

# Kinetic modeling of polyurethane pyrolysis using non-isothermal thermogravimetric analysis



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## ABSTRACT

The pyrolysis of polyurethane was studied by dynamic thermogravimetry analysis (TGA). The studied polyurethane is used as organic binder in casting process to make sand cores and molds. A semi-empirical model is presented that can be used to describe polyurethane pyrolysis occurring during TGA experiments. This model assumes that the polyurethane is pyrolysed by several parallel independent reactions. The kinetic parameters of polyurethane pyrolysis were evaluated by fitting the model to the experimental data obtained by TGA over a wide variety of heating rates. A nonlinear least-squares optimization method is employed in the fitting procedure. A hybrid objectives based simultaneously on the mass (TG) and mass loss rate (DTG) curves has been used in the least-squares method. The values of the activation energy obtained by the non-linear fitting were then recalculated by the methods of Kissinger and Friedmand. Furthermore, the parameters obtained in the present paper were then compared with those reported in the literature.

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## 1. Introduction

Polyurethane is widely used in foundry industry as an organic binder to harden sand cores. The latter are inserted into a metallic mold to obtain internal shapes of casting parts. Pouring of a molten metal into the mold causes the thermal decomposition of polyurethane and gas emissions which can represent a severe problem for the quality of the casting parts. Indeed, under the effect of the thermal decomposition of the polyurethane, the pressure of the cores increases (due to the produced gas). If the local gas pressure in the sand cores exceeds the local metalostatic pressure of the solidifying liquid metal at core-casting part interface, gas bubbles can grow into the metal. Depending on whether the gas bubbles escapes through the metal or not, two possible scenarios can occur. In the first one the gas can escape through the casting part, so its effect might be limited to the formation of bubble trails defect [1,2]. In the second one, the gas bubbles stay entrapped within the solidified metal. The entrapped gas bubbles contribute thus to the formation of blowholes defects in the casting. Both bubble trails and blowholes defects affect the quality of the casting parts by deteriorating their mechanical properties and thus these parts are generally rejected. Nowadays, in order to prevent casting

defects caused by the gas emissions and to assure the soundness of castings, one can use numerical simulation which allows the determination of the velocity and the pressure of the gas in the sand cores. The models used in the numerical simulation of gas emissions are based on differential equations which describe the transport of mass, momentum and energy within the sand cores. These equations contain source terms including the thermal decomposition rate of the organic binder which are calculated using an appropriate kinetic model. The reaction scheme and the parameters of the kinetic model have to be determined experimentally. Therefore, the study of the thermal decomposition of the polyurethane represents a necessary step for the numerical simulation of the gas emissions occurring during the pouring and the solidification of the casting parts.

Generally after pouring the molten metal into the mold, the sand cores are totally covered by the metal. As there is no oxygen within the sand cores, the thermal decomposition of the polyurethane binder can be assumed to be done only by pyrolysis [2]. One of the most common used thermal analysis techniques to study pyrolysis kinetics of organic solids is the thermogravimetry analysis (TGA) [3]. TGA technique consists in measuring the mass of a substance as a function of temperature (or time) while the substance is subjected to a controlled temperature programme. The thermogravimetry analysis of a solid matter can be conducted either at isothermal conditions (constant temperature) or non-isothermal/dynamics

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conditions (generally the temperature varies linearly with time). The investigation of the pyrolysis by TGA is carried out in inert atmosphere such as nitrogen, argon or Helium. However, one can study combustion by using a reactive atmosphere such as oxygen or hydrogen. The results obtained by TGA are principally the curves of mass loss (noted TG) and of rate of mass loss (note DTG) as functions of temperature (or time).

Even though several works have been carried out to determine the kinetic parameters of the pyrolysis of polyurethanes used in applications other than the foundry [4], only experimental results have been reported about the pyrolysis of polyurethanes used in foundry [5–7]. The objective of this work is to propose a kinetic model of the polyurethane pyrolysis and to calculate the kinetic parameters using TG and DTG curves obtained by thermogravimetry analysis of polyurethane. The determined kinetic parameters could be used later within a computational fluid dynamics model for gaseous emissions occurring in sand core during casting process [8].

## 2. Experimental results

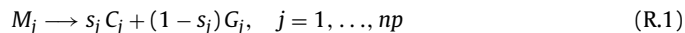
The polyurethane binder studied in this work was prepared by the reaction of phenolic resin and polyisocyanate resin. Both resins are in a liquid form and in combination with organic solvents. A blend of an equal weight of phenolic and polyisocyanate resins was mixed to form a reaction mixture. The formation of polyurethane occurred in the presence of a gaseous amine catalyst (dimethylethanolamine). The obtained solid polyurethane was ground using a mortar and pestle. Three samples were prepared with initial masses of 16.7, 16.0 and 16.4 mg. The analyses of the samples were conducted by a Perkin-Elmer TGA 7 thermobalance. The samples were heated in nitrogen flow at different heating rates: 20, 60 and 80 °C min<sup>-1</sup>. The mass loss and the mass loss rate curves of the polyurethane are given in Fig. 1. The results shows that the average value of the residual mass of polyurethane equals around 26.75% of initial mass of the various samples.

## 3. Kinetic models of organic solid pyrolysis

There are abundance of published research works dealing with the modeling of the pyrolysis of solid matter using TGA. In these works, several kinetic models were employed to describe the pyrolysis of organic solids. We can mention among the used kinetic models: the single global reaction model [9–12], the parallel independent reactions model [13–17], and the distributed activation energy model [18–22]. In the single global reaction model, the pyrolysis of organic solid is described by only one reaction. This model is the simplest kinetic model that one can use. It is generally employed to describe thermal decomposition of a pure homogeneous solid. The parallel reaction model assumes that the organic solid is constituted of many solid fractions (pseudo-components) each of which is decomposed independently by one reaction. Therefore, the interaction of pyrolysis reactions of different pseudo-components is neglected. This model is essentially used to describe the pyrolysis of organic solid blends and mixtures. In the distributed activation energy model, the organic matter is assumed to be decomposed by an infinite number of parallel independent reactions. Each reaction has its own activation energy and the sum of all reactions is given by a distributed activation energy. This model is used generally to take into account the heterogeneity of the studied solid matter.

## 4. Kinetic model of polyurethane pyrolysis

In this section, the kinetic model used in our study to describe polyurethane pyrolysis will be presented. This model is based on a parallel independent reactions model. In this model, the organic solid, noted  $M$ , will be considered as a mixture of  $np$  pseudo-components, noted  $M_j$ . The pseudo-components are supposed to decompose independently from one another, and not to influence each other. The pyrolysis of each pseudo-component produces a gas noted  $G_j$  and a solid noted  $C_j$ . Therefore the pyrolysis of  $M$  could be described by the reaction scheme (R.1)



where  $s_j$  is the mass-based stoichiometric coefficient of pyrolysis reaction of solid pseudo-component  $M_j$ .  $np$  is the number of parallel reactions. The conversion rate of each reaction  $j$  is given by the following equation:

$$\frac{d\alpha_{M_j}}{dt} = k_j (1 - \alpha_{M_j})^{n_j}, \quad j = 1, np \quad (1)$$

where  $n_j$  is the order of the reaction.  $\alpha_{M_j}$  is the conversion ratio of pyrolysable part of pseudocomponent  $M_j$ . It is defined as:

$$\alpha_{M_j} = \frac{m_{M_j}^0 - m_{M_j}}{m_{M_j}^0 - m_{M_j}^\infty}, \quad j = 1, \dots, np \quad (2)$$

where  $m_{M_j}^0$  is the initial mass of  $M_j$ .  $m_{M_j}$  the mass of  $M_j$  during the pyrolysis reaction.  $m_{M_j}^\infty$  is the final mass of  $M_j$  when the reaction is complete.

The kinetic coefficients  $k_j$  are function only of temperature.  $k_j$  are given in an Arrhenius form:

$$k_j = Z_j \exp\left(\frac{-Ea_j}{RT}\right) \quad j = 1, np \quad (3)$$

where  $Z_j$ ,  $Ea_j$  and  $R$  are the pre-exponential factors, activation energies, and the universal gas constant, respectively. The overall conversion rate of the solid matter  $M$  is given by a linear combination of conversion rates of  $M_j$  and, is expressed by Eq. (4)

$$\frac{d\alpha_M}{dt} = \sum_{j=1}^{np} c_j Z_j \exp\left(\frac{-Ea_j}{RT}\right) (1 - \alpha_{M_j})^{n_j} \quad (4)$$

where the coefficient  $c_j$  represents the fraction of the overall mass loss due to the pseudo-component  $M_j$ . The sum of these coefficients has to be equal to unity:

$$\sum_{j=1}^{np} c_j = 1 \quad (5)$$

In the same way, the conversion ratio of the solid matter  $M$  is given by a linear combination of conversion ratio of different pseudo-components  $M_j$ :

$$\alpha_M = \sum_{j=1}^{np} c_j \alpha_{M_j} \quad (6)$$

$\alpha_M$  can be calculated using TGA results by the following equation:

$$\alpha_M = \frac{m_M^0 - m_M}{m_M^0 - m_M^\infty} \quad (7)$$

$m_M^0$ ,  $m_{M_j}^\infty$  and  $m_{M_j}$  are the initial, final and current weights of  $M$ . If we consider that the TGA experiments have been carried out in

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