



Influence of reaction mechanism accuracy on the chemical reactivity prediction of complex charring material in fire condition



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ABSTRACT

The production of combustible gases from solids during thermal decomposition and how these gases feed the flame take an important part in the currently fire research. In this context, the modelling of the thermal, chemical and physical phenomena in the condensed phase constitutes a key step to accurately predict the gases production (source term). This modelling applies to establish a relationship between the kinetics of gases production (thermal decomposition of the matter), the solid temperature and the atmosphere composition (% of oxygen). Due to digital progress, the accuracy of modelistic approaches does not depend on the resolution technique, but rather on the accurate description of the apparent chemical reaction pathway. This mechanism, identified through the matter scale experiment, will define the number of kinetic parameters to be estimated. This study focuses on the complexity level of the reaction mechanism, and its effect on the accuracy of the chemical reactivity forecast. The analysis is thereby performed on a solid material (polyisocyanurate foam) with a complex multi-step mechanism. Several mechanisms complexity with various levels of sophistication (number of linked reactions) are studied while their results are presents and discussed. This work uses a new statistical technic based on statistical criteria to judge the quality of the model and to choose a reaction mechanism with a degree of complexity adapted to fire modelling at large scale. The analysis done reveals a possibility to simplify the initial reaction mechanism's complexity, without influencing the accuracy of forecasts. These works have therefore demonstrated that the use of highly simplified mechanisms enables the reproduction of the complex decomposition kinetics of the PIR foam. On the other hand, the use of a detailed reaction pathway is not always necessary to predict the decomposition of complex material through modelistic methods.

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1. Introduction

Many researches are conducted in order to reduce the fire hazard in the sectors of the transportation (train, ship, aircraft...), energy (storage, extraction...), building or industry. An important part of these researches concerns the prediction of material reactivity during a fire. In fire science, this problem is a great challenge because of the complexity of the physical and chemical processes occurring inside the material [1].

Modelling the thermal reactivity of a material requires to accurately knowing intrinsic properties such as thermophysical properties or kinetic parameter. Unlike thermophysical properties, kinetic parameters associated to the material reactivity cannot be

directly determined through common bench scale experiments. In solid phase, since they do not represent a “real” reaction, these parameter can be freely determine in order to accurately predict all step of the chemical process [2] like the decomposition, the charring or the production of a specific gaseous species. The kinetic properties are represented by a kinetic model which considers a decomposition mechanism of the matter, a kinetic law and different kinetic parameters.

Historically, several inverse methods have been developed to estimate these kinetic parameters from microscale consideration, and have been grouped in two categories [3]: isoconversional methods (also called *model-free*) [4–6] and modelistic methods (also called *model fitting*) [7,8].

1. The “*isoconversional method*” is an analytical method based on graphical analysis which does not require any assumption on the reaction scheme. The approach is among the most reliable

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Nomenclature

A	Pre-exponential factor, s^{-1}
E	Activation energy, $J\ kg^{-1}$
$f(\alpha)$	Differential conversion function
$k(T)$	Constant rate
m	Mass (kg)
N	Number of components (-)
N	Order of reaction (-)
R	universal constant of gases
T	Time, s
T	Temperature, °C
Y	Mass fraction ($kg\ kg^{-1}$)
Y_j	Mass fraction of species j ($kg\ kg^{-1}$)
Y_r	Residual mass fraction ($kg\ kg^{-1}$)
Y_t	Total mass fraction ($kg\ kg^{-1}$)

Greek symbols

α	Degree of conversion
δ	Oxygen reaction order
$\dot{\omega}$	Reaction rate, s^{-1}
β	Heating rate, $K\ min^{-1}$

Subscripts and superscripts

i	i^{th} Reaction
j	Condensed phase species j of the i^{th} reaction
f	Final
0	Initial
O ₂	Oxygen
R	Residue
T	Total
.	Per unit time

ones for simple, non-noisy, well separated consecutive reactions although it remains sometimes inefficient for complex reaction pathways with overlapping [9,10].

2. An alternative consists in using a modelistic approach to estimate parameters of complex kinetics [7,8,11–13]. Basically, this method estimates the kinetic parameters of each heterogeneous reaction in solid phase, minimizing thus the difference between experimentally measured and calculated data of the reaction rate. Unlike isoconversional methods, modelistic ones are able to identify the suitable multi-step reaction models for the description of complex kinetics [10].

Today, progress of the modelistic approach's prediction accuracy of thermal decomposition is no longer hampered by the resolution technique [1,2], but rather by the kinetic model [14] and the description of the solid phase's decomposition process; a description whose degree of complexity and precision may vary. The mechanisms identified from microscale consideration, define the number of apparent chemical reactions and therefore the number of kinetic parameters which have to be estimated. The definition of a reaction scheme depends on the assumptions about the material's reactivity and the available information on its composition.

Detailed descriptions of chemical reaction occurring in solid material can be found in the literature [15–17]. Initially developed for reactions in gaseous phase, software such as Exgas [18] or other [19] can be applied for the reaction of solid materials in order to generate this kind of mechanism according to specific criteria. Several authors have applied these tools to solid materials, such as high density polyethylene (HDPE) [20–23]. These obtained reaction mechanism considers an extremely large number of elementary reactions (sometimes more than 7500 reactions [23]) and species

(more than 1000 [23]) which complicate an eventual application. In this context, several researches have been conducted since many years, in order to propose a reduced mechanism based on a strict method [20–24]. Nevertheless, that technic is difficult to use and only available under the condition that the mechanism is developed and tested. In fire science, various authors proposed semi-detailed kinetic mechanisms based on microscale consideration such as PU [25] or more complex molecules such as wood [26]. Despite the reduction and the rigorous method used to reduce the mechanism, two main problems need to be considered in fire application:

- The Computational fluid dynamics (CFD)-based fire modelling (FDS [27], FireFoam [28]) cannot take into consideration a great number of reaction, since its aim to reduce the calculation time for engineering needs;
- The composition of the studied material is usually unknown and often not pure.

Because of the second point, chemical processes which occur during the decomposition of solid materials are often too complex to be described in detail. Furthermore, with the chemical aspect of the degradation, physical aspects (such as fluid motion) have to be added because in some cases, these phenomena can be neglected. Indeed, the chemical decomposition process is globally described by a series of competing or consecutive heterogeneous reactions which are difficult to identify experimentally.

The description of the problem addresses the following question: how is it possible to reduce the mechanism or create a simplified one that will consider the kinetic behaviour? For reactions in gaseous phase, there are numerous methods for reducing the size of highly detailed schemes [29–32] which are based on the redundancy theory. This approach consists in defining some criteria for the deletion of species and reactions which are not compatible [22]. According to this principle, the most efficient reduction methods are the Detailed Reduction (DR), and Direct relation Graph with error propagation (DGR/DRGEP method) [22,32,33]. These methods are perfectly adapted for reducing detailed reaction pathways. Nevertheless it remains limited in order to reduce the problem up to few apparent reactions.

In order to simplify this problem and due to the modelling constraint with CFD code, the description of a material's chemical decomposition in fire field is formal rather than mechanistic. For this reason, the commonly adopted approach describes the material's thermal reactivity through a "simplified and comprehensible equivalent scheme" which specifies the least number of apparent reactions inside the mechanism [13]. As a result, only one or two reactions are generally considered, but sometimes more. These apparent reactions must capture the main trend [11], or specific phenomena (such as the initial decomposition temperature of the material, the production of a specific species, the charring process, the final residual mass, etc) which may be important at a higher scale, for the prediction of ignition time, gas fuel production etc. Some physical properties are directly dependent on the occurring reaction. In order to achieve this, the reaction pathways of solid material are usually defined according to mass loss rate criteria [11–13]. In contrast to the gas phase, there is no a simplified tool or method able to define mechanisms from MLR results. Consequently, each operator can identify its own mechanism. The use of MLR criteria alone does not guarantee that the identified mechanism and all of the associated parameters will represent the physical phenomenon or give the best fit of the Mass Loss Rate. Recent works have shown the relevance of considering MLR criteria with other influencing factors, such as the gaseous emissions [25], the temperatures or the thickness [34,35].

A trade-off must be found between the consistent level of complexity for modelling and the accuracy of the prediction [1]. This

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