# Characterizing the Degradation of Solid Materials using the Tubular Furnace, Cone Calorimeter, FTIR and Kinetic Modeling

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## 1 Degradation of Solid Materials

The controlling mechanisms in the combustion of solid fuels are of great interest to fire safety. During the burning of a solid fuel, the degradation kinetics governs the emission of pollutants, dictate the heat released and highly influences the dynamics of the process. These kinetics and the expressions describing the degradation behaviour are needed for the understanding and modeling of solid burning and fires. However, this information is not readily available in the literature for most practical materials due to the complexity of the mechanisms and the lack quantified knowledge, especially for fuels such as polymers.

The methodology followed here and results presented involve simulating experimental tests of solid degradation with a kinetics model and using a genetic algorithm to find a set of model parameters that provide the best agreement between the model predictions and the experimental data.

## 2. Experimental Study.

During fire, the thermal degradation of the combustible materials can be assimilated to thin materials (homogenous temperature into the combustible) or thick materials (gradient of temperature into the material). In order to study these two cases, two different experimental devices are used during the present work :

- the thermal degradation of the thin materials are characterized with the tubular furnace : indeed the small mass of combustible used (200 mg) permit to obtain a constant temperature into all the combustible.
- the thick materials are degraded in the cone calorimeter.

The two set-up are on-line associated to combustion gas analysers: chemiluminescence, absorption, FTIR.

## 2.1. Tubular Furnace

A tubular furnace is an experimental apparatus used to study the off-gassing product of a solid sample as it thermally degrades. The central part of a furnace is a horizontal quartz reactor which allows temperature control

of a material sample. The sample is heated and a working gas is flown over it, while the gas products are channelled to out of the furnace. The furnace is coupled with an FTIR analysing the off-gases and providing the concentration of the following gas species: CO, $CO_2$, $CH_4$, $C_2H_2$, $C_2H_4$, $C_3H_8$, $C_6H_6$, HCHO, $H_2O$, HCl, $NO_2$, NO, $N_2O$, HCN, $NH_3$ and $SO_2$.
For the experiments reported here, the furnace temperature was operated in the temperature range from the temperature of pyrolysis to 1200 °C. The temperature of pyrolysis is determined from experiments in DSC or TGA or from the literature. Experiments were run under both, inert and air, atmospheres and the flow rate was varied in the range from 2 and 4 l/min. The control of the atmosphere of degradation, from 0 to 20,9 % is important since a fire can be confined or well ventilated. The solid fuels studied were those of industrial (e.g. transportation and building) interest cardboard, wood and polyurethane foam.

The results and the different species concentrations for the first two materials (cardboard and wood) can be seen in Table 1 (cardboard) and 2 (wood). The results are presented in mg of species formed by gram of combustible burned.

| **Cardboard** | CO | $CO_2$ | $CH_4$ | $C_2H_2$ | $C_2H_4$ | $C_2H_6$ | $H_2$ | NO | HCN | $NH_3$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| mg/g | 280 | 75 | 27 | 7 | 24 | 4 | 10 | 0,4 | 0,7 | 0,2 | 48 |

Table 1. Results for cardboard from tubular furnace tests at 1100°C, inert atmosphere and t=0.4 s.

| **Wood** | CO | $CO_2$ | $CH_4$ | $C_2H_2$ | $C_2H_4$ | $C_2H_6$ | $H_2$ | NO | HCN | $NH_3$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| mg/g | 290 | 77 | 44 | 10 | 32 | 4 | 11 | 0,8 | 1,7 | 0,4 | 54 |

Table 2. Results for wood from tubular furnace tests at 1100°C, inert atmosphere and t=0.4 s.

## 2.2. Cone Calorimeter

The calorimeter used is the ISO 5660, coupled with a module of control of atmosphere. This one is used to determine and to measure the impact of the concentration of oxygen (ventilation of the fire) on the parameters of the degradation. The mass loss rate is calculated form the load cell of the apparatus.
The same combustible are studied.

# 3 Kinetic Model and Genetic Algorithms

The hypothesis in this work is that the gases from the degradation are produced from a set of reactions that can be described with a mechanism of only a few reactions. This mechanism is formulated *a priori* based on fundamental chemical and fire knowledge on solid degradation.

A mathematical model describing the kinetic process taking place inside the furnace is develop. This model account for the production of gas species as a function of the temperature of the furnace and its dilution in the outlet tube. The model requires the parameters describing the reaction rates (Eq. 1) and the species yields according to the degradation mechanism.

$$\dot{\omega}_i = A_i e^{-\frac{E_i}{RT}} m_i y_{o_2} \tag{1}$$

The results of the mathematical model are compared to the experimental results (e.g. shown in Table 1 and 2) and the parameter set providing the best agreement between the two results is consider the solution. For find this solution, it is needed to solve a complex inverse problem composed of non-linear set of expressions.

Classical optimization tools are not appropriate for the present application because the high dimensionality of the problem produces a large search-space and very complicated landscapes of the optimization target, with numerous local maxima and minima. An efficient multidimensional optimization technique such as a genetic algorithm (GA) is therefore necessary. GAs are a heuristic search method that imitates the principles of biological adaptation [1]. GAs efficiently handle intricate and non continuous objective landscapes, multiple local optima, and noise in the data. GAs are found to be valuable for combustion of solids and have been applied to smouldering combustion [2], and fire [3].

## 4 Application of the Results

The completion of the parameter for the mathematical model allows now to predict results are different set of conditions. These predictions can be applied to the furnace test but also to other models where the thermal degradation of the materials studied is involved.
The applicability of the kinetic model to other conditions is shown.

A preliminary used of the results is applied to the cone calorimeter. The new kinetics is coupled with a heat transfer model and applied to simulate the solid behaviour in the cone calorimeter. This allows the prediction of ignition and burning behaviour. It is important to know that the knowledge of composition is essential to establish the concentration of flammable gases that will lead to ignition. Without this information it is impossible to predict piloted ignition, as used in the cone calorimeter. The simulation of the solid degradation and gas combustion is done by using the FDS [4].

The feasibility of the methodology to obtain kinetic models from the furnace test has been demonstrated. Parameters of thermal degradation and fire behaviour are needed for numerical modelling of solid combustion but not easily available. The methodology proposed here can be further applied to other materials, or to estimate other material properties.

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