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Multi-scale modeling of the thermal decomposition of fire retardant plywood

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ABSTRACT

Due to the complexity and costs of full scale fire-test experiments, numerical simulations provide a useful alternative when investigating the fire behavior of new materials. The mass loss rate of the solid is one of the most important parameters in assessing fire behavior as it is directly linked with the pyrolysis gas flow rate and represents the initial factor of the combustion process. In this paper, fire retardant plywood is investigated with a focus on the solid mass loss rate modeling. A multi-scale approach is followed in order to establish the kinetic mechanism of thermal degradation. A combination of small scale and large scale tests were completed to fully develop and validate the proposed kinetic mechanism. For small scale testing, experiments are conducted by using thermo-gravimetric analysis coupled to gas analysis with FTIR technique under nitrogen and air atmospheres. These experiments were completed at several heating rates. Thermo-gravimetric results are used to propose a kinetic mechanism for the thermal decomposition of the solid and the kinetic parameters are calculated by using the genetic algorithms method. For larger-scale testing, experiments were carried out in a cone calorimeter coupled to a FTIR gas analyzer. The experiments were completed in air atmosphere in order to validate the kinetic mechanism developed from small-scale testing. The kinetic model developed is implemented into the general Gpyro model which takes into account both thermal and mass transfer phenomena inside the solid. The results showed good agreement between the model calculations and the experimental data.

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1. Introduction

Today, computational fluid dynamics (CFD) codes are widely used by the fire protection engineers for performance based design as well as disaster analysis. Those codes are composed of several sub-models, each one having a specific function. Among these models, the model of pyrolysis describes the thermal decomposition of the solid: mass loss, mass loss rate, quantity of gas. This model includes the values of flammability and decomposition properties of materials as well as the kinetic parameters of thermal decomposition. Many models exist in the literature and could have different degrees of complexity. These models range from simple model based on empirical laws, to more complex models that describe physical and chemical phenomena.

Typically, pyrolysis models can be divided into two principal categories as follows:

- The semi-empirical models, where the solid is considered as inert until the surface temperature reaches an ignition temperature

(T_{ig}). The mass loss rate (MLR) can be determined from the energy released after assuming the heat of combustion (ΔH_c) as a constant. The heat flux used for this calculation comes from experimental results [1,2].

- Numerical models: The pyrolysis rate is null until the surface reaches a limiting value of the temperature. The degradation is also controlled by the heat transfer into the solid. In these models, the kinetics is fully described as the energy transfer in the solid by solving the heat balance equation. This method is quite simple but requires knowledge of the thermal properties (k , ρ , C_p) [3]. Unfortunately, the kinetic parameters and the thermal property values cannot be measured through one type of experiment. Many experimental techniques are required such as thermo-gravimetric analysis (TGA) and cone calorimeter tests.

TGA is a traditional method to investigate thermal degradation by determination of the weight loss characteristics at different heating rates and atmospheres [4–10]. Also, TGA coupled to Fourier transformed infrared spectroscopy (TGA-FTIR) is one of the most useful methods that scientists have at their disposal to understand thermal degradation of solid materials. This technique brings an understanding about the chemical reactions that occur

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Nomenclature

\dot{w}_{fg}'''	formation rate of all gases from the condensed phase ($\text{kg m}^{-3} \text{s}^{-1}$)	ΔH_k	change in enthalpy of the condensed phase species k (J kg^{-1})
$\bar{\rho}$	weighted bulk density (kg m^{-3})	h_i	enthalpy of the condensed phase species i (J kg^{-1})
ρ_g	density of the gas phase (kg m^{-3})	\bar{h}_g	weighted enthalpy of the gas phase (J kg^{-1})
$\bar{\psi}$	weighted porosity (–)	$h_{g,j}$	enthalpy of the gas phase species j (J kg^{-1})
\dot{m}''	mass flux ($\text{kg m}^{-2} \text{s}^{-1}$)	D	diffusivity ($\text{m}^2 \text{s}^{-1}$)
Y_i	mass fraction of condensed phase species i	P	pressure (Pa)
Y_j	mass fraction of gas phase species j	\bar{M}	weighted molecular mass (kg mol^{-1})
\dot{w}_{fi}'''	formation rate of condensed phase species i ($\text{kg m}^{-3} \text{s}^{-1}$)	R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
\dot{w}_{di}'''	destruction rate of condensed phase species i ($\text{kg m}^{-3} \text{s}^{-1}$)	\bar{K}	weighted permeability (m^{-2})
\dot{w}_{fj}'''	formation rate of gas phase species j ($\text{kg m}^{-3} \text{s}^{-1}$)	ν	viscosity ($\text{m}^2 \text{s}^{-1}$)
\dot{w}_{dj}'''	destruction rate of gas phase species j ($\text{kg m}^{-3} \text{s}^{-1}$)	z	axial coordinate
j_i''	diffusive mass flux ($\text{kg m}^{-2} \text{s}^{-1}$)	σ	Stephan Boltzmann constant ($\text{W m}^{-2} \text{K}^{-4}$)
\bar{h}	weighted enthalpy of the condensed phase (J kg^{-1})	α	conversion factor (–)
\bar{k}	weighted thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	$\alpha_{i,k}$	Conversion factor for species i and reaction k
T	temperature (K)	A	pre-exponential factor (s^{-1})
h_{cv}	heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)	E	activation energy (J mol^{-1})
T_g	temperature of the gas phase (K)	MLR or dm/dt	mass loss rate (g s^{-1})
$\bar{\epsilon}$	weighted emissivity (–)	t	time (s)
\dot{q}_0''	external heat flux (W m^{-2})	β	heating rate ($^\circ\text{C min}^{-1}$)
\dot{q}_r''	radiative heat flux (W m^{-2})	C_p	heat capacity (J K^{-1})
$\bar{\kappa}$	in-depth radiation absorption coefficient (m^{-1})	n	order of the reaction
		TGA	thermo-gravimetric analysis
		FTIR	fourier transformed Infrared spectroscopy
		GA	genetic algorithms

during the thermal decomposition [6]. One advantage of the TGA method is that the conditions of degradation are well known and controlled. Unfortunately, the conditions of decomposition in the TGA apparatus are not representative of those in real fire conditions. The heating rates are low compared to the real heat fluxes and there is no temperature gradient and mass transfer into the sample. Thus, the results obtained from TGA test may not be applied to real-life fire situations. However, the slow heating rates and the milligram size samples of the solid permit identification of the different thermal decomposition steps. This information can then be used to initialize the models and develop an approximate assessment of fire behavior.

In contrast, the cone calorimeter apparatus is a standard large-scale test for materials [11,12]. It measures the evolution of mass loss as well as mass loss rate as a function of time. The conditions of degradation are realistic, with thick materials, large heat fluxes and heat and mass transfer phenomena. However, many required parameters for the development of models of pyrolysis are unknown such as the heat and mass transfer inside the solid matrix. Moreover, the gradient of temperature into the solid sample leads to a superposition in time of the thermal reactions of degradation. However, in order to take into account the different constraints and to be able to develop and validate appropriate models of thermal decomposition at all the conditions, large-scale testing approaches are required [13].

In this paper, the thermal decomposition of plywood was studied using two methods which test at two different scales: TGA (particle scale) and cone calorimeter (material scale). Each of the methods (TGA and Cone) were coupled to a Fourier transformed infrared spectrometer (FTIR gas analyzer) to consider the gaseous emissions evolved. A mechanism of thermal decomposition is proposed by analysis of both the mass loss rates and the gaseous emissions from TGA experiments. The reaction rate is described by a modified Arrhenius law [13,14] with four unknown parameters: the stoichiometric coefficient, the energy of activation, the pre-exponential factor and the order of the reaction.

These kinetic parameters are then determined by the optimization method of the genetic algorithms. A comparison between numerical and experimental evolutions of the mass and the mass loss rate for the different heating rates at the particle scale (obtained from TGA) showed a good agreement which confirms the model was validated at the small scale. It was then incorporated into the Gpyro code [15] in order to simulate the experimental results obtained at the cone calorimeter scale. The numerical evolutions of the mass loss rate are in good agreement with the experimental ones, thus the model is also validated at this larger scale.

2. Experiments

2.1. Materials

Flammability standards (Euroclass system) have been developed to characterize the fire behavior of the materials. This European classification system includes two sub-systems: a main one for all construction products and another one for flooring products. It takes into account the smoke class and the burning droplets class. More details are available in [16,17].

There are seven Reactions to Fire classification levels available – A1, A2, B, C, D, E and F. Additional criteria provide information on a product's tendency to produce smoke and flaming droplets or particles – s1 to s3 criteria. For combustible products, smoke release is an important consideration and is measured for Reaction to Fire classes A2 to D. There are three smoke intensity levels: s1, s2 and s3, with s3 being the worst.

Burning droplets/particles can inflict skin burns and cause further spread of fire. Burning droplets/particles are measured for Reaction to Fire classes A2 to E. There are three classes of burning droplets: d0, d1 and d2, with d2 being the worst. The present work uses a treated plywood (mainly made of oakum) classed B (s3, d1) so combustible with non-flammability.

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