-exponential factor [9]. Further studies can be carried out on this issue to determine the accuracy of the activation energies calculated by the model; for instance, model-free kinetic methods can be applied to the results to obtain the activation energy as a function of conversion, avoiding the compensation effect.

#### 4. Conclusions

The discrete DAEM model showed suitable predictions for the validation thermograms measured for both foams and the lignin reinforcement. The kinetics of the degradation process of the LRPF was modified with respect to the PF foam due to the use of lignin as reinforcement. The range of activation energy for the thermal degradation process of the LRPF calculated by the discrete DAEM model is comprised between the ranges determined for PF and LR. The LRPF cumulative distribution function for the activation energy was shifted to slightly higher values than the PF, and it is affected by the reinforcement. This is clearly shown by the new steps, compared to the reference foam, PF, found in its distribution function, located at the same activation energies than for the LR. Finally, the compensation effect between the pair of kinetic parameters reported in the literature for DAEM models was also found for all the samples under study. Further studies are suggested to verify the results obtained by the discrete DAEM model.

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