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PolyFlame

PolyFlame est une newsletter à destination des chercheurs et des industriels du domaine du « comportement au feu des matériaux organiques ». Cette newsletter périodique est publiée via la Société Chimique de France (SCF).

A travers cette newsletter, vous découvrirez les nouveautés et les dernières avancées dans le domaine du comportement au feu en matière de recherche et développement, la synthèse et la production de nouveaux systèmes de retardateurs de flamme, les besoins industriels. Pour faire avancer la connaissance et l'expertise, une partie de cette newsletter est consacrée à l'écoute des chercheurs et des industriels reconnus dans ce domaine.

Bonne Lecture,

*(This issue is dedicated to "**Smoldering Fires**")*

An interview with Dr V. Babrauskas

Would you please present yourself, your scientific research field and activities?

I am Dr. Vyto Babrauskas. Ever since the 1970s, I have been engaged in a very wide range of fire safety research activities, which includes fire resistance, fire modeling, heat release rate, toxicology, explosions, electrical fires, and smoldering.

Could you define briefly the smoldering phenomena?

Smoldering is defined as a propagating, self-sustained exothermic reaction wave deriving its principal heat from heterogeneous oxidation of a solid fuel. More practically, it can be identified as combustion without a flame. Smoldering is a sub-set of glowing combustion, in that the reaction wave has to be self-sustained; meanwhile, glowing combustion can be self-sustained, or externally driven. The term 'smoldering' is often used loosely by laymen, who tend to refer to any fire where big flames are not present as 'smoldering.' This type of usage should be discouraged.

Which kinds of materials are concerned by smoldering?

A very wide range of materials are susceptible to smoldering. The most important are wood and all forms of wood products, also a wide array of agricultural commodities. Some man-made plastics can smolder under certain circumstances, but the majority of plastics do not.

What are the main differences between the smoldering fires and flaming fires?

In combustion science, the spilt is made into homogeneous fires and heterogeneous combustion. Homogeneous combustion is combustion that takes place throughout a volume; in practice, this is a flaming fire. The contrast is that a smoldering fire does not exhibit flaming. In the real world, however, situations can arise whereby a fuelbed is exhibiting both areas of flaming and areas of smoldering. Perhaps the largest practical difference between flaming and smoldering fires is in their heat release rate (HRR). In a structure fire, a flaming fire may be on the order of 1 MW, while a smoldering fire may be 1 kW.

Which statistics about smoldering and how many kinds of fire are known?

This is a very difficult question. The fire brigade does not get called unless the fire is big. Thus, when the fire service personnel arrive, they see a fire in its later stages, not at its beginnings. As a result, they cannot reliably describe how the fire started. A fire may initially start as flaming or smoldering, but the fire service officer will not see this beginning. As a result, in the USA, statistics are not tabulated on this question, since it is considered that there is no way for fire service officers to reliably make this determination. Nonetheless, expert judgment is that roughly half of structure fires start in the smoldering mode.

How one can control/avoid the flameless fires (before their transition to flaming mode)?

Fires may be avoided by breaking any of the three legs of the fire triangle: fuel, oxygen, and source of heat. Usually it is easiest to control sources of heat, harder to control the availability of fuel, and harder yet to control the availability of oxygen.

Which kinds of flame retardants are principally able to suppress the smoldering phenomena?

Smolder retardants are generally not added to combustible materials or products, except for certain product types which are subject to governmental regulations, e.g., mattresses, upholstered furniture, cellulosic thermal insulation. Boric acid is often added to cellulosic products in the above categories in order to reduce their propensity to smolder. Elemental sulfur has also been found to be useful in reducing smoldering under a wide range of circumstances. Various other chemicals can be found in the patent literature, but none are in widespread use. It

Another topic: Which subjects will be the main challenges of fire science in the next decade?

My own view is that the largest challenge for the fire safety field is to learn how to provide fire safety solutions with a favorable benefit/cost ratio. The world has seen two centuries' worth of fire safety regulations being promulgated without much consideration towards assessing the costs versus the benefits. I think the biggest challenge for the profession is to reorient itself, so that a benefit/cost assessment is performed for any regulation. This, by the way, pertains not only to fire safety, but also to other safety areas, e.g., electrical safety.

A new book on "Smoldering Fires"

"The phenomenon of smoldering, specific to some types of materials, is the cause of many fires. The book entitled "Smoldering Fires "authored by Vytenis Babrauskas is a very useful reference on this topic. It draws up its typology, describes the main stages and identifies the influence of various parameters such as type and geometry of the materials involved, humidity and oxygen concentration, and figures out the points which remain incompletely understood and still require research efforts."

Le phénomène de feu couvant (en anglais smoldering), spécifique à certains types de matériaux, est à l'origine de nombre d'incendies. Le livre de Vytenis Babrauskas constitue une synthèse très utile qui fait le point sur ce phénomène, en dresse la typologie, en décrit les principales étapes et identifie l'influence de divers paramètres (type et géométrie des matériaux impliqués, humidité et concentration en oxygène) sans masquer les points qui restent incomplètement compris et nécessitent encore des efforts de recherche.

More information : https://doctorfire.com/

Smouldering Combustion Phenomena in Science and Technology

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Introduction

Smouldering is a slow, low-temperature, flameless form of combustion, sustained by the heat evolved when oxygen directly attacks the surface of a condensed-phase fuel [1] [2]. It is a hazard of importance to several scientific disciplines but also a novel technological concept under development. Smouldering is the leading cause of deaths in residential fires [3] and causes economics losses of the order of $350 million per year in property damage in the USA alone. The aerospace industry has growing safety concerns regarding in-flight (including space flights) smouldering fires in hidden areas that cannot be detected or properly extinguished using conventional protection systems [4]. Ecologists and forest scientists study smouldering wildfires because they destroy large amounts of biomass and cause greater damage to the soil ecosystem than flaming fires [5]. Atmospheric scientists have studied acute pollution episodes caused by the Indonesian peat fires in 1997 and the destruction of vast amounts of stored carbon in the soil [6]. Earth scientists study smouldering subsurface fires in coal mines and seams that burn for very long periods of time (even centuries) [7]. There are noteworthy new environmental and energy technologies based on the direct application of smouldering combustion. These include remediation of contaminated soils, production of biochar for long term carbon storage, enhanced oil extraction from reservoirs and gasification of coal seams.

Whereas flaming combustion has been widely studied and is the aim of hundreds of papers per year, smouldering combustion has received very little attention as shown in the scientific publishing records in FIREDOC [8]. This lists less than 600 papers on smouldering out of 80,000 on fire sciences published after 1900. Combustion and fire scientists were the first to research the topic in the 50's. It is only in the last decade that smouldering phenomena is been studied significantly by other scientific fields such as ecology or atmospheric and earth sciences.

The first widely available scientific work of merit on the topic was published in 1957 [9]. Palmer's seminal work consisted of burning piles of dust. This pioneering work was followed by a dozen of papers on smouldering of dust and fibrous materials in the 60's. The same low rate of studies per year continued during the first half of the 70's but with the focus switched to polymeric foams and cigarettes. A sudden increase occurred in the second half and about twenty papers per year on average were published with a focus on smoke detection, toxicity, polyurethane foam and cellulose. The publication rate peaked in the 80's and gradually dropped to an approximate average of 10 papers per year from 2001 to date.

This long-term neglect has led to the split of the topic into rather isolated bodies of research in diverse disciplines. Bridging these gaps would stem from a multidisciplinary understanding of the phenomenon and has the potential to lead into important benefits to our safety, economy and environment.

This paper attempts to synthesize a comprehensive view of smouldering combustion bringing together contributions from diverse scientific disciplines. For an in-depth review, the reader is refereed to the work of Ohlemiller [1], which on the date that this paper goes to press still stands as the only review of the fundamental scientific concepts behinds smouldering combustion to date. A more recent review on the issues of smouldering in fire safety engineering is [2].

II. Overall Characteristics of Smouldering

Smouldering is a fundamental combustion problem involving heterogeneous chemical reactions and the transport of heat, mass and momentum in the gas and solid phases.

The fundamental difference between smouldering and flaming combustion is that, in the former, the oxidation reaction and the heat release occur on the solid surface of the fuel or porous matrix and, in the latter, these occur in the gas phase surrounding the fuel. Fig. 1 shows the two burning regimes for forest fuels (top) and the most familiar example of smouldering, coal embers (bottom). The characteristic temperature, spread rate and heat released during smouldering are low compared to those in the flaming combustion of a solid. Typical values in smouldering at ambient conditions are around 500-700 °C for the peak temperature and 6-12 kJ/g for the average heat of combustion; typical values during flaming are around 1500-1800 °C and 16-30 kJ/g respectively. Because of these characteristics, smouldering propagates at low velocities, typically around 10-30 mm/h [2], approximately two orders of magnitude lower than the velocity of typical flame-spread. Significantly higher temperatures and higher heats of combustion can be expected in technological application of smouldering combustion in porous media with forced flows at high pressure (like in-situ combustion for oil extraction or coal gasification) since these reproduce nearly adiabatic conditions and provide large oxygen supplies.

Because of its low temperature, smouldering is characteristically an incomplete oxidation reaction and thus emits a mixture of toxic, asphyxiant and irritant gases and particulates at a higher yield than flaming fires. It favours CO_2 to CO ratios around unity (as opposed to ratios around 10 in flaming combustion), so CO is an important toxic factor in smouldering fires [10], [11].

Figure 1. Left) Snapshot showing the two regimes of combustion for solid fuels; flaming of the grass and smouldering of the organic soil (for scale reference, the flame is about 10 mm in height). Right) Glowing charcoal briquettes (photo by J.B. Nielsen, Public Domain, Wikimedia Commons)

Many solid materials can sustain a smouldering reaction, including coal (see Fig. 1 bottom), cotton, tobacco, dust, paper, peat (see Fig. 1 top), duff and hummus (see Fig. 1 top), wood, board of organic fibres (see Fig. 2 right), synthetic foams and charring polymers including polyurethane foam (see Fig. 2 left). Smouldering fuels are characterized by having a significantly greater characteristic thermal time than fine fuels but allow oxygen transport to the surface. These characteristics lead to the slow but persistent burning typical of smouldering combustion. In general terms, the fuel consists of an aggregate and permeable medium formed by particulates, grains, fibres or a porous matrix. These aggregate fuel elements facilitate the surface reaction with oxygen by providing a large surface area per unit volume. They also act as thermal insulation that reduce heat loss but, at the same time, permit oxygen transport to the reaction sites by convection and diffusion [1].

Synthetic foams, like polyurethane foam (see Fig. 2 left), are highly susceptible to smouldering combustion. The porous nature of the foam allows air to feed the exothermic reaction while protecting the reaction zone from heat losses to the surroundings. Polyurethane foam is the material of choice for most laboratory controlled tests of smouldering combustion because it is easy to ignite, has a high propensity to smoulder, and also because its composition and physical properties are very homogeneous an advantage not present in most natural fuels.

Fig. 2: Left) Cross-section of a partly smouldered polyurethane slab 200 mm high burned in microgravity conditions (photo by NASA, [12]). Right) Smouldering of a 80 by 50 mm sample of woody fiberboard (31 min after hot-coil ignition at the bottom).

The smouldering of liquid fuels soaked in a porous matrix is also possible. There are three examples of this in the literature. Lagging fires, well known in fire and process safety, involve the soaking of a porous insulating material by oil or another self-igniting liquid [13]. In the petroleum industry, smouldering fronts are purposely initiated in underground porous reservoirs to extract oil [14]. More recently, a wide range of liquid contaminants saturated in porous mineral soils has been smouldered at laboratory conditions [15]. The presence of the porous matrix is indispensable for smouldering of these liquids to occur, suggesting that the oxidation takes place at the pore surface in contact with the liquid fuel.

Smouldering ignition requires the supply of heat flux to the solid fuel. The subsequent temperature increase of the solid first sets off the thermal-degradation reactions (mainly endothermic pyrolysis) and then oxidation, until the net heat released by oxidation is high enough to balance the heat required for propagation. This net heat released by the reactions is partially transferred by conduction, convection and radiation ahead of the reaction and partially lost to the environment. The oxidizer is transported to the reaction zone by diffusion and convection, in turn feeding the oxidation reactions. Once ignition occurs, the smoulder reaction advances gradually through the material. It is well established that for most materials and typical conditions, the two limiting factors in smouldering propagation are the oxidizer flux to, and the heat losses from, the reaction zone [1].

The transition from smoulder to flaming is a spontaneous gas-phase ignition supported by the smoulder reaction which acts both as the source of gaseous fuel (pyrolyzate, CO, etc.) and of heat to carry the reaction. Fig. 3 shows snapshots of an experiment of smouldering propagation over a period of several seconds and the transition from smouldering to flaming in a polyurethane foam sample. The transition occurs when critical conditions inside the pores of the solid are met, triggering the onset of gas-phase reactions [16], [17] [18]. These conditions include the flammability of the gas mixture inside the pores and a net excess of heat released by strong solid-phase oxidation reactions. Increased levels of oxygen and airflow (e.g. caused by wind) can strongly influence transition. Transition to flaming has only being observed to date to occur in forward propagation mode because the hot gases preheat the fuel ahead. But currently understanding of the process is rather limited and more research is required on the topic. In particular, the transition from smouldering to flaming cannot be predicted in practical terms since it is not well described by any model to date.

The heat flux needed to attain smouldering ignition is significantly lower than that for flaming ignition. For instance, smouldering ignition of polyurethane foam has been reported to occur with a heat flux of 2 kW/m^2 using a contact heater [12], while direct flaming ignition with a radiant heater occurs only above 10 kW/m^2 [19]. Thus, the transition from smouldering to flaming combustion provides a hazardous shortcut to flaming fires, which could be initiated with heat sources that are too weak to directly ignite a flame on the solid fuel.

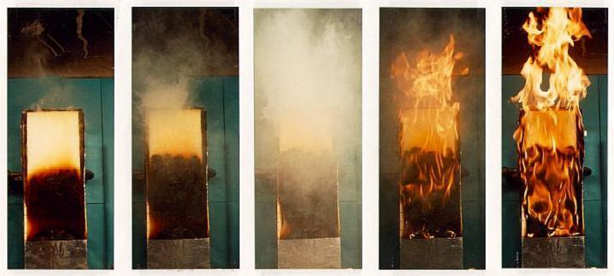

Fig. 3: Series of photographs of a combustion experiment illustrating the transition to flaming in a smouldering polyurethane slab 40 cm high (photo by NASA, [18]). After 1 hour of burning only half the sample has smouldered (photo 1). When transition takes place (photos 2 and 3), the whole sample is engulfed in flames in a few seconds (photos 4 and 5).

When studying smouldering propagation through the interior of combustible materials, it is common to consider the simpler one-dimensional process and to classify it in two main configurations: opposed and forward propagation. These are defined according to the direction in which the smoulder reaction propagates relative to the oxidizer flow. Fig. 4 shows the two 1D configurations. In opposed smoulder, the reaction front propagates in the direction opposite to the oxidizer flow, and in forward smoulder, the front propagates in the same direction.

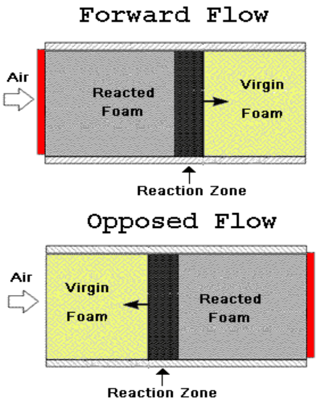

Fig 4: Configurations in one-dimensional smouldering; forward and opposed.

These two configurations are distinguished by the roles played by heat and mass transport mechanisms and chemical reactions. In forward propagation, the oxygen flows through the char, reacts at the smoulder zone and then the oxygen-depleted gas flow continues through the virgin fuel. Convective heat transport is towards the virgin fuel ahead and results in preheating. In opposed propagation, the oxygen flows through the virgin fuel and reacts at the smoulder zone. Then the oxygen-depleted gas flow travels through the char. Convective transport is towards the char left behind the front, reducing the preheating of the fuel.

III. Structure of a Smouldering Front

Figure 5 shows a photograph of a sample of peat (porous biomass fuel) where a smouldering front has been initiated and is propagating laterally. Superimposed on the photograph is a schematic of the smouldering front structure that can be observed with the naked eye.

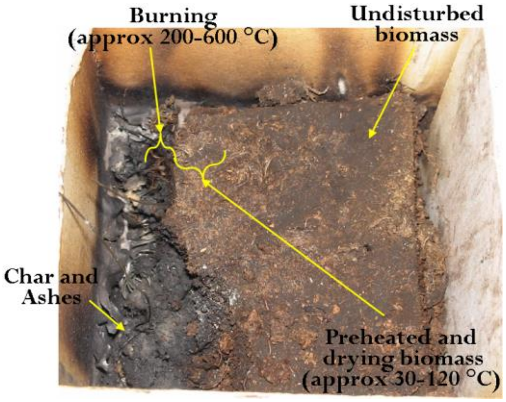

Fig 5. Front and temperature ranges in a smouldering peat sample 100mm long [5].

Generally speaking, there are four visually discernable regions propagating in a smouldering front. These are:

1. Preheating of the undisturbed fuel: heat from the reacting front is transported ahead preheating the fuel up to temperatures where water evaporation takes place. This front does not emit gases in any significant quantity.

2. Evaporation: this endothermic reaction occurs within a range of temperatures from approximately 80 to 100 °C, emitting water vapour. In this front the mass loss depends on the moisture content.

3. Burning region: this front is where the pyrolysis and oxidation reactions take place and net heat is released. Pyrolysis reaction absorbs heat and converts the fuel into volatile gases, polyaromatic hydrocarbons, trace levels of CO and CO_2, and water vapour. It leaves behind a solid carbonaceous char. Pyrolysis starts approximately at temperatures above 200-250°C. Subsequent heating above this temperature increases the pyrolysis rate if fuel is available. Pyrolysis is stronger at deeper layers of the fuel where oxygen transport is reduced and oxidation rate is lower. The oxidation involves the exothermic reaction of the fuel and char left by the pyrolysis front. The peak temperature is found in this region and is where most of the fuel mass is lost. This reaction overlaps with the pyrolysis depending on the propagation mode and oxygen availability [20]. The oxidation reaction occurs at temperatures over 300 °C and is the main source of CO and CO_2. More CO_2 is formed where the oxygen supply is large (e.g. closer to the oxygen supply or free surface) and more CO where it is limited (e.g. further from the oxygen supply or deeper into the fuel layers).

4. Char and ash region: this is where the smouldering has ceased and the remaining matter cools down to ambient temperature. The ash left is the mineral content present in the original fuel and the char is the result of incomplete burning.

The propagation rate of self-sustained smouldering is typically controlled by oxygen transport and net heat losses (see Section VI). Yet, heterogeneous chemical kinetics governs the front structure and dictate the effective value of the global heat released. The degradation of a solid fuel involves multiple pathways to chemical changes (pyrolysis and oxidation), and these pathways are not yet fully understood. In spite of the complex kinetic behaviour, experimental evidence suggests that mechanisms consisting of only a few global reactions capture the most important characteristics of the decomposition process [20, 21, 22, 25, 27].

The polymers for which smouldering kinetics are best known are cellulose and polyurethane foam. Reference [21] provides a quantified mechanism for cellulose pyrolysis, and [22] provides the mechanism and parameters for its thermal degradation in air (includes pyrolysis and oxidation). The mechanism includes cellulose pyrolysis, cellulose oxidation and char oxidation, accounting for three solid species; cellulose, char and ash. However, this mechanism has never been used to predict experimental results of cellulose smouldering. Rein et al. [20] provided a 5-step mechanism for polyurethane consisting of two foam pyrolysis, two foam oxidations and one char oxidation reaction, and accounting for four solid species (foam, β-foam, char and residue). This mechanism has been validated against experiments of polyurethane smouldering [23].

Well established kinetic mechanisms are lacking and thus smouldering combustion is frequently described as a function of the propagation mode. Forward is described using a 2-step mechanism having pyrolysis and oxidation reactions [24], [25], whereas in opposed smouldering these two paths are lumped together in a global single reaction [26], [27]. Only recently, the same kinetic mechanism and parameters was shown to be able to predict both forward and opposed smouldering [23].

In forward smouldering propagation (Fig. 6, right), the oxidation and the pyrolysis reactions form two distinct propagating fronts. The pyrolysis front arrives first to the virgin foam and then followed by the oxidation front. This is in agreement with experimental measurements of forward propagation [25] and [28] where two distinct fronts are observed in the temperature profiles. In opposed smouldering (Fig. 6, left), the oxidation and the pyrolysis reactions overlap to form a single propagating front. This is also in agreement with experimental observations in opposed propagation [27], [29], where a single front is observed in the temperature profiles.

Fig 7 shows the one dimensional representation of a smouldering front in a fuel rod and the approximate correspondence with a burning cigarette (one of the most common examples of smouldering). As shown by the results in Fig 6 for forward smouldering, the pyrolysis front is located at the leading edge of the cigarette burning front since it does not need oxygen to permeate into the solid. The oxidation reaction takes place at the trailing edge of the burning cigarette, where the oxygen supply is available from the surrounding environment, and the heat released is transferred ahead of the front into the virgin fuel and pyrolysis front to drive the propagation.

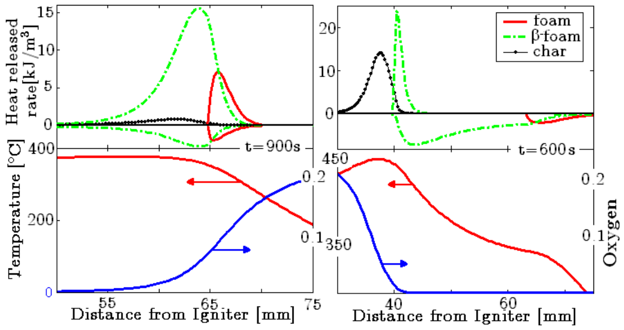

Fig 6. Numerical results for the front structure during self-propagation [23]. Left) Opposed smouldering; and Right) Forward smouldering. Top) The heat-released rate of each reaction (positive for oxidation, negative for pyrolysis). Bottom) The temperature and oxygen profiles.

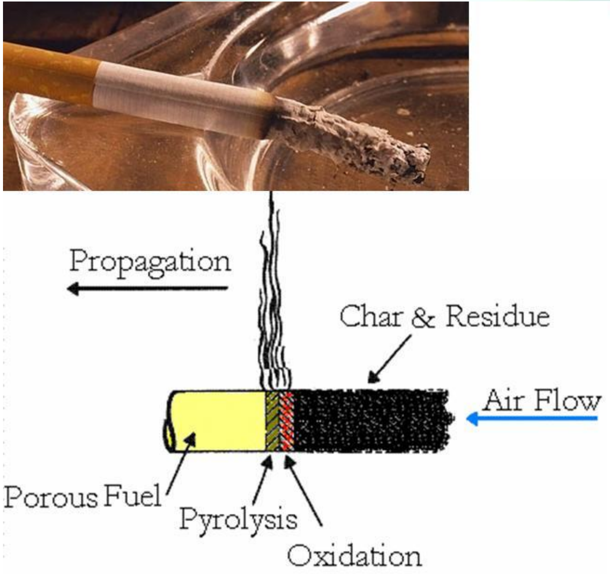

Fig 7: Structure of a one-dimensional reaction front in forward smouldering and the correspondence in a burning cigarette.

V. Governing Equations

The set of governing equations presented here accounts for the most complete description of the transport mechanisms in smouldering combustion. This model has been shown to reproduce the most important features of the process and can predict the thermal and species structure of the reaction-front, the onset of smouldering ignition, the propagation rate and the temperature profiles. Only an overview is presented here. A detailed discussion can be found in [32], and other supporting references are [1] [33] [34] [35] [23] and [36].

The governing equations consist of the conservation of energy of the solid (Eq. 1), energy of the gas (Eq. 2), continuity of the gas (Eq. 3), solid species (Eq. 4) and gas species (Eq. 5).

$$\frac{\partial h_s'''}{\partial t} = \nabla \cdot \left(k_s \nabla T_s\right) + \tau_{gs}\left(T_g - T_s\right) - \rho_0 \sum_i \dot{\omega}_i \Delta h_i \quad (1)$$

Where h''' is the enthalpy per unit volume, ρ_0 is the initial density of the solid and *t* is the time. *T* is the temperature, with the subscript *s* for solid and *g* for gas. The temperature can be calculated from the corresponding enthalpy dividing it by the specific heat. The conservation equation includes the transport terms (in order of appearance on the right hand side) of heat transfer by conduction, between gas and solid matrix, and the source term of heat released by chemical reactions on the solid surface. The conductivity k_S includes the radiative conductivity in the optically thick limit, which can be estimated using electron-microscopy photos of the porous matrix [20, 32]. The transfer of heat between gas and solid matrix is quantified via the efficient coefficient τ_{gs}. The reaction rates and heats of reaction are defined according to the kinetic mechanism assumed (see Section 4) and the kinetic parameters of the fuel.

Similarly, for the gas, the conservation equation becomes:

$$\frac{\partial}{\partial t}\left(\phi h_g'''\right) = \nabla \cdot \left(\phi k_g \nabla T\right) + \\ + \nabla \cdot \left(\phi \rho_g \frac{K}{\mu} c_{pg}\left(T_g - T_0\right)\nabla p\right) - \tau_{gs}\left(T_g - T_s\right) \qquad (2)$$

where ϕ is the porosity, c_{pg} the specific heat, *p* the pressure, *K* the flow permeability of the matrix, μ the viscosity. This equation takes into account the transport of heat by convection, conservation of momentum by Darcy's law in which the gas velocity is calculated as a linear function of the pressure gradient in the porous medium. No energy released by any gas reaction is included since a smouldering process that is far from transitioning to flaming is driven only by heterogeneous reactions on the surface of the solid.

The gas continuity is given by:

$$\frac{\partial}{\partial t}\left(\phi \rho_g\right) = \nabla \cdot \left(\phi \rho_g \frac{K}{\mu} \nabla p\right) + \rho_0 \sum_i \dot{\omega}_i \nu_{g,i} \qquad (3)$$

where the reaction rates and yields are defined according to the kinetic mechanism assumed and the kinetic parameters of the fuel. Buoyancy-induced flows are not included here but can be added using the Boussinesq approximation.

The conservation of the solid species is

$$\frac{\partial m_j}{\partial t} = \sum_i \dot{\omega}_j \nu_{j,i} \qquad (4)$$

The conservation of the gas species is

$$\frac{\partial}{\partial t}\left(\phi \rho_g yi\right) = \nabla \cdot \left(\phi \rho_g \frac{K_x}{\mu} y_{O_2} \nabla p\right) + \\ + \nabla \cdot \left(\phi \rho_g D_{diff} \nabla y_{O_2}\right) - \rho_0 \sum_i \dot{\omega}_i \nu_{O_2,i} \qquad (5)$$

The most important gas species in smouldering is oxygen, which feeds the combustion process. Also important for emission and toxicity studies and for the transition to flaming are the gas product species. The pressure of the gas phase can be calculated using the ideal gas law once the gas composition is known.

To complete the mathematical representation of the problem, the most important conditions will be those describing the ignition protocol, the influx of oxygen and the heat losses at the boundaries with the exterior domain.

Figure 8 shows the numerical results from integrating Eqs (1-5) for a 1D rod made of polyurethane foam [32]. These results have been validated against experimental measurements and shown to capture the ignition, propagation and front structure in both forward and opposed propagation modes [23].

VI. Simplified Analysis

The complexity of the smouldering process requires the use of approximations in the theoretical models and simplifications in the experiments (see Section 4 for ideal experimental environment) to study the fundamentals. The propagation rate of self-sustained smouldering is typically controlled by two mechanisms: oxygen transport and net heat losses [1]. This can be shown by conducting a simple global energy balance at the smouldering front. This yields a simple mathematical representation of the propagation that serves to quantify the controlling mechanisms involved in the process.

In a control volume that contains the smouldering front, the propagation rate is determined by the balance between the heat released per unit mass of oxygen reacted, the energy required to heat the virgin fuel and the incoming air to the smoulder temperature, and the heat losses to the environment [27], [29]. Assuming that all oxygen is consumed, the application of such an energy balance into mathematical terms provides the following expression for the smouldering propagation velocity in opposed configuration [29]:

$$u_{sml} = \frac{\dot{m}''_{O_2} Q_{sml} - \dot{m}''_g c_{pg}\left(T_{sml} - T_0\right) - \dot{q}''_{loss}\, {}^{A_L}\!/_{A_c} + \dot{q}''_{ig}}{\rho_s c_{ps}\left(1 - \phi\right)\left(T_{sml} - T_0\right)} \qquad (6)$$

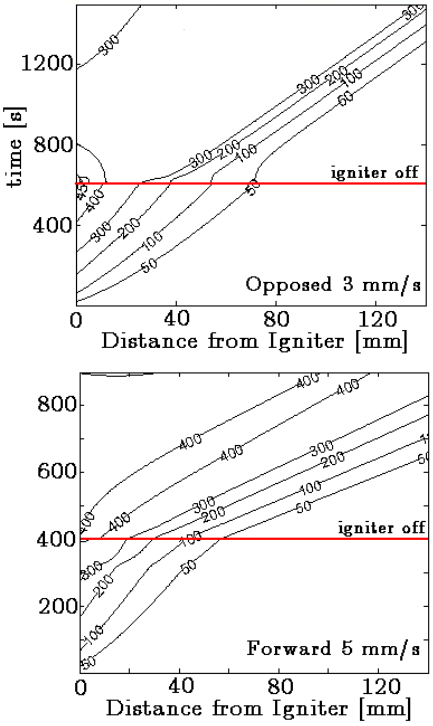

Fig 8. Numerical results for temperature contour lines as a function of time and space in a 1D rod of polyurethane foam and 140 mm in length [32]. Top) Opposed smouldering with an inlet airflow of 3 mm/s; and Bottom) forward smouldering with an inlet airflow of 5 mm/s. The slope of each contour lines gives the propagation velocity.

The heat transferred from the igniter $\dot q''_{ig}$ can be neglected when studying self-sustained smoulder because the propagation occurs far from the igniter influence. For the typical range of gas velocities, the energy required to heat the incoming airflow to the smoulder temperature ($\dot m''_g c_{pg}(T_{sml} - T_0)$) is small in comparison with the other energy terms. Consequently, in the above expression, Eq. (6), the two major terms determining the smoulder propagation velocity are the heat released by the reaction ($\dot m''_{O_2} Q_{sml}$) and the heat losses to the external environment ($\dot q''_{loss} \, {}^{A_L}\!/_{A_c}$). The heat loss coefficient ${}^{A_L}\!/_{A_c}$ expresses the ratio of the lateral area to the cross-sectional area at the smoulder front. The properties of the solid ($\rho_s c_{ps}(1-\phi)$) only scale the magnitude of the velocity. Then, considering only the major terms, Eq. (6) simplifies to:

$$u_{sml} = \frac{\dot m''_{O_2} Q_{sml} - \dot q''_{loss} \, {}^{A_L}\!/_{A_c}}{\rho_s c_{ps}(1-\phi)(T_{sml} - T_0)} \qquad (7)$$

According to Eq. (7), the propagation velocity in the oxidizer-limited regime is linearly proportional to the mass flux of oxidizer, as it has been verified experimentally [37], [27], [29]. It external is seen in Eq. (7) that the effect of the heat losses to the environment is to hamper smouldering propagation. The heat losses term includes the effect of the size of the fuel sample through the ratio ${}^{A_L}\!/_{A_c}$. This ratio reflects that heat loss is proportional to the surface area whereas heat generated is proportional to the volume. As the sample is made smaller, the ratio ${}^{A_L}\!/_{A_c}$ increases, and the effect of the heat losses increases until smoulder propagation cannot occur below a critical size. The critical size for smouldering propagation can be analyzed by making Eq. (7) equal to zero (limit of no propagation). For a slab of square cross-sectional area, side length *L* and smouldering front thickness δ , the ratio ${}^{A_L}\!/_{A_c}$ becomes equal to ${}^{4\delta}\!/_{L}$. The rate of heat loss can be expressed as the function of a global heat-losses coefficient U_{loss} and the temperature gradient with the exterior. Then, setting u_{sml} in Eq. (7) to zero and rearranging the expression, the critical sample size L_c is expressed as:

$$L_c = \frac{4\delta}{Q_{sml}} \frac{U_{loss}(T_{sml} - T_0)}{\dot m''_{O_2}} \qquad (8)$$

The expression Eq. (8) can be used to provide an estimate of the critical size. The smoulder-zone thickness δ , the smoulder temperature T_{sml} and the heat of smouldering Q_{sml} depend on the smouldering properties of the fuel. For example, for polyurethane foam the required parameters are available from Bar-Ilan et al. [29] [28] and yields the critical size of 160 mm. The analysis of experimental studies of smouldering indicates that the critical size for rectangular polyurethane foam samples under natural convection is 150 mm [38]. Thus, for a polyurethane-sample which size is below this critical value, achieving self-sustained smouldering requires the reduction of the heat losses or the increase of the heat generated, or both. The former can be accomplished by thermally insulating the sample and the latter by increasing the oxidizer flux [16], [17].

VII. Smouldering Phenomena

VII.1.Fires in the Built Environment

Fire statistics draw attention on the frequency and danger of smouldering fires. They are the leading cause of fire deaths [3] and [39] with more than 25% of the annual fire-deaths. During

2001 alone, there were an estimated 31,200 smouldering fires in structures and US$386 million in property damage [3] in the USA alone. A fire-initiation scenario that is particularly common is when a weak source of heat (e.g. a cigarette) ignites a piece of porous combustible material (e.g. upholstered furniture). This can lead to a smouldering fire that lasts for a long period of time (hours or even days), spreading slowly until critical conditions are attained and flames suddenly erupt.

The inherent danger of smouldering fires in the built environment stems from four particular characteristics [40]: 1) they can be initiated by weak sources of heat, too weak to immediately start a flaming fire; 2) they produce relatively cooler plumes of smoke which composition and lack of buoyancy makes detection difficult by standard fire detection devices; 3) gases produced by smouldering pose a toxic hazard; and 4) they can abruptly transition to a flaming fire.

Smouldering intrinsically emits products of incomplete oxidation and thus emits a mixture of asphyxiant and irritant gases and particulates at a higher yield than flaming fires [10]. The productions rate is lower and the growth slower than flaming fires but it poses a serous threat to sleeping, incapacitated, trapped or otherwise immobilized occupants. The studies of Hilado et al. [41] on mice addressed the lethal toxicity of smouldering gases from a wide range of polymers. Mice were exposed to the smouldering gases from a piece of upholstery. With cotton fabric and polyurethane foam cushion, 12% of the mice died in the 90 min of the experiment and an additional 40% died in the following 14 days after the exposure was discontinued. With cotton fabric and cotton cushion, all the mice died during the first 35 min of experiment due to CO poisoning. Quintiere et al. [42] studied the hazard to humans of smouldering fires in enclosure due carbon monoxide. They determined that life-threatening conditions from CO doses occurred in most cases in the 50-150 minute range of the experiment. They also noted that the time to transition to flaming occurred within the same time window.

The ability of standard smoke detectors to activate in the presence of a smouldering fire is undermined since smoke from smouldering fires behaves differently to the smoke generated by flaming fires [40]. This is due to two main reasons: (a) the low temperature and weak plumes of smoke thereby produced; and (b) the smoke composition. Smoke detectors for flaming fires are typically designed and installed taking into account that the hot products of fires move up with the flame-induced buoyant flows and depend on the convective movement of combustion products from the fire to the detector. The positioning of these detectors is based on the need to minimize this travelling time. In an enclosure, the hottest gas and the greatest concentration of smoke collect at the highest locations. It is at these locations that smoke detectors are generally installed. However, the low heat release rates of smouldering fires and the resulting weak plumes imply that the gaseous combustion products are quickly cooled by the ambient air and therefore do not follow the same path as flaming fires. As a result, smoke from a smouldering fire takes considerably longer times to move to the smoke detector system [43], [44]. The plume may never reach detectors situated on the ceiling but may disperse or become stagnant at a lower level. Smouldering intrinsically emits smoke made of products of incomplete combustion and thus the composition is different from the smoke from flaming fires. The size of the smoke particulates and their spatial distribution in the fire plume from a smouldering source varies greatly from flaming fires. Because conventional smoke detectors are usually calibrated using flaming sources, they might not work properly with smouldering sources [45], [46].

There are several works in the literature comparing the effect of fire retardants on flaming against the effect on smouldering [40]. Some suggest that fire retardant treatments to reduce flame ignition also reduce smouldering ignition [47]. Many flame retardants promote the char formation that is considerably richer in carbon content per unit mass than the original fuel. It has often been experimentally observed that materials with good resistance to flaming ignition have poor resistance to smouldering ignition and vice versa [48, 49, 50, 47, 17]. By enhancing the charring tendency, flaming combustion rates may be reduced, but perhaps at the expense of creating a source of smouldering combustion that would not otherwise have existed [51]. Inhibition of smouldering combustion requires different types of chemical retardant mechanisms than those required for inhibition of flaming combustion. The analysis in [52] of polyurethane foams shows that flame-retarded foams transition to flaming over a wider range of conditions than non flame-retarded foam this is primarily due to the higher yield of char of the former [49]. Wang et al. [50] studied wood ignition and showed that Borax tends to reduce flame spread but promotes smouldering, conversely boric acid suppresses smouldering but has little effect on flame spread. This conflictive interaction of current flame-retardants with smouldering and flaming ignitions poses a dilemma in fire safety and requires further research.

VII.2. Aerospace Fire safety

Smouldering combustion is a fire-safety concern in the aerospace sector, including space flights. The aircraft industry suffers many smouldering incidents every year and although most do not grow beyond the point of origin or are detected on time, avoiding major disruptions, on some occasions smouldering has led to fatal accidents. One example is the 1998 Swissair flight 111 aircraft fire [53] which, according to investigations, was caused by faulty wiring which resulted in smouldering ignition of adjacent polymer insulation sheathing. The smouldering fire transitioned to flaming after some time.

There is concern for an accidental fire occurring in a space-based facility [54], [55]. In the closed environment of a spacecraft or extraterrestrial base, with no avenue for escape, a fire to be greatly feared [56]. Should a fire occur in a space facility, there is a strong probability that it would be a smoulder-originated fire [4]. The Space Shuttles have registered on average one charred-cable incident for every ten missions [57], [58]. A charred cable is symptomatic of smoulder-prone conditions and could lead to sustained smouldering or ignition of nearby fuels. The MIR orbital station and other USSR/Russian spacecraft have also suffered several smoulder-related incidents [59]. The impact of smouldering during a space mission is also critical from the points of view of the impact on the environmental health of the astronauts [60] and the difficulty to detect and extinguish a smouldering fire [61]. These topics need to be assessed in the context of long-term space habitation. With the currently orbiting International Space Station and future long-term missions (i.e., mission to the Moon and Mars), there is an increased interest in the study of smouldering in reduced gravity because of the need to pre-empt the possibility and to minimize the effect of a smoulder-initiated fire during the operation of a space-based facility. Thus, it is of great interest to understand and characterize the smouldering behaviour of materials used in these facilities under the expected ambient conditions of absence of gravity, but also of reduced pressure and increased oxygen concentration.

impact of the flaming front but is nonetheless an important factor in wildfires and the subsequent damage to the forest. Large smouldering fires are rare events at the local scale but occur regularly at a global scale. Once ignited, they are particularly difficult to extinguish despite extensive rains or firefighting attempts and can persist for long periods of time (weeks and up to years; [6], [62], and spread over very extensive areas of forest and deep into the soil. By propagating below the surface, smouldering fires offer the means for flaming combustion to re-establish during wildfires in unexpected locations (e.g. across a fire break) and at unexpected times (e.g. long after burn out of the flaming front). These fires represent a large contributor to biomass consumption and a significant source of combustion emissions to the atmosphere [6], [63], [11].

The effects of smouldering fires on the landscape can range from the small scale (pockets of burning in superficial layers or the root of a single tree), to the large scale (burning of a hill-top or the destruction of the root network of a complete forest stand). In general, smouldering fires have a severe impact on the local soil system, because the burning fuel is the organic portion of the soil itself. The prolonged heating from the slowly propagating fire can kill roots, seeds and plant stems and the affected layers of soil sustain large losses of biomass. This coupled with expositing of underlying layers increases the likelihood of long term damage and erosion.

Forest fuels prone to smoulder during wildfires can be divided in two categories; thick fuels and organic soils. Natural thick fuels are stumps, snags, downed logs, large branches and roots [64]. These are characterized by having a significantly greater thermal time than finer fuels, which favours the slow burning of smoulder combustion. Organic soils are hummus, duff, peat, coal seams and others. Smouldering fires of organic soils can burn in shallow or deep fronts. Each has different dynamics. A shallow front burns near the free surface and are open to the atmosphere, thus having large supplies of oxygen available but exposed to convective heat losses. A deep subsurface fire burn many meters below the ground, and thus have a limited supply of oxygen but are insulated from heat losses to the atmosphere. In this section, only shallow fuels are discussed and deep fires are treated in section 7.4.

It has been measured that smouldering can consume around 50% or more of the total burned biomass in temperate and fires [65], [63], and in Amazonian tropical-woodland fires [66]. Bertschi et al. [63], Rabelo et al. [64] and Carvalho et al. [67] report high fuel-consumption fractions by smouldering fires. Smouldering of forest fuels is also responsible for a significant fraction of the pollutants emitted into the atmosphere during a wildfire. Bertschi et al. [63] studied the emissions from smouldering biomass fuels and calculated the emission from real wildfires. Based on their results and compared to the emissions from the flaming phase of a tropical savanna fire, smouldering produces 130% more CO and 670% more hydrocarbons, but 15% less CO_2 and no NO_x. Compared to the emissions from a boreal fire, smouldering produces 30% more CO and 20% more hydrocarbons, but 13% less CO_2 and no NO_x. Many smoke management problems in the US associated with prescribed fires involved smouldering emissions [68].

The changes to the soil produced by smouldering fires in organic soils are driven by two factors: the high temperatures reached and the large loss of soil mass. The most important physical change produced by smouldering fires is that affecting the stability of the ground. The removal of soil layers at the surface leads to enhanced erosion and the destruction of deeper layers can lead to structural collapse. Over-hangs, holes in the ground and pan-shape voids around tree bases are commonly produced during smouldering fires and can lead to local subsidence of the soil and damage to roots, threatening tree stability and disturbing hydrological dynamics. Heating of the soil by wildfire produces changes of chemical nature (loss of carbon, nitrogen and organic phosphorus) and biological nature (modification of nutrient availability, perturbation of microbial dynamics and plant species). In general terms, flaming fires produce very high temperatures away from the ground for short periods of time. Smouldering fires, however, lead to enhanced heat transfer to the soil for much longer durations (i.e. in the order of one hour) that can lead to sterilization of the soil [5], [69]. The longer duration and the higher heat transfer to the forest floor by smouldering has been identified as an important factor in fire mortality (comparable to damage to tree crowns by flaming fires) [70].

The moisture and the organic content have been identified as the main controlling parameters for smouldering ignition of biomass. Frandsen [71] determined that the smoulder-ignition limits of Canadian boreal peat are a moisture content lower than 110% (dry base) and an mineral content lower than 82%. Contents higher that these were shown to result in no ignition.

In the organic layers of the ground, the smoulder front propagates downward and laterally consuming the fuel (Fig 8). The front structure is similar to a forward-smouldering configuration: the drying and the pyrolysis fronts move ahead of the oxidization front which stays in contact with the oxygen in the open air.

A recent case of a smouldering fire causing major damage to the landscape and the ecosystem is a wildfire that occurred in a 40 year old, 15 ha plantation of lodgepole pines in Rothiemurchus near Aviemore, Scotland, during July 2006 [5]. The flaming fire was extinguished by the fire service within 3 days, but the peat underneath the forest continued to smoulder for more than 40 days despite the occasional rains (see Fig 9). To stop the smouldering spread, the fire service dug a fire-break trench 5 m wide and 0.5 to 2 m deep at the perimeter of the burning areas to remove the peat and expose the mineral soil. Fig. 3 shows photographs of adjacent forest stands after the fire. While the flaming fire scorched the trees up to 1 m from the floor and consumed some of the grass, the smouldering fire burned the peat up to depths of 0.5 to 1m removing large quantities of the soil. The root systems and tree bases were by far the most affected areas by smouldering. Many smouldering pan-shape voids were seen around forest stands and single trees. These were formed by the burning of large portions of soil in approximately circular areas 0.5 to 3maround the tree bases and exposing the mineral soil layers beneath. A dependence of peat consumption patterns on the distance from the base of the trees was also observed in several areas of the forest (not shown in Fig. 9), in a similar pattern to that noted by Hille and Stephens [72] and Miyanishi and Johnson [73]. Near the bases of trees, where crown cover reduces the rainfall and roots take up water, there is a much higher degree of peat consumption and the fire spread following the roots. This suggests that the fire pattern in Rothiemurchus was largely influenced by the moisture distribution of the peat.

Fig 9: Photographs of adjacent forest stands from the July 2006 Rothiemurchus peat fire in Scotland, UK [5]. The fire involved flames for three days and smouldered for six weeks. Top) Stand not affected by the fire showing the trees and the peat layer. Bottom) Stand of trees trunks charred by the flames and the soil destroyed by smouldering fire.

The transition from smouldering to flaming is also observed in forest fires. Logs can naturally burn for long periods of time oscillating between flaming and smouldering combustion after the flame front has passed [64]. Smouldering can also re-ignite previously extinguished wildfires. For example, this mechanism led to the re-ignition of the 1991 Oakland Hills Fire, California [74]. The re-ignited fire destroyed nearly 2,000 homes and caused up to US$10 billion in damages. Hot embers are another method by which wildland fires can spread due to smouldering. These embers are lofted by the fire plume and transported some distance away from the originating fire front [75]. Once landed, the hot ember heats the underlying litter, underbrush or grass and can initiatie a smouldering fire, which could transition to flaming.

VII.4. Subsurface Fires

Smouldering fires of peat and coal can penetrate many meters below the ground (see Fig. 10) and can cause large perturbations in the global atmospheric chemistry and a long term safety hazard to local population.

When active, the burning of ground and subsurface layers can last for long periods of time and emit large quantities of combustion products causing the deterioration of the air quality. Carbon emissions from peat fires are equivalent to approximately 3,000 times the normal flux due to natural decomposition at ambient conditions [11]. After the 2002 study of the Borneo fires [6], subsurface fires have started to be seen as an emerging threat, posing a global risk with social, economic and environmental consequences in both the short and the long terms.

Peat is an accumulation of partially decayed vegetation matter. Peatlands cover more than 3% of the Earth's land surface. They are important ecosystems for a wide range of wildlife habitats supporting biological diversity, hydrological integrity and carbon storage. Peatlands play an important role in the global carbon balance and recent environmental changes, such as climate change and human activities including drainage, peat harvesting and air pollution have raised questions regarding the long term stability of these carbon sinks.

The largest peat fires registered to date took place in Indonesia during the El Niño dry season of 1997 (previously occurred in 1972, 1974, 1982, 1991 and 1994, and later repeated in 1998, 2002, 2004 and 2006) and lasted for several months, destroying over 2,441,000 ha of peat with a loss of ground layers between 0.2 and 1.5 m deep [6]. Smouldering accounted for 80% of the emissions to the atmosphere.

The smoky haze covered large parts of South East Asia for weeks, disrupting shipping and aviation and causing large economic losses, long term damage to the environment and healthcare problems. It has been estimated that the 1997 fires released between 0.8 to 2.6 Gton of carbon emissions into the atmosphere, equivalent to 13-40% of the global fossil fuel emissions for that year [6].

Coal seams and coal mines and other fuel accumulations like landfills also burn in smouldering mode. Thousands of underground coalmine fires have been identified around the world [7]. Some of the oldest and largest coal fires in the world occur in China, the United States, and India. Elusive, unpredictable and cost prohibitive, coal fires may burn indefinitely, choking the life out of a community and its environs while consuming a valuable natural resource. Fires lasting more than 46 years are well documented [76].

In China alone, subsurface fires account for 2 to 3% of the annual world emission of atmospheric CO_2 [7].

Associated financial run into millions of dollars from loss of coal, closure of mines, damage to environment and fire fighting efforts. There are some well-documented cases. In 1962, an abandoned mine pit in Centralia, Pennsylvania, USA was accidentally lit. Several unsuccessful attempts were made to extinguish it, but the fire continues to burn after more than forty years. It is currently being monitored with the front advancing approximately 20 m/year [76]. In 2005, the State of Colorado, USA, reported more than 30 actives subsurface fires [77], involving 2% of all known abandoned coal mines in the state.

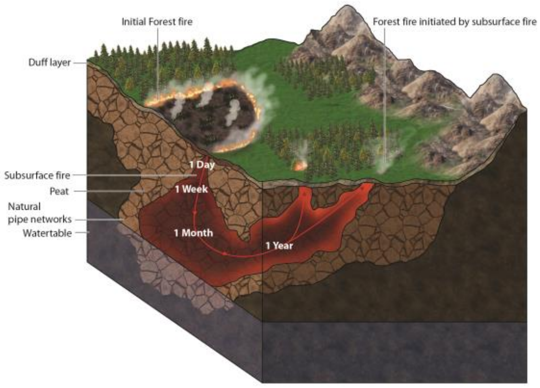

Fig 10. Illustration of a subsurface fire initiated at the surface that propagates into the ground and emerges months later (illustration by E. Burns 2008 and commissioned by G. Rein)

The primary controlling mechanisms of subsurface smouldering fires are the net fuel load, the oxygen transport, (predominantly dictated by the distance to a free surface and the permeability of the medium) and the heat losses (predominantly by water evaporation and conduction). Thus, the fuel properties affecting these mechanisms are, the moisture and inert contents, organic composition, bulk density, flow permeability, and the presence of cracks or deep channels. These properties dictate the smouldering dynamics controlling the ignition, depth, duration, and extent of smouldering fires. Subsurface fires are fed by small quantities of air flowing through fractured strata, cracks, natural pipe networks [78], openings or mines shafts and galleries, which permit oxygen to circulate to the subsurface. The reduced heat losses and the high thermal inertia of the underground material, together with the high fuel availability and the small oxidizer flow promote long-term smouldering combustion and allow for creeping but extensive propagation both in depth and in area. These fires prove difficult to be detected and frustrate most efforts to be extinguished. Little technical research has been undertaken on the subject and as a result, the understanding of how to tackle these fires is very limited [79].

VII.5. Technological Applications

There are beneficial applications of smouldering combustion to technological advances in energy, environment science and forest management. An overview of those noteworthy is included here.

Smouldering of fossils fuels in the subsurface is of interest for optimal exploitation and cleaner use of energy sources. In-situ combustion in oil fields is a method of thermal recovery in which a forward smouldering fire is generated in one side of the reservoir and is feed by injecting a gas containing oxygen [14]. Part of the oil is cracked and burned and converted into lighter hydrocarbons, carbon monoxide, carbon dioxide and water at high pressure. As the smouldering front moves, heat is transported ahead and reduces oil viscosity, in turn displacing it and creating a flow of oil towards the production well. In-situ oil combustion is being used more often for oil recovery when traditional-extraction methods become inefficient or too costly. Underground coal gasification is an in-situ process carried out in deep coal seams (deeper than 30 m) using injection and production wells drilled from the surface, which enable the coal to be converted into product gas for power generation [80]. The coal seam is ignited via the injection well and a forward smouldering front is fed by injecting a gaseous mixture containing oxygen. The products of combustion at high pressure are collected at the production well. Hydrogen, carbon monoxide, and methane are useful as gas fuels produced by this process. Underground gasification allows development of new sources of energy from coal that could be cleaner than traditional coal burning.

In the field of environmental science, smouldering is of interest in waste treatment, soil contaminant remediation, and biochar production and storage.

Smouldering of tires can be employed for tar and energy production, fostering the recycling of tires and partially avoiding their waste [81]. Smouldering combustion can be used for remediation of contaminated soils [15] and associated laboratory experiments (see Fig 11) show that the smoulder front can be controlled to consume most of the liquid contaminant and clean the porous matrix soil. This is a promising environmental technology.

Biochar is a fine-grained, highly porous charcoal produced from biomass that helps soils retain nutrients and water. Charcoal is rich in carbon content and a long-term stable solid resisting degradation, and thus, can be used to lock carbon in the soil [82]. Biochar is of increasing interest because of concerns about global warming being caused by emissions of CO_2 and other greenhouse gases. On the one hand, smouldering can provide energy-efficient conversion of biomass into biochar by the pyrolysis. Thus, one process that promotes biochar with the advantage of minimal or zero energy costs is a smouldering process where the energy supply is released from the slow oxidation of a part of the biomass itself. Small reactors, easy to operate and to maintain, can be designed to be run by local communities. On the other hand, biochar can sustain a smouldering combustion and thus smouldering fires present a significant hazard where Biochar is to be stored in quantities or at high concentration [83]. If a smouldering fire was to occur in a biochar field, a fire could propagate through the surface and subsurface layers destroying the biochar and releasing the stored carbon as gas emissions. This is about the only hazard that could led to an accidental release of the stored carbon to the atmosphere.

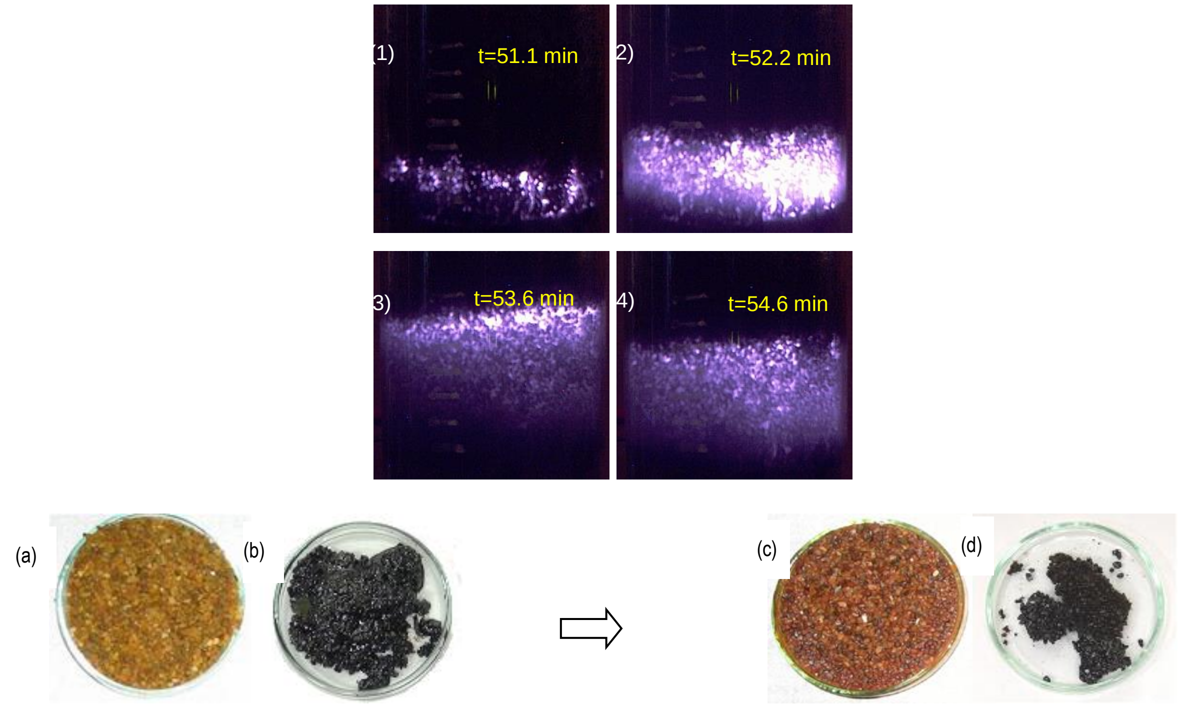

Fig 11. Smouldering combustion as a remediation technology for contaminated soil [15]. (Top) Series of images showing the onset and propagation of the visible front in soil contaminated with 25% coal tar (Images show an area of about 30x30 mm of the sample. Ignition was initiated at t=50 min). (Bottom) Comparison between samples of soil before and after the treatment: (a) Clean soil, (b) soil mixed with fresh coal tar, (c) treated soil from the reactor core, and (d) treated soil from the periphery of the reactor.

In forest management, controlled smouldering fires can be used to reduce shallow layers of natural fuels at slow propagation rate [84]. These fires have two benefits when kept in very shallow layers: they are easy to control and result in little damage to the forest stand.

VII.6. Other Smouldering Phenomena

Smouldering combustion is referred in the literature by other names. It is referred to as filtering combustion [85], a term used for surface combustion in porous metal matrixes, glowing combustion, which is an intense smouldering process that has heated the solid surface to the point that it radiates to the environment in the visible spectrum. Other names are found in fire safety practice, where the issue of smouldering fires in residential environments is called ‘the smoking problem’ [3]. A phenomenon that is intrinsically linked to smouldering combustion is the self-heating of a solid fuel [86]. In this case, the heterogeneous oxidation reactions and heat losses governing self-heating are of similar nature to those in smouldering combustion and if the process is strong enough it may lead to the ignition of a smouldering front or/and the transition to a flaming fire. Other names are deep seated fires in landfill sites under overextraction conditions (i.e. when air is being entrainment into the pile lagging fires in the process industries, low oxygen combustion in the biochar community and fire flooding or fireflood in in-situ combustion by petroleum industry.

Peat fires under anomalous climate conditions are also responsible for the rare event, first reported in 1999, of a smouldering wild-urban interface fire. This occurred in St. Petersburg, Russia during a spell of unusually hot, dry weather [87]. Peat fires south of the city burned for weeks during the summer period and haze covered five districts. The smouldering fire was seen 300 m from the concrete residential buildings in 10 m deep peat lands.

An unusual case of subsurface fire is the burning of the debris of the World Trade Center. After the attack, fire and subsequent collapse of the Twin Towers on September 11th, 2001, the immense pile of debris left on the site smouldered for more than five months with occasional burst of flames near the free surface [88]. It resisted attempts by the fire fighters to extinguish it until most of the rubble was removed. Outdoor pollutant levels in lower Manhattan returned to urban background levels after about 200 days [89]. The effects of the gaseous and aerosol combustion products on the health of the emergency workers were patent but the details are still a matter of debate. There is very little information on this fire.

VIII. Concluding Remarks

Smouldering combustion is studied by a number of rather isolated disciplines but which fundamentals remain mostly unknown to the scientific community. This paper provides an overview of smouldering problems in the different disciplines, in an attempt to bridge the gaps between them and bring together current and future research efforts.

From a fundamental scientific point of view, the most studied smouldering materials to date are cellulose and polyurethane foam. The most carefully conducted and comprehensive experiments of smouldering combustion are those of NASA conducted in microgravity and ideal flow conditions. But this is not enough to foster a multidisciplinary approach to smouldering. The study of the state of the art shows that current body of knowledge cannot provide good understanding. More experimental and theoretical studies are needed, especially to explore the issues of ignition, combustion emissions and extinction and the transition to flaming.

Fundamental research in these topics will facilitate further applied research in the fields reviewed in this paper and will allow better tackling the problem of gas emissions from subsurface fires, the loss of carbon pool and how to extinguish them. These topics will become even more important if, as climate experts predict, warmer and drier summers over large areas of the planet might be expected in the future which would bring an increased subsurface fire frequency.

Moreover, the production and safe storage of biochar, in-situ oil recovery and in-underground coal gasification are promising technological solution to solve current energy and environmental problems but that required further scientific development to allow optimized operations of the technology, increase efficiency and reduce the economic and environmental costs. The prospects of new opportunities for science and engineering in smouldering combustion are noticeable, but a much larger international research effort is required to increase the number of multidisciplinary studies.

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TCC 918 – Avoiding Fire with Toxic Smoke Caused by Electronic Components

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Introduction

Plastic materials in general are excellent insulators. Due to their high mechanical strength and low weight, they are particularly suited for the electric and electronics (E&E) market as well as the transportation and appliances industries. One commonly used plastic material for such applications is from the polyamide family: PA 6, which features good surface quality, processability and slightly lower prices than other PAs, is especially well suited. In many of these applications, the plastic materialis reinforced with short glass fibers to further improve mechanical performance.

However, these materials can catch fire when close enough to an ignition source like an electric spark. One common measure for ensuring fire safety is the addition of flame retardants (FR). The type and amount of flame retardant used depends on the application and the associated requirements set forth by various flammability standards. In general, a low amount of flame retardant is desired, in order to have the least effect on the plastic's properties and processing behavior. Like any additive, flame retardants increase the viscosity of polymer melts, which is especially critical in the electronics industry where minia- turization and thus very thin walls are standard. A variety of flame retardants exists for PA 6.

Fires initiated by even a single electric spark develop smoke right from the outset. What's why most fire victims are killed by toxic smoke. Furthermore, the smoke can get dense enough to make visual orientation difficult or even obstruct the escape of a trapped person. Cor- rosive substances in the smoke can also damage equipment otherwise not affected by the fire. The toxicity and corrosiveness often observed come from halogenated polymers or flame retardants. For that reason, special non-halogenated flame retardants and graphite-based flame retardants are used to avoid these problems.

Figure 1: Cone Calorimeter TCC 918

Measurement Conditions

To highlight the effect of different non-halogenated flame retardants on the fire behavior of PA 6, samples of the different compounds were injection-molded into

100 x 100 x 4-mm^3 plates and tested in the TCC 918 (figure 1). The instrument allows for the determination of the heat release, mass loss and density and composition of the smoke gas. The samples were positioned on a horizontal sample holder that is placed in the load cell. The load cell monitors the sample mass during the measurement. A conical radiant electrical heater uniformly irradiates the specimen from the top. A spark igniter is located between the specimen's surface and the cone heater. This ignites the flammable gases evolving from the specimen when it is heated. The combustion gases produced pass through the heating cone and are collected by an exhaust duct system with a centrifugal fan and hood. In the measuring section of the exhaust duct, the mass flow and temperature of the smoke gas can be measured, as well as O_2, CO_2, and CO concentrations and laser light transmission through the smoke gas.

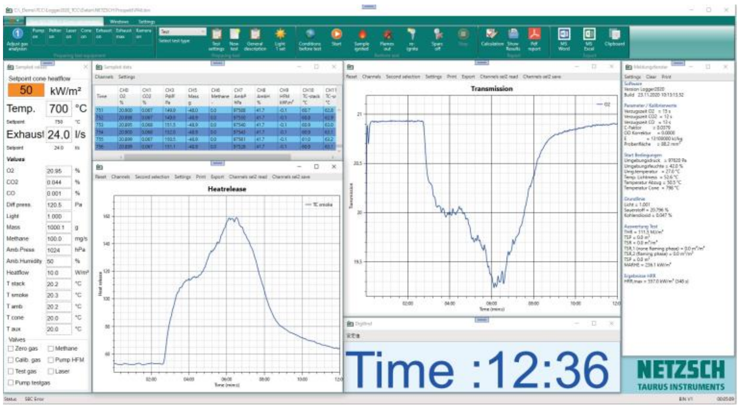
Before starting the tests, the gas analysis system (Siemens Oxymat/Ultramat) was calibrated with calibra- tion gases and the C-factor was checked by using the methane burner with a defined heat release. The gas analyzer used was equipped with O and a CO_2 option.

After heating up the cone heater, the shutter was closed, and the prepared sample holder was positioned onto the ground plate. Then, the system automatically removed the shutter for the start of the measurement. The evaporated gases were ignited by the automatic ignition system. The measurement conditions are sum- marized in table 1.

Figure 2 shows the results of the measurement on neat PA 6 and the visualization in the TCC software. The left column shows the measurement input data; in the middle, a table with the measured values from 751 to 756 s can be seen along with two example graphs of the measured data; and, the right column presents an overview of the selected analysis values for this particular measurement.

Table 1 Measurement conditions

Sample holder	Horizontal
Heat flux	50 kW/m²
Nominal duct flox rate	24.0 L/s


Setpoint cone heatflow 50 kW/m²
Temp. 700 °C
Setpoint 750 °C
Exhaust 24.0 l/s
Setpoint 24.0 l/s

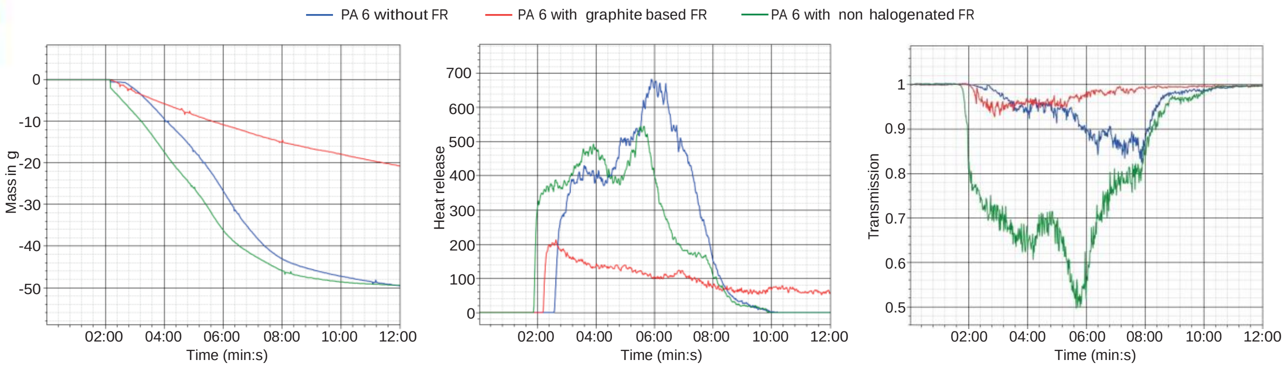
Values

O2	20.95	%
CO2	0.044	%
CO	0.001	%
Diff press.	120.5	Pa
Light	1.000	
Mass	1000.1	g
Methane	100.0	mg/s
Amb.Press	1024	hPa
Amb.Humidity	50	%
Heatflow	10.0	W/m²
T stack	20.2	°C
T smoke	20.3	°C
T amb	20.2	°C
T cone	20.0	°C
T aux	20.0	°C

Valves
☐ Zero gas ☐ Methane
☐ Calib. gas ☐ Pump HFM
☐ Test gas ☐ Laser
☐ Pump testgas

Time :12:36

Figure 2: Overview of the TCC measurement on neat PA 6 in the TCC software



a) b) c)

Figure 3: a) Mass loss, b) heat release rate and c) transmission of a neat PA 6 (blue), PA 6 w/graphite-based flame retardant (red) and PA 6 w/non-

Figure 3 allows a closer look at the results. Figure 3a shows the mass loss, b) shows the heat release rate and c) shows the transmission as a function of time for the three different samples.

It can be seen that the PA 6 sample with 20 wt% graphite-based flame retardant (red curve) shows the lowest mass loss, heat release and smoke release (lowest reduction in transmission) of all the samples. In comparison, the sample with 20 wt% non-halogenated flame retardant (green curve) behaves very similarly to the neat PA 6 material (blue curve). As pertains to the heat release, it shows slightly lower values and also the heat release ends earlier. As per- tains to transmission, however, the smoke emission is much higher than for the neat PA 6.

Summary

These investigations show that in the case of this particular PA 6 as well as the investigated FR loadings, the graphite- based flame retardant performs much better and signifi- cantly reduces the detrimental effects a fire can have on its surroundings. In the case of the non-halogenated FR, additional loadings would need to be studied to identify a composition with better performance.

Save the date

3rd International Conference on Eco-Friendly Flame Retardant Additives and Materials (ECOFRAM 2022)

17th and 18th may 2022, Alès (France)

IMT Mines Alès, and the French Chemical Society group on “Degradation and fire behavior of organic materials” are pleased to announce that the Third International Conference on Eco-Friendly Flame Retardant Additives and Materials (ECOFRAM) will take place in Alès, France on the 17th and 18th May 2022. Over the two days, the conference will be devoted to fundamental and applied research works concerning the development of eco-friendly flame retardant additives and materials. The addressed topics will be the following:

- Sustainable FR additives
- Biobased FR polymers and composites
- Global approach: recycling, ageing, end of life, circular economy
- Toxicity and environmental issues
- Fire safety regulation and environmental issues

Invited speakers:

- Dr Sabya Gaan (EMPA, Switzerland)
- Pr Baljinder Kandola (University of Bolton, UK)
- Dr Sandrine Therias (University of Clermont Auvergne, France)
- Pr Jérémie Pourchez (Mines Saint Etienne, France)

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