Processes Defining Smouldering Combustion:

Integrated Review and Synthesis

José L. Torero, Jason I. Gerhard*, Marcio F. Martins, Marco A.B. Zanoni, Tarek Rashwan, Joshua Brown

* Department of Civil and Environmental Engineering, Western University, London, Ontario N6A 5B9, Canada
b Department of Postgraduate Studies in Mechanical Engineering, Laboratory of Combustion and Combustible Matter (LCC), Federal University of Espírito Santo, Vitória-ES, Brazil
c Department of Civil, Environmental and Geomatic Engineering, University College London, UK

* Corresponding author at: Department of Civil and Environmental Engineering, Western University, Spencer Engineering Building, Rm. 3029, London, Ontario N6A 5B9, Canada. Tel.: +1 (519) 661 4154; fax: +1 (519) 661 3942. E-mail address: jgerhard@uwo.ca (J. I. Gerhard).

Abstract

Smouldering combustion is an important and complex phenomenon that is central to a wide range of problems (hazards) and solutions (applications). A rich history of research in the context of fire safety has yet to be integrated with the more recent, rapidly growing body of work in engineered smouldering solutions. The variety of disciplines, materials involved, and perspectives on smouldering has resulted in a lack of unity in the expression of key concepts, terminology used, interpretation of results, and conclusions extracted. This review brings together theoretical, experimental, and modelling studies across both fire safety and applied smouldering research to produce a unified conceptual understanding of smouldering combustion. The review includes (i) a synthesis of nomenclature to generate a consistent set of terms for the underlying processes, (ii) an overview of smouldering emissions and emission treatment systems, (iii) a distillation of ignition and extinction research, including the role of heat losses and factors underpinning smouldering robustness, (iv) a review of the temporal and spatial distribution of heat and mass transfer processes as well as their solution using analytical and numerical methods, (v) a summary
of smouldering chemical kinetics, and (vi) a summary of key gaps and opportunities for future research. Beyond merely review, a new conceptual model is provided that articulates similarities and critical differences between the two main smouldering systems: porous solid fuels and condensed fuels in inert porous media. A quantitative analysis of this conceptual model reveals that the evolution of a smouldering front, while a local process, is determined by a global energy balance that is cumulative in time and has to be integrated in space. As such, the fate of a smouldering reaction can be predicted before the effects of global heat exchange have affected the reaction. This approach is relevant to all forms of smouldering propagation (including fire safety), but it is particularly important when using smouldering as an engineered process that results in the positive use of the energy released by the smouldering reaction (applied smouldering). In applied smouldering, predicting the fate of a reaction ahead of time allows operators to modify the conditions of the process to maintain self-sustained smouldering propagation and thus fully harness the benefits of the reaction.

Keywords: Smouldering Combustion, Porous Medium, Heat Transfer, Land Remediation, Energy Recovery
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1 Symbols and Nomenclature

Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CFIPM</td>
<td>Condensed fuels in inert porous media</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative thermogravimetry</td>
</tr>
<tr>
<td>DT</td>
<td>Dimensionless time</td>
</tr>
<tr>
<td>GA</td>
<td>Genetic Algorithms</td>
</tr>
<tr>
<td>IPM</td>
<td>Inert porous media</td>
</tr>
<tr>
<td>LM</td>
<td>Levenberg-Marquart</td>
</tr>
<tr>
<td>LTE</td>
<td>Local thermal equilibrium</td>
</tr>
<tr>
<td>LTNE</td>
<td>Local thermal non-equilibrium</td>
</tr>
<tr>
<td>MC</td>
<td>Moisture content</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>PSF</td>
<td>Porous solid fuel</td>
</tr>
<tr>
<td>REV</td>
<td>Representative elementary volume</td>
</tr>
<tr>
<td>SHS</td>
<td>Self-propagating high-temperature synthesis</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
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</table>

Latin Letters

<table>
<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>A_s</td>
<td>Surface area, m²</td>
</tr>
<tr>
<td>A_cs</td>
<td>Cross-sectional area, m²</td>
</tr>
<tr>
<td>Ar</td>
<td>Arrhenius number</td>
</tr>
<tr>
<td>A</td>
<td>Pre-exponential factor, s⁻¹</td>
</tr>
<tr>
<td>a</td>
<td>Strain rate, s⁻¹</td>
</tr>
<tr>
<td>Bi</td>
<td>Biot number</td>
</tr>
<tr>
<td>c</td>
<td>Constants of integration</td>
</tr>
<tr>
<td>C_p</td>
<td>Specific heat capacity, J kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>d_p</td>
<td>Particle diameter, mm</td>
</tr>
<tr>
<td>d_void</td>
<td>Void space diameter, mm</td>
</tr>
<tr>
<td>Da</td>
<td>Damköhler number</td>
</tr>
<tr>
<td>D_t</td>
<td>Diffusion coefficient, m² s⁻¹</td>
</tr>
<tr>
<td>D_d</td>
<td>Taylor dispersion coefficient, m² s⁻¹</td>
</tr>
<tr>
<td>d</td>
<td>Darcy resistance, Pa m⁻¹</td>
</tr>
<tr>
<td>e</td>
<td>Natural logarithm</td>
</tr>
<tr>
<td>E</td>
<td>Energy, J</td>
</tr>
<tr>
<td>Ė</td>
<td>Energy rate, J s⁻¹</td>
</tr>
<tr>
<td>E_p</td>
<td>Pyrolysis activation energy, kJ mol⁻¹</td>
</tr>
<tr>
<td>E_o</td>
<td>Oxidation activation energy, kJ mol⁻¹</td>
</tr>
<tr>
<td>frCO</td>
<td>Fraction of C oxidized to CO</td>
</tr>
<tr>
<td>frCoxid</td>
<td>Fraction of C consumed</td>
</tr>
<tr>
<td>frO2oxid</td>
<td>Fraction of O₂ consumed</td>
</tr>
<tr>
<td>FK</td>
<td>Frank-Kamenetskii number</td>
</tr>
<tr>
<td>h</td>
<td>Heat transfer coefficient, W m⁻² K⁻¹</td>
</tr>
<tr>
<td>h_m</td>
<td>Mass transfer coefficient, kg m⁻² s⁻¹</td>
</tr>
<tr>
<td>h_{ig}</td>
<td>Interfacial heat transfer coefficient, W m⁻² K⁻¹</td>
</tr>
<tr>
<td>k</td>
<td>Thermal conductivity, W m⁻¹ K⁻¹</td>
</tr>
<tr>
<td>k_p</td>
<td>Intrinsic permeability, m²</td>
</tr>
</tbody>
</table>
\( k_\phi \) Dimensionless porosity function
\( l \) Characteristic length, m
\( Le \) Lewis number
\( M \) Molar weight, g mol\(^{-1}\)
\( n, m \) Reaction order
\( Nu \) Nusselt number
\( P \) Pressure, Pa
\( Pr \) Prandtl number
\( Pe \) Peclet number
\( \dot{q}_{in} \) Heat flux, W m\(^{-2}\)
\( Q \) Source/sink term, W m\(^{-3}\)
\( Q_{cr} \) Critical rate of heat generation per unit volume, W m\(^{-3}\)
\( r \) Radius, m
\( r_0 \) Initial radius, m
\( \dot{R} \) Reaction rate, s\(^{-1}\)
\( Re \) Reynolds number
\( R_g \) Ideal gas constant, J K\(^{-1}\) mol\(^{-1}\)
\( R_s \) Specific gas constant, J kg\(^{-1}\) K\(^{-1}\)
\( S \) Saturation
\( t_g \) Air-on time, s
\( t_h \) Heater-off time, s
\( t_f \) Final time, s
\( T_{max} \) Maximum temperature, K
\( T_0 \) Initial ambient temperature, K
\( u_g \) Air flux, m s\(^{-1}\)
\( U \) Global heat loss coefficient, W m\(^{-2}\) K\(^{-1}\)
\( v \) Mass yield/consumption of species per mass of reactant
\( v_f \) Front velocity, m s\(^{-1}\)
\( V \) Volume, m\(^3\)
\( X \) Mass fraction
\( Y \) Mass fraction/loss
\( \dot{Y} \) Mass fraction/loss rate, s\(^{-1}\)
\( Y_{O2,0} \) Initial oxygen mass fraction
\( Y_{O2,f} \) Final oxygen mass fraction
\( Z \) Arrhenius equation

**Greek Symbols**
\( \Delta H \) Heat of reaction, MJ kg\(^{-1}\)
\( \lambda \) Correction of material geometry
\( \phi \) Porosity
\( \gamma \) Optimization constant
\( \varphi \) Optimization function
\( \chi \) Mixture fraction
\( \rho \) Density, kg m\(^{-3}\)
\( \sigma \) Stefan–Boltzmann constant, W m\(^{-2}\) K\(^{-4}\)
\( \theta \) Dimensionless temperature difference
\( \delta \) Dimensionless heating rate
\( \mu \)  Dynamic viscosity, Pa s

**Subscripts/Superscript**

- \( A \): Ash
- \( b \): Bitumen
- \( bk \): Bulk
- \( Ch \): Char
- \( calc \): Calculated
- \( cl \): Cylinder
- \( cond \): Conduction
- \( conv \): Convection
- \( cr \): Critical
- \( eff \): Effective
- \( exp \): Experimental
- \( F \): Fuel
- \( f \): Final
- \( FC \): Fixed carbon
- \( g \): Gas
- \( gen \): Generation
- \( GP \): Gaseous products
- \( in \): Inlet
- \( ig \): Ignition
- \( l \): Liquid
- \( max \): Maximum
- \( N \): Normalized
- \( out \): Outlet
- \( oxid \): Oxidation
- \( pyr \): Pyrolysis
- \( rad \): Radiation
- \( s \): Solid
- \( sf \): Surface
- \( sp \): Sphere
- \( void \): Void space
- \( 0 \): Initial
- \( \bar{x} \): Non-Dimensional Parameter
1.0 Introduction

Smouldering combustion is a fascinating, important, and complex phenomenon. It has played a key role in the relationship between humans and fire for millennia [1, 2] and is recognized as a natural part of terrestrial ecosystems [3]. Smouldering as a combustion problem was first acknowledged by Palmer [4] and has been studied mostly in the context of fire safety because it is recognized as a relevant process of destructive fires. Applied smouldering is now emerging as a tool for engineers to address a wide range of environmental and industrial challenges.

Smouldering – combustion in the absence of flames – has been studied from many perspectives and in many contexts: from microscopic considerations (single grain or pore) to peat mega-fires smouldering across hundreds of thousands of hectares; from natural convection in foam to forced convection in cigarettes; from unintentional self-heating of waste piles to intentional treatment of contaminated soil; from out-of-control underground coal seam fires to intentional applications for underground oil and gas recovery. It has been studied in micro-gravity, analyzed with combustion theory, modelled with simple and complex approaches, and scaled up by 5 orders of magnitude from laboratory to field-scale applications. The disciplines taking interest in smouldering extend beyond the fire and combustion communities to chemistry, soil science, energy, space engineering, heat transfer, mechanical engineering, petroleum engineering, hydrogeology, environmental engineering, and porous media processes among others.

The variety of disciplines, materials involved and perspectives on smouldering phenomena has resulted in a lack of unity in the expression of key concepts, in the terminology used, in the interpretation of the results, and in the conclusions extracted. Smouldering has been named in situ combustion, glowing combustion, fire flooding, and filtration combustion in different contexts. There are many ideas in the literature that could appear contradictory and many questions that remain unresolved. The recent introduction of applied smouldering research is informed by, and also informs, traditional smouldering research, yet the results of research in this area have also never been integrated to other smouldering related findings.

The complexity of smouldering processes relative to those of flaming combustion, and the nuanced interplay of physical and chemical processes in smouldering, changes the scope of the necessary science. Traditional treatment emphasizes the importance of local and temporal phenomena as is commonly done for most combustion processes. However, there is limited appreciation for the fact
that smouldering behaviour at the scale of a system depends on the integral, in space and time, of many key processes. Smouldering is a process that is defined by the result of continual feedback between heat and mass transfer processes and chemical kinetics that can determine the fate of smouldering and its propagation. The outcomes can be drastically different: increasing temperatures leading to super-adiabatic conditions and/or flaming, self-sustaining propagation with steady temperatures, or decaying propagation leading to extinction. As a result of our disjointed understanding of smouldering, our ability to interpret conditions, recommend actions, and intentionally control smouldering is limited. On one hand, a smouldering reaction may be considered weak, with relatively low temperatures and propagation rates that suggest it is perpetually on the verge of quenching. On the other hand, the same reaction may be recognized as remarkably robust with the potential to sustain itself for centuries with no intervention, or even survive every attempt at suppression.

As a discipline, fire science still has much unresolved complexity relative to most others [5]. And, despite being one of the most relevant and complex fire processes, smouldering science has received much less attention than most other aspects of fire [6]. Smouldering has always had a relatively minor profile in the fire discipline. However, that is changing. In the 1950s and 60s, the percentage of fire papers about smouldering was virtually zero. Despite a rapid rise in the total number of fire papers, the percentage about smouldering increased to 0.08% by 1970, to 0.8% by 1980 and to over 1% in 2018. The first substantial review of smouldering appeared in 1985: a pioneering study by Ohlemiller [7] that provided the first theoretical framework to describe smouldering combustion. Subsequent reviews [6, 8, 9] present summaries of studies conducted after 1985 but retain the framework proposed by Ohlemiller [7].

All previous reviews agree that the universal characteristic of smouldering is the presence of a porous medium of sufficient permeability to air, ensuring sufficient oxygen is available to the reaction. That oxygen diffuses into the surface of the reacting fuel, driving its exothermic oxidation. When the rate of heat generated and retained exceeds that lost to endothermic processes and the environment, smouldering can be self-sustaining.

Traditionally, smouldering research focused on porous solid fuels (hereafter referred to as PSFs). These include textiles (linen, cotton, wool, paper, leather), synthetic materials (expanded thermosetting plastics, polyurethane foam, foam rubber, polyisocyanurate foams,
phenolformaldehyde foams, wood fibre insulation boards), fuels (coal, oil shale, charcoal, oil sands, wood, granular carbon), plants and grains (tobacco, hay, brewing grains, sawdust), soils (peat, forest litter such as leaves and pine needles), and foods (corn starch, sugar, fish meal). The primary objective was to understand the risk of fire from PSFs and consider means to prevent ignition (including self-ignition) or achieve suppression [10-21]. The potential for cigarettes to cause ignition of bedding and upholstery is a classic example [22-27]. Also studied in this context was oil-soaked ‘lagging’ (pipe insulation), one of the few cases in which liquids were considered the fuel [3, 28]. Given that the motivation for studying smouldering has been intimately related to the material burning, smouldering literature is very material specific. Most studies address issues pertaining to a specific material, and only in very few occasions are conclusions drawn that have explicit applicability across different materials.

Two key aspects of smouldering that make it such a serious fire risk are (i) it can initiate from heat sources that are insufficient to cause flaming, and (ii) once initiated it is extremely difficult to suppress [7, 17]. Thus, smouldering is known to be responsible for recurrent coal seam fires burning for centuries [29, 30] and for peat megafires visible from space [14], both with extremely serious implications for environmental and human health.

Recently, smouldering has been recognized as a process that can be harnessed for human benefit. The reason it is such a fire risk is also one reason it is so valuable: materials that have too low calorific value or are too wet to flame can be smouldered. Since the process can be engineered to be self-sustaining, it can have a very low energy and carbon footprint. When used for waste management, for example, the competing technologies are usually thermal processes, such as pyrolysis, volatilization, or incineration. These processes are energy intensive because they are endothermic and/or suffer from significant heat losses. The large and unmanageable losses result in the need for continuous inputs of supplemental heat or fuel. Applied smouldering is also highly controllable, since the rate of fuel consumption is generally proportional to the air mass flow rate [7] and this is easily controlled in engineered systems. All of these suggest significant benefit for those responsible for organic materials that need disposal, volume reduction, and/or conversion to heat and gas.

There are many examples of applied smouldering. Use of in situ combustion, or fire-flooding, to recover crude oil from reservoirs has been extensively investigated (e.g., [31-39]). This has been
combined with other approaches, such as steam injection, to maximize oil production ahead of the combustion front [34]. Smouldering has also been proposed for recovering metals from heavy oil waste [40], for sintering of iron ore [41, 42], for underground coal gasification [43], for landmine detection [44], for recycling shredded tires [45], and for reducing the volume of landfills [46]. Smouldering has been applied commercially for in situ (i.e., on site, below ground) remediation of industrially polluted soil [47-54]. Commercial smouldering systems have been developed to treat waste industrial liquids, such as crude oil tank bottoms, in above ground systems [55]. In addition, smouldering has been proposed for managing sewage sludge (in some cases termed biosolids), the dominant waste from industrial waste water treatment plants [56], and for recovering energy from pine bark waste [57]. Recently smouldering has been applied as an energy efficient destruction technique for human faeces [58-61]. This has led to the development of a continuous smouldering reactor that recovers and reuses the excess energy as part of an innovative, off-grid toilet designed to address the sanitation challenges of impoverished countries [62].

Applied smouldering requires a thorough understanding of the process in order to optimize the operational conditions in the context of an industrial application. In several of the cases above, the fuel is a liquid (e.g., coal tar, creosote, petroleum hydrocarbons) that is found already embedded in a porous medium (soil). However, in other applications (e.g., crude oil, biosolids, pine bark, faeces) the fuel is intentionally mixed with an inert porous medium, such as quartz sand. In contrast to PSF, these systems will be collectively referred to as Condensed Fuels in Inert Porous Media (CFIPM). All of these smouldering applications employ a relatively short, intentional ignition event followed by a forced, continued air supply. CFIPM present some different conditions than PSF in traditional smouldering studies, including different heat transfer characteristics, much lower porosity (e.g., 98% in foam vs. 35% in sand), lower permeability to air, and higher airflow rates (resulting in, for example, reduced buoyancy effects). Also, sensitivity to key process variables is important, such as moisture content and enriched oxygen concentration; variables that are less relevant to a fire safety context. Moreover, a substantial subset of fire safety studies have studied opposed smouldering, where the oxygen feeding the reaction is flowing in the direction opposite to the reaction’s propagation. In contrast, engineered smouldering research focuses on forward smouldering, where air is injected behind the front and flows in the same direction as the propagating reaction.
Taken together, the wide range of available studies provide a comprehensive picture of the different processes affecting smouldering. However, there has been no synthesis of the available research into a holistic understanding of smouldering. This review aims to bring together the diversity of studies – theoretical, experimental, and modelling – across both natural and engineered smouldering research to produce a unified conceptual understanding of smouldering combustion. While recognizing that different materials will emphasize or de-emphasize certain phenomena, this review will focus on a conceptual understanding and therefore will only use material dependent studies to illustrate specific phenomena. This will inevitably exclude certain studies where the phenomena has already been described by means of examples illustrated by different materials. A novel aspect of this review is to articulate the state of the art in considering smouldering as an energy balance integrated in time and space. This conceptual model has important implications for managing fire risk and effectively harnessing smouldering to solve engineering challenges.

The framework for discussion is one-dimensional smouldering. However, many of the concepts are relevant to the spectrum of conditions including multi-dimensional smouldering. The general framework proposed here is based on a smouldering front that spans the sample cross-section utilizing oxygen delivered through the effective porosity of the porous medium to the reaction zone. Surface smouldering, such as that which occurs on the surface of wood or incense is a limit state of this process. Numerous studies have examined these valuable phenomena and two excellent examples (e.g., [7, 63]), serve to illustrate this limit behaviour. Nevertheless, the flow fields and the PSF characteristics of such systems are relatively unique and are not truly related to smouldering but to the external flows induced by the environment and/or the smouldering front. Therefore, this limit behaviour represents a special case outside a general conceptual understanding of smouldering, and thus it is only covered briefly.

Section 2 provides essential background, including introducing key processes and nomenclature. It serves to introduce main concepts that are expanded upon in subsequent sections. The nomenclature establishes a consistent terminology used throughout the paper. Moreover, this section summarizes the stoichiometry and kinetics of smouldering chemistry. This is a highly studied field and the review attempts to summarize the diversity of approaches and highlight the costs and benefits of the degree of complexity included in kinetic schemes.
Section 3 summarizes the research into ignition and extinction. It discusses the traditional, local analyses of ignition and extinction. Moreover, it highlights both theoretical consideration and experimental studies of ignition and extinction. Key dimensionless numbers in smouldering are reviewed and linked to the concepts in this section. Finally, the topic of the transition of smouldering to flaming combustion is reviewed.

Section 4 presents a general conceptual model of smouldering combustion, detailing key similarities and differences between PSF and CFIPM systems. Moreover, it presents these in the context of understanding smouldering as a process that depends on heat and mass transfer processes integrated in time and space. The traditional local energy balance is discussed in the context of a bed-integrated, or global, energy balance for the system. The global energy balance concept is then presented as central to differentiating a self-sustaining from a non-self-sustaining smouldering system. This conceptual model is new and articulates an understanding of smouldering that has emerged from the extensive body of research underlying this review. The energy balance concept is then employed to explain the role of heat losses, of ignition, and of extinction on the self-sustainability of a smouldering system. Moreover, the concept of smouldering robustness – as a measure of how far system conditions are from extinction – is articulated in the context of a system energy balance.

Section 5 focuses on smouldering emissions, the sensitivity of emissions to fuel types and smouldering characteristics, and emission treatment systems. Particular attention is given to the emissions of metals and nitrous oxides. The review concludes by summarizing the research gaps and opportunities for the smouldering field, covering hazard management as well as practical applications moving forward.

Self-propagating high-temperature synthesis (SHS) [64-67], packed bed incinerators [68-70], porous media burners [71, 72] and fixed bed catalytic reactors [73, 74] among others are process that share many commonalities with smouldering combustion and have led to important breakthroughs in the understanding of smouldering. As such, relevant information from these areas of research will be invoked throughout this review. Nevertheless, extensive literature that includes many review papers have been published on these subjects; therefore, a review of these research areas will be considered outside the scope of this study.
2.0 Fundamental Processes

2.1 Key Processes

Smouldering combustion differs from other forms of combustion (ex. premixed combustion, non-premixed flaming combustion, etc.) in several key ways. First, smouldering characteristic time scales are consistent with diffusive processes. Characteristic rates for radiative and convective transport as well as reaction rates can all be quantified by diffusive approximations [7, 75]. Heat exchange minimizes losses by radiation, conduction and convection allowing chemical reactions to proceed at rates and temperatures typically too low to sustain other combustion processes. A second unique feature of smouldering combustion is that different reactions can occur simultaneously but spatially distributed in regions that do not necessarily correspond to the region of maximum temperature. In flaming combustion, reactions are spatially distributed but around the region of maximum temperature. Therefore, in traditional combustion processes, the flame thickness is very thin, so all chemical processes compete in close proximity. The spatial distribution of the chemical reactions in smouldering can result in the suppression of some reactions and the promotion of others at very different locations. This can affect heat and mass transfer processes as well as the resultant products of combustion. Third, in smouldering, the porous medium serves as a heat exchanger; therefore, filtration and re-condensation are common mechanisms that further complicate the spatial distribution of the reactions. The result is a temporal evolution of the smouldering front, and of the products generated, as the front progresses. While the chemical mechanisms associated with any combustion process might be relevant for smouldering, these particular features of smouldering can result in outputs that are very different from any conventional combustion process.

Smouldering has been examined at a variety of scales. Pore-scale systems are required when considering such processes as chemical reaction kinetics and the diffusion of oxygen into the fuel surface [76]. Macroscopic systems, such as those defined by a Representative Elementary Volume (REV) [77], are valuable for considering bulk properties (e.g., porosity, permeability, bulk density, thermal conductivity), the corresponding flux-gradient relationships (e.g., Darcy’s Law for fluid flow, Fourier’s Law for heat conduction), and the conservation of mass and energy model formulations that employ them [78, 79]. Bed-scale systems are needed for smouldering propagation (average peak temperature, front velocity) and energy balance considerations [80, 81].
Field scale systems are relevant for studying large engineering problems where the scale of the problem is larger than the scale of heterogeneity of key properties, e.g., coal seam burning [29, 30], in situ combustion for oil recovery [31-39], in situ and ex situ contaminated soil treatment [49, 53]. This review does not aim to summarize all of this work. Rather, it tries to summarize key aspects that form a common theme and link the smouldering propagation process across scales.

Indeed, the chemical mechanisms referred to above are a local phenomenon. “Local” will be a key word used in this review to describe any process that can be considered at a small scale with respect to space (relative to the scale of the system) and occurring at a specific time. For example, processes happening within a thin reaction front are considered local, such as reaction rates, mass transfer, and heat exchange. However, the output of a smouldering system referred to above is a global phenomenon. “Global” will be a key word referring to processes that must be considered as integrated over space (e.g., over the fuel bed/entire system) and/or over time. Examples of global phenomena include net energy production, total fuel mass destruction, and cumulative gasses produced. Some processes can be considered either at the local or the global scale, such as heat transfer. One of the goals of this review is to clearly differentiate local from global smouldering behaviour, so the key words will appear regularly to underscore this distinction.

In smouldering combustion, chemical reactions are inextricably coupled with heat and mass transfer mechanisms. Thermogravimetry (TG), Differential Thermogravimetry (DTG), and Differential Scanning Calorimetry (DSC) have been extensively employed to isolate the chemistry from the heat and mass transfer mechanisms. They provide an environment of controlled atmosphere and heating rate, with negligible thermal gradient and species transport. Moreover, only heterogeneous reactions are measured due to the short residence time of air in the sample [7]. The use of these techniques along with bench scale experiments have been central to defining key processes, both local and global, related to smouldering.
2.2 Process Nomenclature

Inconsistencies in terminology and confusion in the concepts related to smouldering are common in the literature. This section attempts to establish a consistent nomenclature for key processes so as to provide a foundation for the rest of the paper.

For the purposes of this review, seven distinct processes are identified related to smouldering: inert heating, endothermic pyrolysis, exothermic degradation, assisted thermal degradation, self-sustaining thermal degradation, self-sustaining smouldering, and smouldering propagation. In smouldering, spatial distribution of chemistry and temperature means they are not always coupled; therefore, it is necessary to separate heat and mass transfer from chemistry. This is the main reason to define these seven processes. These processes will then be used, in combination with heat and mass transfer considerations, to describe different smouldering regimes. These processes should not be directly related to ignition, extinction or transition to flaming but purely relate (with the exception of smouldering propagation) to local thermochemistry.

Note that the temperature ranges at which these processes occur are variable, may overlap, and depend on fuel composition, atmosphere, and heating rates [7, 82]. Literature on solid and liquid fuels (when appropriate) will be used to define each of these processes. However, most of the examples will be taken from biomass decomposition literature, which provides substantial research relevant to smouldering combustion.

If the heat provided either by an external source or by exothermal processes is insufficient to overcome the activation energy of the endothermic pyrolysis and oxidative reactions these reactions will not occur. Under these conditions, temperature changes only relate to enthalpy changes and mass loss is associated only to phase change. Both processes are driven by thermodynamics. This process is herein referred to as inert heating. A review of most of the relevant literature associated to inert heating is provided by [83] and [84] together with experimental results that indicate that the evaporation of relatively stable high molecular weight species occurs below 220°C, generating numerous products. Decomposition of biomass containing compounds such as starch, cellulose, hemicellulose, lignin, and pectin occurs mostly at temperatures higher than 220°C. Oja et al. [83] and Schulten [84] provide a detailed analysis of these products. Further analysis is beyond the scope of this study except, given their importance,
it is worth briefly discussing water, glycerol and nicotine (typical of tobacco products, where
extensive literature is available).

Inert heating can include low temperature endothermic processes such as the evaporation of water,
nicotine or glycerol. Fig. 1 shows the comparative degradation of tobacco, glycerol and a mixture
of tobacco and glycerol. The evaporation of water appears as an endothermic process at
approximately 100°C for tobacco and tobacco-glycerol mixtures. At temperatures between 120-
250°C the endothermic evaporation of glycerol is observed for all three materials with the mixture
showing an endothermic peak in between the tobacco and the pure glycerol. The evaporation of
nicotine is not obvious on TGA/DSC curves, nevertheless many studies have shown that the
endothermic evaporation of different forms of nicotine compounds occurs in a range of
temperatures between 110°C and 220°C [85]. Analysis of gas emissions show that these three
compounds do not undergo any chemical transformation, thus thermodynamics controls
evaporation and mass loss occurs purely due to inert heating. Inert heating will produce emissions
that will most likely re-condense within the relatively cool porous medium ahead of the
smouldering front unless the processes are very close to the surface or the flow drives them away
from the porous medium. In experiments using reactors where the flow drives emissions towards
the porous medium, then these emissions will not appear until the front approaches the end of the
reactor [50].

Fig. 1. TGA and DTG-curves of tobacco, glycerol and glycerol–tobacco mixture (reprinted from
[86] with permission of Elsevier).
As the temperature increases beyond those of inert heating, but below oxidation temperatures, thermal degradation of the fuel – i.e., the decomposition of the fuel into different, typically shorter-chain compounds – will occur. There is no evidence in the biomass literature that indicates that self-sustaining smouldering can occur as a single-step oxidation with no thermal degradation, nevertheless thermal degradation can occur without self-sustaining smouldering. Most solid (e.g., coal, oil shale) or liquid hydrocarbons (e.g., crude oil, bitumen, coal tar, etc.) can be endothermically degraded into heavy liquids (tar) and porous solids (char). Tar is any high molecular weight product that is volatile at these intermediate temperatures but condenses near ambient temperatures. Char is a solid porous material with large surface-to-volume ratio and variable structure, reactivity, and composition (containing not only carbon but varying amounts of C, H, N, and O). In liquid hydrocarbons, tars are described as a mixture of maltenes (liquid phase that is soluble in n-heptane) and asphaltenes (solid particles, insoluble in n-heptane, dispersed in the liquid phase) [87-98]. Maltene degradation results in asphaltenes and asphaltene degradation yields char [89, 92, 97, 99-104]. Different types of tar and char (and fractions) can be produced from different types of fuels, atmosphere (inert or oxidative) and heating rates [7, 82, 105]. Ohlemiller and Rogers [82] describe different char vs tar formation paths for solid hydrocarbons. Foams, cellulosic materials, and many rigid polyurethanes typically form only a solid char in either oxidizing or inert atmospheres [16, 106-112]. In contrast, flexible urethane foams may form both tar and char in variable fractions [110-112].

Pyrolysis has been used in the literature as an all-encompassing term for the generation of thermal degradation by-products. As a result, pyrolysis has been used to define both endothermic and exothermic processes, which can cause confusion. In this review, these subsets of thermal degradation are clearly distinguished: Endothermic degradation processes are referred to as *endothermic pyrolysis* while exothermic thermal degradation processes are referred to as *exothermic degradation*.

For biomass specifically, Tumuluru et al. [113] provide a detailed review of low temperature biomass degradation as part of a discussion on torrefaction, i.e., thermal degradation typically between 200-320°C. Fig. 2 compares the degradation paths for hemicellulose, cellulose, lignin and pectin (typical components of biomass). While the onset of degradation for cellulose occurs above 300°C, and this degradation corresponds to endothermic pyrolysis, hemicellulose and pectin
undergo exothermic degradation between 220°C and 250°C as does lignin, but as early as 150°C. The composition of the gas products of degradation below 300°C is provided by [114] for different biomass products, showing the presence of CH₄, CO and CO₂. Typical mass loss in this stage can reach approximately 10% of the biomass [115]. Yang et al. [116] attribute the exothermic degradation of hemicellulose to the larger presence of organic compounds containing C–O, while the presence of methoxyl–O–CH₃ with lignin might be responsible for these earlier degradation steps. *Exothermic degradation* reactions include de-polymerisation and the production of altered and rearranged poly-sugar structures but do not involve an external oxidizer (even if they produce CO or CO₂). There is currently no evidence that the net energy resulting from exothermic degradation and endothermic pyrolysis is capable of proceeding towards oxidation with no external heat supply [7, 117-120]. This separation of endothermic pyrolysis and exothermic degradation processes is necessary because self-sustained smouldering requires an energy balance that is positive enough to raise the temperature of the chars/tars formed to levels were oxidation can occur.
Fig. 2. (a) DSC curves of hemicellulose, cellulose and lignin pyrolysis (reprinted from [116] with permission of Elsevier), (b) Thermal degradation of citrus pectin with DSC, TG and DTG curves (reprinted from [121] with permission of Elsevier).

At this stage we can introduce three different processes, assisted thermal degradation, self-sustaining thermal degradation, self-sustaining smouldering. These are local processes that describe three different possible outcomes of the local energy balance. This review will refer to the overall combination of exothermic degradation and endothermic pyrolysis that leads to a negative energy release as assisted thermal degradation. As an example, in Fig. 2a, below 300°C-350°C, endothermic pyrolysis reactions dominate over exothermic degradation reactions requiring an external heat supply to sustain the fuel degradation. It might be possible that, for certain fuels, exothermic degradation overwhelms the endothermic nature of pyrolysis and the result is an
exothermic process that releases a surplus of heat (Fig. 2b). In that case, if this surplus of heat is less than the apparent activation energy of all combined degradation chemical reactions occurring near the released heat, the process remains as *assisted thermal degradation*. Whereas if the net heat generated by the process surpasses the apparent activation energy of all degradation chemical reactions combined, the degradation process has the potential to become self-sustaining. This review will refer to this latter process as *self-sustained thermal degradation*. If the net energy production exceeds the energy required to activate oxidative chemical reactions, then *self-sustained smouldering* can occur.

It is important not to confuse *self-sustained smouldering* with the self-sustained propagation of a smouldering reaction, herein referred to as *smouldering propagation*. Self-sustained smouldering is an intrinsic (i.e., local) chemical process that does not consider heat and mass transfer throughout the porous fuel bed. Smouldering propagation is the result of complex heat and mass transfer processes (including an exchange of heat, oxygen and combustion products) that allows a self-sustained smouldering reaction to propagate through a porous bed [7, 64, 107, 110, 119, 122-130]. Thus, smouldering combustion is not local but global, in that it requires integration of processes in time and in space throughout the fuel bed. In biomass materials, heat losses are unavoidable and transport of oxygen and gaseous reaction products is never ideal. Therefore, the conditions leading to smouldering propagation always involve inefficiencies associated with heat and mass transfer that do not need to be considered when analysing the conditions leading to intrinsic self-sustained smouldering. Hence, while the local reaction is always referred to as self-sustained smouldering, the global process of smouldering propagation can be self-sustained or non-self-sustained (further discussed in Section 4.0).

2.3 Reaction Zones

Fig. 3 shows the TG-DTG-DSC curves associated with the thermal decomposition of Bright and Burley tobaccos [131] that serves to illustrate the different processes described above. More recent studies report similar observations [132-134]. Zone I represents the inert heating zone where endothermic evaporation of volatile compounds occurs. Zone II represents the exothermic degradation while Zone III and Zone IV correspond to endothermic pyrolysis. Despite the minor differences, both tobaccos show exactly the same degradation sequence. In both cases moisture evaporation is not present (biomass was dried prior to the test).
Fig. 3. TG-DTG-DSC of Bright and Burley tobaccos heated at 20°C min\(^{-1}\) in the atmosphere of helium (reprinted from [131] with permission of The Japan Society of Calorimetry and Thermal Analysis).

Fig. 4 compares degradation in the presence of oxygen with degradation in a nitrogen atmosphere [132, 133]. As soon as oxygen is present Zone III separates from Zone IV showing the presence of a new and very significant peak (~ 480°C) and a second minor peak (~650°C). These peaks correspond to self-sustained smouldering. Since smouldering propagation incorporates heat and mass transfer, it cannot be analysed using TGA. While it is clear that self-sustained smouldering does not necessarily lead to smouldering propagation, these temperatures represent the lower limit where the chemistry is net exothermic. Thus, emissions from smouldering propagation can be traced ultimately back to these temperatures. There is no need for higher temperature chemistry for smouldering propagation to exist.
Fig. 4. (a) TG-DTG curves for tobacco leaves ($\beta = 10^\circ C \text{ min}^{-1}$) (reprinted from [132] with permission of John Wiley and Sons), (b) DTG curves obtained for tobacco (reprinted from [133] with permission of Elsevier).

In many forms of biomass, the rate of mass loss shows three major peaks (Figs. 5 and 6) under $N_2$ and four peaks under air [134-136]. The two low temperature major degradation steps ($115^\circ C$ and $250^\circ C$) correspond to the inert heating zone (water and glycerol evaporation), as shown in Fig. 1. The third step corresponds to assisted thermal degradation as illustrated in Figs. 1 to 4. Under air, the fourth step corresponds to the self-sustained smouldering (oxidation) step.

The heat flow curve (Fig. 7) shows two visible peaks under $N_2$ with the common lags of a few degrees typical of high heating rates and/or large particle size. In the absence of a well characterized baseline, it is not possible to establish if any of the individual peaks might be endo- or exothermic. However, comparison with Figs. 1 and 2 allows inferring that the lower peaks might
correspond to products such as nicotine evaporation [85] and that the higher peaks could correspond to exothermic degradation of hemicellulose and lignin or pyrolysis of cellulose [116].

Fig. 5. (a) TGA and (b) DTG for a tobacco sample heated at 10°C min⁻¹ in a nitrogen and air atmosphere. Lines with downward peaks correspond to the weight loss rate and the decaying lines to the residual weight (reprinted from [134] with permission of American Chemical Society).
Fig. 6. TGA curves of the (a) reconstituted tobacco material and (b) reconstituted tobacco material with added paper wrapper heated in both air and nitrogen (reprinted from [136] with permission of Elsevier).

Fig. 7. DSC for a sample heated at 10°C min⁻¹ in a nitrogen (continuous line) and air atmosphere (dotted line) (reprinted from [134] with permission of American Chemical Society).

The studies by Barontini et al. [134] and Park [135] show that in the presence of oxygen a fourth peak above 400°C appears. This is the clearest difference between the mass loss rate traces in nitrogen and air presented in Figs. 6 and 7. The behaviour below 400°C seems to remain unaffected by the presence of oxygen. These observations are consistent with those of [132] and [133].
presented in Fig. 4. Yang et al. [116] report peaks in the same range for the exothermic degradation of hemicellulose and Einhorn-Stoll et al. [121] for pectin (see Fig. 2). Furthermore, in the presence of oxygen extrinsic to the fuel the second and third peak result in exothermic reactions. The heat flux (Fig. 7) from these reactions increases strongly with the heating rate showing that they are weakly exothermic. However, in some new materials such as real human, animal feces [137], or biosolids [138] the exothermic degradation is strong and inherent in the conversion process of such materials (Fig. 8).

![DSC under N₂](image)

Fig. 8. DSC under N₂ from (a) human, (b) chicken and (c) pig feces at 10°C min⁻¹ (adapted from [137]).

It is likely that these reactions will not be able to sustain propagation through the biomass, nevertheless, it is not possible to establish this unless a detailed solution to the mass, momentum and energy equations is obtained for the exact configuration of the porous matrix.

The strongest oxidative reaction appears between ~434°C and 460°C. This peak is consistent between the results reported in Fig. 4 and those reported by [134] and [135]. This second reaction is what most studies in the literature will classify as the second step of a two-reaction model such as the one presented below. Many studies will refer to this step as “char oxidation”. The temperatures presented above are just indicators of the reaction, “char oxidation” can manifest itself during smouldering at much higher temperatures [38, 40, 45].

\[
\begin{align*}
\nu_F[Fuel] + \nu_{O_{2,1}}[Oxidizer] & \rightarrow \nu_{Ch}[Char] + \nu_{GP_1}[Gaseous\ Products] + \Delta H_{pyr}\nu_FM_F \\
\nu_{Ch}[Char] + \nu_{O_{2,2}}[Oxidizer] & \rightarrow \nu_A[Ash] + \nu_{GP_2}[Gaseous\ Products] + \\
\Delta H_{oxid}\nu_{Ch}M_{Ch}
\end{align*}
\]
The first step will encompass, within a global heat of pyrolysis ($\Delta H_{pyr}$), the endothermicity associated to inert heating and assisted thermal degradation. Meanwhile the second term will incorporate, within a global heat of combustion ($\Delta H_{oxid}$), all exothermic terms associated with self-sustained smouldering. As described before, biomass does not necessarily fit this simple formulation in that all endothermicity ($\Delta H_{pyr}$) seems to occur below 200ºC and that assisted thermal degradation incorporates also exothermic steps (Figs. 1 to 4).

It is currently not clear the necessary number of steps required to model smouldering propagation and how this is affected by the fuel type and environmental conditions (further discussed in Section 2.4). Reduction of steps seems to be only possible when heat and mass transfer enables spatially resolving inert heating and assisted thermal degradation together ahead of a highly exothermic front. Nevertheless, other factors such as oxygen concentration in the gas phase or compounds intrinsic to the fuel can drive these decomposition steps complicating the step reduction process. It is important to note that the literature does not provide any fundamental method to deliver a reduced chemical kinetic model for smouldering. The combination of Kissinger and Genetic Algorithms was first suggested by Rein et al [108] to extract kinetic parameters from best fits to TGA data (further discussed in Section 2.4). These mathematical fits, in combination with previously proposed reduced reaction models [7, 117, 139] helped deliver adequate predictions of smouldering temperatures and propagation rates as well as to infer chemical explanations for observations such as the enhancement of the rate of decomposition that occurs when oxygen is present in the gas phase [106]. While there is value to this approach, it is clear that, as a mathematical fit to highly non-linear equations, it is not always a reliable approach to justify where multiple steps are necessary to describe fully the degradation of a material [140].

To get further information on the different chemical processes occurring at temperatures lower than the highest temperature peak (~434ºC and 460ºC), it is necessary to look at the production of CO and CO$_2$ (Fig. 9). The production of CO$_2$ in nitrogen covers the entire temperature range above 100ºC while the production of CO only begins above 225ºC. The same trend can be observed for the production of CO and CO$_2$ in air, where the main difference is the magnitude of the peaks and the presence of a new peak at ~425ºC. As mentioned above, several reactions in the thermally assisted regime can lead to the production of CO and CO$_2$ [113-116], nevertheless, above 280ºC-
290°C (Fig. 4) the presence of extrinsic oxygen starts having a significant effect on the degradation process.

Fig. 9. (a) CO$_2$ in Nitrogen, (b) CO$_2$ in air, (c) CO in nitrogen and (d) CO in air for a sample heated at 10°C min$^{-1}$ (reprinted from [134] with permission of American Chemical Society).

The CO/CO$_2$ ratio is commonly used as a signature of the presence of oxidation reactions and in particular smouldering (whether self-sustained smouldering or smouldering propagation) seems to deliver well-defined CO/CO$_2$ ratios for solid fuels [18]. For the ~130°C peak the ratio is zero therefore it can be assumed with certainty that CO$_2$ emerges from the assisted thermal degradation of the biomass but is not the product of oxidative reactions. The second peak appears at ~325°C, for this peak the CO/CO$_2$ ratio is approximately 0.25 for both air and nitrogen. The production of CO and CO$_2$ increases in magnitude with a larger supply of oxygen but the CO/CO$_2$ ratio remains approximately constant. This shows that this reaction is oxygen limited but it is the same reaction for nitrogen and air. This peak could potentially be associated to transitions from the decomposition of hemicellulose (lower temperature) to that of lignin and cellulose (higher temperature) (Fig. 2 and [113]). Nevertheless, it is not possible to discard the presence of
smouldering reactions. For the final peak (~425°C), the CO/CO\textsubscript{2} ratio is 0.05. After all the lignocellulosic biomass (hemicellulose, cellulose, and lignin) has been thermally degraded to char, increasing the surface to volume ratio for the biomass, greater supply of oxygen to the surface follows promoting complete combustion of the remaining char and resulting in a smaller CO/CO\textsubscript{2} ratio. Despite being smaller, these ratios are still within typical ranges for smouldering combustion. For smouldering of organic material embedded within an inert sand matrix, CO/CO\textsubscript{2} values can be variable depending on fuel type and system conditions, ranging from 0.05 to 0.40, with lower values favoured by higher air flow rates and larger scales; a value of 0.20 at the laboratory scale for smouldering faeces-in-sand [62] is an example.

2.4 Chemistry

A research topic that has received great attention in the context of smouldering is the definition of the kinetic mechanisms that describe the main chemical reactions [7, 76, 106, 107, 109, 110, 130, 141, 142]. These kinetic mechanisms generally describe competing exothermic and endothermic reactions, that combined, can result in net consumption or generation of heat. They also can aim to describe the production and consumption of key by-products. In virtually all instances, they represent a simplification of the true (complex) chemical systems they represent. Ideally, they provide information on the main reactions dominating the smouldering system at various temperatures and locations within the preheating and reaction zones (see Section 4.0 General Conceptual Model of Smouldering).

The interest in smouldering chemistry stems from the opportunities presented by the capability of numerical models to reproduce the temporal and spatial evolution of smouldering propagation [76, 110] that was evidenced experimentally with polyurethane foams [143, 144]. However, and as explained above, since they are generated from non-smouldering data purely as an optimization exercise [110], it remains an open question the degree to which they accurately represent smouldering phenomena (further discussed below).

The chemical reactions that could possibly occur within pyrolysis, assisted or self-sustained thermal degradation of fuels are multiple [113]. Oxidative reactions tend to be much faster than pyrolysis reactions, so strong simplifications are possible and the literature provides kinetic models
of different levels of complexity [16, 106-109]. These models range from simple one-step (global)
reactions to complex systems with multiple steps. Table 1 provides a compilation of kinetic
mechanisms from one to nine steps for a variety of solid and liquid hydrocarbons (peat,
polyurethane foam, biomass, cellulose, cardboard, wood, tire waste, crude oil, heavy oil, bitumen,
tar sands, oil shale, and asphalt). The aim of Table 1 is to show groups of Generic Mechanisms,
providing a synthesis of the disparate studies in the literature.
### Table 1. Generic kinetic mechanisms for smouldering combustion

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Eq.</th>
<th>Steps</th>
<th>Reaction Type</th>
<th>Generic Mechanism</th>
<th>Fuel</th>
<th>Gas</th>
<th>Liquid</th>
<th>Solid</th>
<th>Highlights</th>
</tr>
</thead>
<tbody>
<tr>
<td>[64, 122, 123, 125-130, 145-149]</td>
<td>(3)</td>
<td>1-step</td>
<td>Oxidation</td>
<td>( \text{Fuel} + \text{O}_2 \rightarrow \text{Char} + \text{H}_2\text{O} + \text{Gases} + \text{Heat} )</td>
<td>Carbon [126-130, 149], Hydrocarbon mixture (C,H,O), Diesel Particulate Filters [146], Wood [123], Cellulosic material [122], Porous solid fuel [64, 125, 147]</td>
<td>( \text{CO}, \text{CO}_2, \text{N}_2, \text{H}_2\text{O}, \text{O}_2 )</td>
<td>-</td>
<td>Ash</td>
<td>Widely used kinetic mechanism due to its simplicity. It is mostly employed in analytical smouldering models. Kinetic parameters are typically estimated through analytical methods. As pyrolysis reactions are not included, adjustment of the heat of oxidation is necessary to avoid extremely high temperatures.</td>
</tr>
<tr>
<td>[75, 80, 81, 117-119, 124, 150-152]</td>
<td>(4)</td>
<td>2-step</td>
<td>One pyrolysis and one oxidation</td>
<td>( \text{Fuel} + \text{Heat} \rightarrow \text{Char} + \text{Gases} )</td>
<td>Oil shale [150], Polyurethane foam [118, 119, 124, 151], Cellulosic materials [75, 117], bitumen [80, 81, 152]</td>
<td>( \text{CO}, \text{CO}_2, \text{O}_2 )</td>
<td>-</td>
<td>( \text{CaCO}_3, \text{CaO}, \text{Char}, \text{Ash} )</td>
<td>Fuel pyrolysis is included in Eq. (4) and (5). Eq. (4) implies that char oxidation can be neglected and Eq. (5) indicates that fuel oxidation is not relevant. For oil shale and any other material with inorganic content, an endothermic decarbonation (carbonates decomposition) can be introduced, Eq. (6). Eq. (7) neglects pyrolysis reactions and takes into account fuel and char oxidation.</td>
</tr>
<tr>
<td>[7, 76, 106, 120, 141, 142, 153-157]</td>
<td>(5)</td>
<td>2-step</td>
<td>One pyrolysis and one oxidation</td>
<td>( \text{Char} + \text{O}_2 \rightarrow \text{Ash} + \text{Gases} + \text{Heat} )</td>
<td>Polyurethane foam [76, 120, 157], Cellulosic materials [7, 141, 153], Wood [154], Biomass [106, 156], Peat [142], Porous solid fuel [155]</td>
<td>( \text{CO}, \text{CO}_2, \text{N}_2, \text{H}_2\text{O}, \text{O}_2 )</td>
<td>-</td>
<td>Char, Ash</td>
<td>Competition between fuel pyrolysis and fuel oxidation is introduced in Eq. (8), whereas in Eq. (9) drying is included neglecting fuel oxidation. Although drying is a phase-change process, it is typically assumed as an Arrhenius-type reaction in TG analysis. However, when applied into smouldering simulations, it fails to simulate properly the drying process [107].</td>
</tr>
<tr>
<td>[158, 159]</td>
<td>(6)</td>
<td>3-step</td>
<td>One pyrolysis and two oxidations</td>
<td>( \text{Char} + \text{O}_2 \rightarrow \text{Ash} + \text{Char} + \text{Gases} + \text{Heat} )</td>
<td>Polyurethane foam [76, 120, 157], Cellulosic materials [7, 141, 153], Wood [154], Biomass [106, 156], Peat [142], Porous solid fuel [155]</td>
<td>( \text{CO}, \text{CO}_2, \text{N}_2, \text{H}_2\text{O}, \text{O}_2 )</td>
<td>-</td>
<td>Char, Ash</td>
<td>Three oxidation reactions are introduced in Eq. (10): fuel (heavy oil), tar (light oil), and char (coker) oxidations. Eq. (11) shows that oil shale undergoes drying, fuel pyrolysis yielding tar (mixture of oily hydrocarbons) and char (fixed carbon). Char is oxidized and an endothermic decarbonation takes place. Both mechanisms were reformulated in terms of generic terms.</td>
</tr>
<tr>
<td>[158, 159]</td>
<td>(7)</td>
<td>3-step</td>
<td>Two oxidations</td>
<td>( \text{Fuel} + \text{O}_2 \rightarrow \text{Char} + \text{Gases} )</td>
<td>Polyurethane foam [76, 120, 157], Cellulosic materials [7, 141, 153], Wood [154], Biomass [106, 156], Peat [142], Porous solid fuel [155]</td>
<td>( \text{CO}, \text{CO}_2, \text{N}_2, \text{H}_2\text{O}, \text{O}_2 )</td>
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<td>(8)</td>
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<td>One pyrolysis and two oxidations</td>
<td>( \text{Char} + \text{O}_2 \rightarrow \text{Ash} + \text{Char} + \text{Gases} + \text{Heat} )</td>
<td>Polyurethane foam [76, 120, 157], Cellulosic materials [7, 141, 153], Wood [154], Biomass [106, 156], Peat [142], Porous solid fuel [155]</td>
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</tr>
<tr>
<td>[158, 159]</td>
<td>(9)</td>
<td>3-step</td>
<td>One pyrolysis, one oxidation, and one decarbonation</td>
<td>( \text{Fuel}<em>{(\text{char})} + \text{Heat} \rightarrow \text{Fuel}</em>{(\text{char})} + \text{H}_2\text{O} )</td>
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<tr>
<td>[158, 159]</td>
<td>(10)</td>
<td>4-step</td>
<td>One pyrolysis and three oxidations</td>
<td>( \text{Fuel} + \text{Char} + \text{Gases} )</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[158, 159]</td>
<td>(11)</td>
<td>4-step</td>
<td>One pyrolysis, one oxidation, and one decarbonation</td>
<td>( \text{Fuel}<em>{(\text{char})} + \text{Heat} \rightarrow \text{Fuel}</em>{(\text{char})} + \text{H}_2\text{O} )</td>
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</table>
1  Table 1. Continued.

<table>
<thead>
<tr>
<th>Ref.</th>
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<th>Steps</th>
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<th>Generic Mechanism</th>
<th>Fuel, Gas, Liquid</th>
<th>Solid</th>
<th>Highlights</th>
</tr>
</thead>
<tbody>
<tr>
<td>16, 104-110</td>
<td>(12)</td>
<td>5-step</td>
<td>Two pyrolyzes and three oxidations</td>
<td>Fuel + Heat $\rightarrow$ $\beta$ + Fuel + Gases</td>
<td></td>
<td></td>
<td>The concept of $\alpha$, $\beta$, and $\gamma$-fuel (or char) is introduced in Eq. (12) and Eq. (13) and applied hereafter. Different thermochemical processes that may or may not consume $O_2$ can create fuel or char with different structures and compositions. Char elemental analysis shows traces of C, H, N, and O [82, 106].</td>
</tr>
<tr>
<td>[106-112]</td>
<td>(14)</td>
<td>5-step</td>
<td>Three pyrolyzes and two oxidations</td>
<td>$\alpha$ – Fuel + Heat $\rightarrow$ $\beta$ – Fuel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[99]</td>
<td>(15)</td>
<td>6-step</td>
<td>Three pyrolyzes and three oxidations</td>
<td>$\alpha$ – Fuel + Heat $\rightarrow$ Char + Gases</td>
<td></td>
<td></td>
<td>The mechanism showed in [99] was reformulated and presented in a generic format in Eq. (15). It introduces new heavy oil (or bitumen) decomposition products such as maltene, asphaltene, and char (coke).</td>
</tr>
<tr>
<td>[160]</td>
<td>(16)</td>
<td>7-step</td>
<td>Three pyrolyzes and four oxidations</td>
<td>Fuel + Heat $\rightarrow$ $\beta$ – Fuel + Gases</td>
<td></td>
<td></td>
<td>The processes that lead the transition from smouldering to flaming might be analyzed by the incorporation of char and $\alpha$-char oxidation reactions in Eq. (16).</td>
</tr>
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<td>Table 1. Continued.</td>
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<td></td>
</tr>
<tr>
<td>[161]</td>
<td>(17)</td>
<td>8-step</td>
<td>Three pyrolyzes and four oxidations, and one gas oxidation</td>
<td>$\text{Fuel} + \text{Heat} \rightarrow \beta - \text{Fuel} + \text{Gases}$</td>
<td>$\beta - \text{Fuel} + \text{Heat} \rightarrow \gamma - \text{Char} + \text{Gases}$</td>
<td>$\gamma - \text{Char} + \text{Heat} \rightarrow \text{Gases}$</td>
<td>$\text{Fuel} + \text{O}_2 \rightarrow \text{Char} + \text{Gases} + \text{Heat}$</td>
</tr>
<tr>
<td>[106]</td>
<td>(18)</td>
<td>9-step</td>
<td>One drying, three pyrolyzes, five oxidations</td>
<td>$\text{Fuel}<em>{(wet)} + \text{Heat} \rightarrow \text{Fuel}</em>{(dry)} + \text{H}_2\text{O}$</td>
<td>$\alpha - \text{Fuel} + \text{Heat} \rightarrow \alpha - \text{Char} + \text{Gases}$</td>
<td>$\beta - \text{Fuel} + \text{Heat} \rightarrow \alpha - \text{Char} + \text{Gases}$</td>
<td>$\gamma - \text{Fuel} + \text{Heat} \rightarrow \alpha - \text{Char} + \text{Gases}$</td>
</tr>
</tbody>
</table>
The majority of the mechanisms presented in Table 1 were proposed based on the seven main smouldering processes (see Section 2.2 Nomenclature) and using TG, DTG, and DSC data (under air, \( \text{N}_2 \), and \( \text{O}_2 \) atmospheres, heating rates from 1 to \( 80^\circ\text{C} \) min\(^{-1} \), and sample mass between 2 and 50 mg [89, 90, 96, 97, 100-102, 105, 106, 110, 159, 162-175]) along with SARA (Saturated, Aromatics, Resins, and Asphaltenes [91, 95, 176]) analysis (i.e., a technique that separate liquid compounds into fractions according to the solubility in solvents of different polarity). Examples of TG, DTG and DSC data are provided in Sections 2.1-2.3. Most of the cited studies had the end goal of simply fitting kinetic reaction parameters against TG/DTG data without applying them to smouldering numerical models [103].

A one-step oxidation reaction mechanism (Eq. 3) is widely used in the forward and opposed smouldering literature [64, 122, 123, 125-130, 145-149] due to its simplicity. Such global reactions blend endothermic pyrolysis, exothermic degradation, and oxidation components [122, 123]. One-step mechanisms are popular in analytical smouldering models [64, 122, 123, 125, 146-149] and in models that investigate factors affecting self-sustaining smouldering behaviour without directly considering the effect of pyrolysis [145]. The absence of pyrolysis reactions in analytical models is understandable since more reactions introduce non-linearity in the governing equations. Numerical models usually neglect pyrolysis reactions based on the assumption that the heat of pyrolysis (\( \Delta H_{\text{pyr}} \)) is relatively small when compared with the heat of oxidation (\( \Delta H_{\text{oxid}} \)) [7, 64, 118, 119, 122, 123, 125-130, 145-150] thus treating its endothermicity as a correction to the energy released by oxidation can be deemed appropriate. Under robust smouldering conditions this is usually a valid approach (e.g., [80, 81]). However, it is known that pyrolysis is an important energy sink since, near extinction, oxidation reactions decrease to such an extent that pyrolysis may no longer be a negligible component of the energy balance [7, 76, 108, 124, 151, 155, 177]. In addition, the understanding of pyrolysis has been considered necessary to simulate ignition of a smouldering front [76, 105, 106, 151, 177-179]. Model solutions of a smouldering front in the absence of pyrolysis and heat losses show that the peak temperatures tend to increase excessively due to the large \( \Delta H_{\text{oxid}} \). Thus, such one-step oxidation models [64, 122, 123, 125-130, 145-149] may need to adjust \( \Delta H_{\text{oxid}} \) heuristically to avoid high temperatures.

Two-step mechanisms are presented in Eqs. (4-6). Eq. (4) shows a simplified mechanism for opposed smouldering, where fuel is endothermically pyrolyzed and oxidized (exothermic
degradation) at the same time. In opposed smouldering, char oxidation is considered negligible due to slow kinetics [180] (note that in opposed smouldering heat transfer is toward the burned region, Fig. 19b), and all of the energy released comes from exothermic degradation (i.e., fuel oxidation) [7, 118, 124, 151, 153]. In this configuration oxygen will be mostly consumed at the smouldering front leaving the char in an oxygen deficient environment. This prevents char oxidation. This mechanism adds pyrolysis only as a heat sink.

Moussa et al. [117] also proposed a two-step mechanism (Eq. 5) for cellulosic materials. First, fuel is pyrolized, creating char, which is subsequently oxidized. This mechanism is mostly used in forward smouldering because heat is transferred towards the virgin fuel which finds itself in an oxygen deficient environment that favours pyrolysis. The two-step mechanism does not take into account exothermic degradation (negligible energy release [152]). Recently, Zanoni et al. [152] confirmed that the same two-step mechanism (Eq. (5)) was able to simulate self-sustaining forward smouldering and smouldering propagation for bitumen embedded in a sand matrix. The main energy release was attributed to char oxidation [80].

The literature shows the addition or elimination of steps for specific fuels. For example, in Eq. (6) (e.g., oil shale smouldering [150]), a new heat sink was introduced: the endothermic decomposition of carbonates, which is different from endothermic pyrolysis. In Eq. (7) pyrolysis is deemed negligible and the process is governed by two exothermic reactions; exothermic degradation and char oxidation [118].

Observing two exothermic peaks in DSC experiments for polyurethane foams, Ohlemiller [7] first proposed a three-step mechanism (Eq. (8)), which was an improvement of Eq. (5), defining smouldering as a competition between endothermic pyrolysis and exothermic degradation (first exothermic peak). Both reactions form char, which is completely or partially oxidized (second exothermic peak), resulting in self-sustained smouldering [7, 99, 103, 110, 112, 118, 124, 141, 142, 151, 170, 176, 181, 182].

Rein et al. [110] proposed and optimized more complex kinetic mechanisms for polyurethane foam. Based on TG experiments, they concluded that a five-step mechanism (Eq. (12)) was more appropriate to phenomenologically predict the experimental observations of the species distributions in both opposed and forward smouldering. This was determined after Rein et al. [157], where a three-step mechanism (Eq. 8)) for foam was tested in a smouldering model and
resulted in the under-prediction of char production. The model limitations were attributed to the application of only one pyrolysis reaction.

Research on smouldering of wet fuels (e.g., biomass, peat, etc.) resulted in the introduction of water evaporation (Eqs. (7, 9, 11, and 16), typically assumed as a chemical reaction [106-108, 159, 163] rather than a phase-change process (inert heating). Thus, most of the kinetic mechanisms including water evaporation, when applied into smouldering combustion models, are not able to capture the temperature plateau around 100°C. Moreover, they would not be able to consider the effect of water on the energy balance (i.e., as described in Section 4.0). It is important to note that some fuels (e.g., peat) have a significant fraction of water and its movement by condensation and evaporation can alter the energy balance in the ignition, propagation, and extinction of the smouldering front [7, 108, 183] (see Section 3.0 for further discussion).

Complex kinetic mechanisms with seven (Eq. 16), eight (Eq. 17) reactions were used with the intention of predicting the transition to flaming [155, 160, 161]. More reactions have the tendency of fitting TG data with more precision. However, when employed in smouldering combustion models, these extra reactions generally produce negligible effects on the predicted smouldering process. For example, Rein et al. [110] concluded that the oxidation of the virgin foam in forward smouldering (exothermic degradation) may be virtually neglected since all of it was converted to β-foam. In addition, β-foam was consumed by the oxidation reaction instead of its competing pyrolysis reaction. Another example can be found in [160], in which the model was very sensitive to the first char oxidation but not sensitive to the final step of pyrolysis and final char oxidation.

The mechanisms presented in Table 1 were developed based on experimental observations of TG/DTG data and accepted mathematical formulations for the decomposition chemistry. These mathematical formulations are necessary to incorporate the chemical reaction into smouldering propagation models. Chemistry theory describes such mechanisms in terms of reaction rates ($\dot{R}$):

$$\dot{R}[s^{-1}] = Z[Y_F]^n[Y_{O_2}]^m$$

(19)

where $n$ and $m$ are the reaction orders, $Y_F$ and $Y_{O2}$ are the mass fractions of fuel and oxygen, respectively. “$Z$” is the temperature-dependent component of the reaction rate and it is generally described by means of the Arrhenius equation:
where \( A \) is the pre-exponential factor, \( E \) is the activation energy, \( R_g \) is the ideal gas constant, and \( T \) is the temperature. Pyrolysis reaction rates are represented by Eq. (19) with \( Y_{O_2}=0 \).

The application of such kinetic mechanisms in smouldering numerical models requires the estimation of the kinetic parameters, i.e., activation energy \( (E) \), pre-exponential factor \( (A) \), and reaction orders \( (n,m) \), as described in the Arrhenius equation. These expressions are continuous functions, therefore a unique temperature for the onset of these reactions is difficult to establish. Characteristic temperature values obtained from TG/DTG/DSC data are generally used to describe the temperature at which each process occurs. Nevertheless, these temperatures depend on the heating rates and sample sizes employed in the testing.

Several methods may be used to calculate/estimate the Arrhenius parameters from TG/DTG/DSC data: Kissinger, Ozawa, Freeman-Carroll, Coats-Redfern, Genetic Algorithms (GA), Levenberg-Marquart (LM) algorithm, etc. [105, 106, 110, 159, 162-165, 184-192]. Limitations can be found in almost all of them. For example, graphical methods (e.g., Kissinger, Ozawa) are only suitable for reactions that are simple, non-noisy and non-overlapping. LM algorithms converge quickly but are sensitive to the initial guess. GA can be used for a large number of unknown kinetic parameters; however, it is time consuming and stochastic, i.e., the solution uniqueness is not guaranteed [105, 110, 159, 184]. It is important to further discuss the methodologies used to obtain the kinetic parameters because the applicability of these values to the modeling of smouldering propagation is intimately related to the way in which they were obtained.

Figs. 10 and 11 show an example of the kinetic parameter calculation for the pyrolysis of cellulosic paper [193] via the Kissinger method [185]. Note that, although pyrolysis is shown as an example, kinetic parameter for oxidation reactions can also be calculated via the Kissinger method [185]. Fig. 10 describes one main peak in the DTG. Therefore, a one-step pyrolysis mechanism similar to the first reaction of Eq. (4) (Table 1) was used. The Kissinger method is presented in Fig. 11, where \( \ln\left(\frac{(dT/dt)T_{max}^2}{T_{max}}\right) \) is plotted against \( 1000/T_{max} \). Here, \( dT/dt \) is the heating rate and \( T_{max} \) is the maximum temperature (temperature at the DTG peak). The slope of the linear regression is \( E/R_g \), where \( R_g \) is the ideal gas constant, and the intercept is \( \ln\left(AR_g/E\right) \). Then \( E \) and \( A \) were calculated as 220 kJ mol\(^{-1}\) and 1.2x10\(^{19}\) (min\(^{-1}\)), respectively.
Fig. 10. Normalized sample weight loss rate for cellulosic paper changing with temperature at three different heating rates under nitrogen (reprinted from [193] with permission of Elsevier).

Fig. 11. Kissinger's plot under nitrogen to obtain the kinetic parameters for pyrolysis for cellulosic paper (reprinted from [193] with permission of Elsevier).
In cases with more complex chemistry, such as in polyurethanes foams, numerous chemical reactions can take place, some competing with others. Therefore, analytical methods cannot be employed and more robust techniques, such as Genetic Algorithms (GA), are valuable to determine a set of kinetic parameters. Fig. 12 and Table 2 show an example of the estimation of kinetic and stoichiometric parameters for polyurethane foam via GA [110]. The optimization process used the 5-step mechanism shown in Eq. (12), Table 1. Twenty parameters (log$_{10}$A, E, n, and v) were optimized at the same time (Table 2) by minimizing the difference between experimental data (mass loss ($Y$) and mass loss rate ($\dot{Y}$)) and numerical results:

$$\phi = \left( \int |\dot{Y}_{calc} - \dot{Y}_{exp}| dT \right)^{-1} + \gamma \left( \int |Y_{calc} - Y_{exp}| dT \right)^{-1}$$

(21)

where the constant $\gamma$ represents the relative influence of $Y$ over $\dot{Y}$; typical $\gamma$ values range from 50 to 100 [110, 192]. Further details on the set of ordinary differential equations, reaction rates, and GA optimization approaches can be found in [110].
Fig. 12. Polyurethane foam (a,c) mass-loss and (b,d) mass-loss rate in (a-b) nitrogen and (c-d) air as a function of temperature for three heating rates. Symbols: experimental [194]; solid lines: calculations [110] (reprinted from [110] with permission of Elsevier).
Table 2. Kinetic and stoichiometric parameters for polyurethane foam optimized via GA (reprinted from [110] with permission of Elsevier).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Best</th>
<th>Range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p$</td>
<td>148</td>
<td>[136, 160]</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\log_{10}(A_p)$</td>
<td>11.3</td>
<td>[10.4, 12.5]</td>
<td>log$_{10}$(s$^{-1}$)</td>
</tr>
<tr>
<td>$n_p$</td>
<td>0.21</td>
<td>[0.13, 0.31]</td>
<td>-</td>
</tr>
<tr>
<td>$v_{\beta,p}$</td>
<td>0.70</td>
<td>[0.69, 0.71]</td>
<td>kg kg$^{-1}$</td>
</tr>
<tr>
<td>$E_{\rho\beta}$</td>
<td>124</td>
<td>[121, 127]</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\log_{10}(A_{\rho\beta})$</td>
<td>8.2</td>
<td>[7.8, 8.5]</td>
<td>log$_{10}$(s$^{-1}$)</td>
</tr>
<tr>
<td>$n_{\rho\beta}$</td>
<td>1.14</td>
<td>[1.12, 1.18]</td>
<td>-</td>
</tr>
<tr>
<td>$v_{c,\rho\beta}$</td>
<td>0.05</td>
<td>[0.04, 0.06]</td>
<td>kg kg$^{-1}$</td>
</tr>
<tr>
<td>$E_o$</td>
<td>194</td>
<td>[161, 220]</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\log_{10}(A_o)$</td>
<td>15.4</td>
<td>[12.6, 16.7]</td>
<td>log$_{10}$(s$^{-1}$)</td>
</tr>
<tr>
<td>$n_o$</td>
<td>0.52</td>
<td>[0.47, 0.69]</td>
<td>-</td>
</tr>
<tr>
<td>$v_{c,o}$</td>
<td>0.57</td>
<td>[0.55, 0.57]</td>
<td>kg kg$^{-1}$</td>
</tr>
<tr>
<td>$E_{o\beta}$</td>
<td>194</td>
<td>[161, 220]</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\log_{10}(A_{o\beta})$</td>
<td>15.4</td>
<td>[12.6, 16.7]</td>
<td>log$_{10}$(s$^{-1}$)</td>
</tr>
<tr>
<td>$n_{o\beta}$</td>
<td>0.52</td>
<td>[0.47, 0.69]</td>
<td>-</td>
</tr>
<tr>
<td>$v_{c,o\beta}$</td>
<td>0.57</td>
<td>[0.55, 0.57]</td>
<td>kg kg$^{-1}$</td>
</tr>
<tr>
<td>$E_c$</td>
<td>201</td>
<td>[193, 220]</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\log_{10}(A_c)$</td>
<td>15.2</td>
<td>[14.5, 16.7]</td>
<td>log$_{10}$(s$^{-1}$)</td>
</tr>
<tr>
<td>$n_c$</td>
<td>1.23</td>
<td>[1.10, 1.49]</td>
<td>-</td>
</tr>
<tr>
<td>$v_{r,c}$</td>
<td>0.23</td>
<td>[0.21, 0.25]</td>
<td>kg kg$^{-1}$</td>
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</table>

Although the literature on kinetic parameters estimation is extensive, there are reasons to be cautious in applying them to smouldering systems. First, TG/DTG/DSC experiments use low and constant heating rates ([O(10$^0$-10$^1$)]), whereas smouldering typically occurs at high heating rates ([O(10$^1$-10$^3$°C min$^{-1}$)]) [106]. Such low heating rates favour some minor, low temperature reactions that often loose relevance at high heating rates, causing some discrepancy in the calculation of the Arrhenius parameters [152]. Second, TG/DTG/DSC experiments use a small
particle (μm scale) of fuel and thus are not able to incorporate the role of an inert matrix; thus, potentially important heat and mass transfer and surface area effects on the reactions may be neglected [7]. Third, the compensation effect (i.e., any variation in the activation energy ($E$) will cause also a change in the pre-exponential factor ($A$), which partially compensates for the effect of the activation energy change) may occur since $\ln (A)$ has a linear relationship with $E$ [195]; this is especially relevant to complex mechanisms, in which several reactions may have similar decomposition temperature intervals. The compensation effect may arise as a result of either the influence of experimental factors (e.g. heating rates) or the mathematical nature of the Arrhenius equation [105, 110, 129, 141, 150, 196-199]. Fourth, some studies [76, 151] have suggested that kinetic parameters associated with a specific reaction mechanism might have no fundamental physical meaning, and, even if carefully estimated, they may have to be significantly changed in order to produce the best possible description of reality.

Clearly chemical mechanisms and kinetic parameters depend on the type of fuel, TG/DTG/DSC heating rates, chosen kinetic mechanism complexity, and methods of estimation. The appropriateness of the final chemical scheme must be considered carefully in the context of the intended application. It is not expected that the same set of kinetic parameters will be sufficient to describe different scenarios (i) TG/DTG data, (ii) TG/DTG/DSC data, (iii) analytical descriptions of self-sustaining smouldering, (iv) smouldering propagation under robust conditions, (v) smouldering propagation under non-robust conditions, (vi) smouldering propagation of wet fuels, (vii) smouldering propagation including energy balance, and (viii) smouldering propagation predicting emissions/by-products (see Section 5.0 Emissions), to name only a few scenarios. It is an open question as to the appropriateness of the existing schemes for many of these uses and the degree of simplification that can be employed while still producing meaningful predictions. Currently, this question cannot be addressed because mass transfer effects between the different phases has not been studied in detail. The reaction rates depend on the supply of reactants to the reaction zone (Eq. (19)) and the reaction occurs in the solid phase, therefore, without detailed quantification of mass transfer between phases it is not possible to ascertain if the mathematical expression and embedded parameters properly quantify the reaction rates. This is a matter that needs further study.
Biomass is a fuel that has received extensive attention in the last few years. The focus has been to improve the numerical model first proposed by Leach et al [122] and apply it to biomass with significant moisture content and susceptible to smouldering such as peat. While numerous studies and configurations have been explored (e.g., [108, 109, 111, 156, 200, 201]) and compared to different experimental results (e.g., [202-204]), the basis for the numerical scheme, the methodologies for the extraction of chemical kinetic parameters, the numerical treatment of moisture evaporation and the reaction mechanisms are fundamentally the same. The general conclusion of these studies is that the most appropriate kinetic scheme to reproduce the experimental results depends on the specific configuration and the characteristics of the fuel. It is important to note that, in these models, the numerical scheme used to describe smouldering includes numerous parameters that do not allow one to fully separate the role of chemistry from that of heat and mass transport.

3.0 Ignition, Extinction, and Transition to Flaming

3.1 Ignition

Ignition of a porous solid fuel is a problem that has been of interest for the last century and is deeply imbedded in general combustion ignition theories. The first studies of combustion ignition were undertaken to understand coal mine explosions [205-208]. While theoretical and numerical formulations of combustion ignition have proposed criteria for ignition and detailed combustion ignition measurements have delivered insight on the underlying physical processes applicable to smouldering, there are still many unanswered questions concerning ignition.

Ignition of a smouldering reaction follows the same fundamental principles as solid ignition, thus can potentially be described by the same methods. However, smouldering ignition is complicated by the intricacies of heat and mass transfer. Since smouldering is a heterogeneous reaction, diffusion of oxygen through the fuel surface defines the supply of oxidizer and the release of energy. Characteristic time scales for diffusion tend to be longer than those associated to convection and radiation and therefore heat losses are of greater significance. Smouldering is therefore commonly found only within porous media where heat transfer away from the reaction is limited by Darcy’s law [77] while oxygen diffusion is still enabled by the presence of oxygen in the pores.
This section will present classic porous solid fuels ignition theory to provide insights into the ignition process and to establish its limitations when addressing smouldering. A numerical analysis that introduces transport processes then provides additional parameters controlling ignition of a smouldering reaction. Subsequently, Section 4.7 will provide a complementary understanding of ignition in the context of local and global energy balances.

3.1.1. Fundamental Principles of Ignition

Homogeneous ignition of a non-premixed flame is attained by heating the solid until it undergoes pyrolysis [209]. The released volatiles will combine with oxygen and as the temperature continues to increase a series of chemical reactions will occur leading to the net release of energy [210]. In contrast, heterogeneous ignition involves a solid exposed to oxygen that undergoes oxidation if the oxygen diffuses through its surface faster than the rate at which heating can induce pyrolysis [211-213]. The heat released by the heterogeneous reaction can continue to support the oxidation of the solid or can induce pyrolysis in a sufficient rate that released volatiles can lead to a homogeneous reaction [207].

Since smouldering combustion is a heterogeneous reaction, ignition will follow the same processes as for heterogeneous combustion of any solid; nevertheless, transport processes tend to be complicated by the fact that the fuel is a porous medium. Furthermore, the transition from heterogeneous to homogeneous combustion (i.e. transition to flaming) is not only a function of the characteristics of the solid fuel and the heating rates but it is also strongly dependent on the transport mechanisms within the porous medium. The analysis of smouldering as a fire safety problem has searched for simple criteria that define whether ignition or transition to flaming will occur. Ignition and transition to flaming have thus been treated as secondary objectives in smouldering research with the characterization of the reaction’s propagation being the primary focus. When smouldering is used as a controlled process [47, 58, 214] then the understanding of ignition and transition to flaming becomes a primary objective.

There are not many experimental studies on smouldering ignition, and without exception they are phenomenological in nature. Ohlemiller [215] examined the effect of igniter geometry on smoulderignition of cellulose. Kitano and Nagano [216], Anthenien and Fernandez-Pello [217] and Anderson et al. [218] have studied energetic requirements for initiation of a self-sustaining smoulder reaction under natural and forced convection flow conditions. These studies examine the
parameters and factors that control smouldering ignition and propagation. All of these studies stem from experimental observations and therefore are limited by the specificities of the fuels used and the conditions of the studies. Nevertheless, they provide insights on the various relevant processes. The main conclusion stemming from these studies is that smouldering ignition is a consequence of a very fine balance between heat supply and heat losses to and from the reactive front and the heat generated by the reaction. While this is no different from any ignition event, what differentiates smouldering is the effect of the porous medium on the energy balance and the conditions leading to a heterogeneous or a homogeneous reaction.

Both Anderson et al. [218] and Anthenien and Fernandez-Pello [217] identified critical values of external heat input that resulted in flaming combustion. Nevertheless, the role of the porous medium was only described in a qualitative manner. Torero and Fernandez-Pello [143, 219] and Torero et al. [144, 220] showed for polyurethane that a smouldering reaction will only propagate if the reaction was deep in the porous media. This was explained by the insulating nature of the char minimizing heat losses. In the case of peat, similar experiments were conducted, showing that the thickness of the necessary insulating layer decreased as the oxygen concentration (and subsequent char oxidation) increased [142]. For high oxygen concentrations (above ambient) almost no insulating layer was necessary and smouldering behaves almost as a surface process propagating into the porous medium leaving behind almost no char. Similar observations have been reported by others [180, 218, 221, 222]. Bar-Ilan et al. [223] explored the role of edge heat losses in a one-dimensional smouldering reaction. The authors introduced a simple heat loss term to quantify the boundary condition and attributed to these losses the need for a minimum size for the porous medium that will sustain smouldering.

In summary, experimental studies indicate that smouldering ignition can be described in a similar manner to any other ignition event. As opposed to homogeneous ignition, there is an upper bound to heterogeneous ignition, where excessive heat supply favours pyrolysis and therefore leads to flaming ignition. The heat released by smouldering reactions is relatively small, therefore it is necessary to consider the impact of the porous medium’s characteristics as well as its size and boundary heat losses.

Theoretical studies of ignition are more extensive and are generally based on the framework proposed by Semenov [224]. This is consistent with the experimental observations above but it is
limited by its simplicity. While the principles of Semenov’s theory are applicable, their use in
smouldering ignition is limited because most materials susceptible to smouldering will degrade
following complex chemical pathways, therefore it is not possible to obtain an unique rate of heat
release as used in Semenov’s theory [210, 213, 224, 225]. Furthermore, transport of energy and
species are usually the dominant factors defining the conditions for ignition. The literature lists a
number of parameters generally involved in the theoretical characterization of smouldering
ignition. These parameters are presented in Table 3 and represent all main forms of transport as
well as the reaction kinetics.

Simple criteria based on an energy balance and small values of Biot number, $Bi \to 0$ (see definition
of Biot number and several other dimensionless parameters in Table 3), prove to be insufficient.
The result is that many authors have reported a range of conditions under which ignition can occur
that are outside the bounds of Semenov’s definition [207, 211, 212, 224, 225].
Table 3. Dimensionless Parameters in Smouldering Combustion

<table>
<thead>
<tr>
<th>Dimensionless Number</th>
<th>Formulae</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluid flow (Pore Scale)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Void space</td>
<td>$\phi = \frac{(A_{void} \Delta x)}{A \Delta x}$</td>
<td>[79]</td>
</tr>
<tr>
<td>Ratio of the diameters</td>
<td>$\frac{d_p}{d_{void}} = \frac{1}{(1 - \phi)^{1/3}}$</td>
<td>[78, 226]</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>$Re = \frac{\rho u_g d_p}{\mu_g (1 - \phi)}$</td>
<td>[226]</td>
</tr>
<tr>
<td>Darcy resistance</td>
<td>$d = \frac{\phi \mu_g}{d_p^2 k \phi}$</td>
<td>[226]</td>
</tr>
<tr>
<td><strong>Heat Transfer (Pore Scales)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity ratio</td>
<td>$\frac{\phi \rho_g C_{pg} + (1 - \phi) \rho_s C_s}{\rho_g C_{pg}}$</td>
<td>[78, 79]</td>
</tr>
<tr>
<td>Effective thermal conductance ratio</td>
<td>$\frac{k_{eff}}{k_g} = \phi + (1 - \phi) \frac{k_s}{k_g}$</td>
<td>[226]</td>
</tr>
<tr>
<td>Peclet number</td>
<td>$Pe = \frac{r (\rho C_p)_g u_g}{(k_g) \frac{1}{1 - \phi}}$</td>
<td>[79, 226]</td>
</tr>
<tr>
<td>Prandtl number</td>
<td>$Pr = \frac{C_{pg} \mu_g}{k_g}$</td>
<td>[226]</td>
</tr>
<tr>
<td>Axial diffusion coefficient</td>
<td>$\left( \frac{k}{\rho C_p}_g \right) = \frac{1}{48} Pe^2$</td>
<td>[226]</td>
</tr>
<tr>
<td>Dimensionless solid conductivity</td>
<td>$\bar{k}<em>s = \frac{k_s}{4 d_p \sigma T</em>{max}^3}$</td>
<td>[227]</td>
</tr>
<tr>
<td>Nusselt</td>
<td>$Nu = \frac{h_{sg}}{k_g}$</td>
<td>[226]</td>
</tr>
<tr>
<td>Lewis number</td>
<td>$Le = \frac{\left( \frac{k}{\rho C_p}_g \right)}{D_g}$</td>
<td>[226]</td>
</tr>
<tr>
<td><strong>Chemical Reactions/Heat Transfer (Particle Scales)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Damköhler number</td>
<td>$Da = \frac{(1 - \phi) \rho_s Y_f \Delta H A e^{\frac{-E}{R_g T_0 l}}}{(\rho C_p)_g u_g T_0}$</td>
<td>[228]</td>
</tr>
<tr>
<td>Arrhenius number</td>
<td>$Ar = \frac{E}{R_g T_0}$</td>
<td>[28]</td>
</tr>
<tr>
<td>Frank-Kamenetzki number</td>
<td>$FK = Da Ar$</td>
<td>[229]</td>
</tr>
<tr>
<td>Biot number</td>
<td>$Bi = \frac{h_l}{k}$</td>
<td>[229-231]</td>
</tr>
</tbody>
</table>
Main dimensionless parameters for the analysis of a 1D smoldering front propagation. This table assumes: (i) local thermal equilibrium, (ii) negligible pressure drop across the smoldering front (i.e., high permeability bed) – Darcy’s law becomes trivial [123], (iii) one-step global reaction and (iv) the pore space is saturated with gas. Therefore, the dimensionless numbers can be grouped into: fluid flow (pore scale), heat transfer (pore scale), and chemical reactions and heat transfer (particle scale). Note that the dimensionless numbers definitions presented here may vary depending on the length scale used. See Symbols and Nomenclature for variable definitions. More details on each dimensionless number can be found in the references presented in the table.

The modified formulation proposed by Frank-Kamenetskii [232] that allows for a high Biot number \( (Bi) \) is potentially more appropriate for the analysis of smouldering ignition. Nevertheless, the formulation by Frank-Kamenetskii is also limited in that (i) it proposes a purely thermal analysis that ignores mass transfer limitations, and (ii) heat losses from the ignition region normally only include conduction through the porous medium. Therefore, convection through the porous medium and thermal non-equilibrium between solid and gas phase cannot be resolved by a Frank-Kamenetskii formulation. Furthermore, the temperature at the surface of the porous medium and the ambient atmosphere have to be equal which tends to only be the case for \( Bi > 10 \).

For smouldering, these assumptions are not generally valid. Thomas [233] introduced intermediate Biot numbers to account for a different boundary condition. Thomas added a simple but more realistic physical treatment which considers conduction through the solid and convective heat loss from the surface, i.e., a Robin boundary condition type [234, 235]. This approach adds some relevant physics, nevertheless it does not fully address the complexity of heat and mass transfer associated to smouldering.

The objective of all these analyses was to extract a critical parameter for ignition. Table 4 summarizes the different critical parameters developed in the literature. As can be seen from the table, the critical parameter for ignition can be expressed in various ways (i.e., the critical rate of heat generation, critical environmental temperature, and critical dimensionless rate of heating).

The variety of forms for the critical ignition parameters reflects different representations of the conditions leading to ignition. While different in form, they all deliver a common parameter – a critical temperature – that reflects a local energy balance at the reaction. Thus, the critical parameters presented in Table 4 are also valid for a smouldering reaction. However, the conditions that lead to that critical parameter are limited. None of the formulations stemming from a local energy balance are capable of describing the effect that thermal and species transport between gas and solid phases in the porous medium can have on the reaction.
The identification of the roles of global and local energy balances on the onset of *self-sustained smouldering propagation* makes evident the need for a much more precise understanding of heat and mass transfer processes within porous media. Existing ignition criteria presented in Table 4 remain valid for the ignition of *self-sustained smouldering*, nevertheless these criteria are only relevant to *self-sustained smouldering propagation* if heat and mass transfer processes pertaining to the global energy balance are properly quantified. Recent contributions on the actual experimental and numerical status of ignition research can be found in [236] and [209, 237].
Table 4. Critical parameters referent to theoretical ignition studies.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Assumption</th>
<th>System Equations $^a$</th>
<th>Critical condition $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[207, 210, 213, 224]</td>
<td>- External thermal resistance only.</td>
<td>$\delta = \theta e^{-\theta}$</td>
<td>$Q_{cr} = Ae^{-\frac{E}{R_g T_{cr}}} = \frac{R_g T_{cr} U A_s}{E V e^s}$</td>
</tr>
<tr>
<td></td>
<td>- Small volume of solid.</td>
<td>$\theta = \frac{E}{R_g T_0^2} (T - T_0)$</td>
<td>$\log \left( \frac{T_{cr}^2 A_s}{V} \right) = c_1 - c_2 \frac{1}{T_{cr}}$, where $c_1$ and $c_2$ are constants.</td>
</tr>
<tr>
<td></td>
<td>- Single Arrhenius expression.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Zero-order reaction.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Oxidation occurs at low ambient temperatures, at negligible rate.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- No reactant consumption.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- $Bi &lt; 1$.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td>[232, 238, 239]</td>
<td>- Internal thermal resistance only.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Symmetrical heating.</td>
<td>$\theta = \frac{E}{R_g T_0^2} (T - T_0)$</td>
<td>$\log \left( \frac{T_{cr}^2 A_s}{V} \right) = c_1 - c_2 \frac{1}{T_{cr}}$, where $c_1$ and $c_2$ are constants.</td>
</tr>
<tr>
<td></td>
<td>- Single Arrhenius expression.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Zero-order reaction.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- No reactant consumption.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- $Bi &gt; 1$.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Constant thermal properties.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- $ln \left( \frac{E A \Delta H [Y_0]^n}{k R_g} \right)$ is constant.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td>[228, 233]</td>
<td>- Both internal and external thermal resistance.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Zero-order reaction.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Symmetrical heating.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Absolute reference temperature.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- $Bi \sim 1$.</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- For slab, $\lambda=1$:</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\theta = \ln A - 2 \ln \cosh \left[ z \sqrt{\frac{\delta c_1}{2}} + c_2 \right]$</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\ln \delta = \ln \left( \frac{2D_\delta}{\cosh^2 D_\delta} \right)$</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha = \frac{D_{cr} \sinh D_{cr} \cosh D_{cr} + D_{cr}^2}{\left(1 - D_{cr} \tanh D_{cr}\right) \cosh^2 D_{cr}}$</td>
<td>$\delta = \left( \frac{E A V}{R_g T_0^2} U A_s \right) e^{-\frac{E}{R_g T_0}}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ See Symbols and Nomenclature for variable definitions
3.1.2. Experimental Studies of Ignition

Most experimental studies on smouldering focus on characterizing the reaction’s propagation. Nevertheless, before propagation is attained, ignition has to be achieved. For this purpose, detailed protocols have been described in the literature. These protocols reflect the need to achieve a positive local energy balance at the reaction so that self-sustained smouldering can be attained, nevertheless, it has also been recognized, while not explicitly, that the overall energy input also needs to be sufficient to initiate the self-sustained propagation of the smouldering reaction.

Fig. 13 summarizes the main experimental ignition protocols used in the literature. In Fig. 13a, the radiation source is placed a few centimetres above the fuel surface. This setup is similar to the cone heater used in [38, 240]. The radiation source is an electrical thermal resistance arranged in a conical shape so that a calibrated amount of radiative energy (kW m⁻²) can be supplied to the surface of the fuel. Typically, the external heater irradiates between 10 kW m⁻² and 70 kW m⁻² [48] but for materials such as polyurethane, heat fluxes as low as 2-10 kW m⁻² have been reported [241]. The configuration shown in Fig. 13a corresponds to a radiative flux traversing a semi-transparent medium (i.e., quartz window) used to seal the top of the reactor to allow for a downward airflow. In this configuration, the surface absorbs most of the radiation because typical porous media associated to smouldering have small radiative extinction depths. In-depth radiation is neglected at the surface and the heat input is treated purely as a boundary condition. Heat is then transferred inwards by means of conduction, radiation between the pores and convection. Any radiative transfer from the external source is treated in this manner and as a result the rate of in-depth heat transfer is limited by the surface temperature.

Once the reaction starts, the reaction zone rapidly becomes the hottest region in the porous medium, and therefore becomes the source from which heat is transferred to other regions. To attain a positive energy balance at the reaction front it is necessary to reduce heat transfer to regions that are not in the propagation path and maximize high temperatures along the bed depth. Studies indicate that the location of the reaction relative to the boundaries was critical to achieve ignition [144]. The lower bound of the ignition window is therefore defined by attaining a positive energy balance at the initial location of the reaction front. The other parameters influencing temperatures along the bed depth and the potential of radiation as an ignition source are the properties of the fuel bed such as porosity, effective thermal inertia ($k\rho C_p$), particle diameter and solid-to-fluid
conductivity ratio [242-246]. This approach implicitly reflects the need for a positive global energy balance.

To understand ignition, it is necessary to evaluate the energy balance at the reaction zone. This requires a variety of simplifications. A common assumption is to consider an overall thermal conductivity resulting from the local thermal equilibrium of solid and gas. As established by Nield and Bejan [79], if heat conduction in the solid and fluid phases occurs in parallel, the effective thermal conductivity of a porous medium $k_{\text{eff}}$ is the weighted arithmetic mean of the conductivities $k_s$ and $k_g$: $k_{\text{eff}} = (1 - \phi)k_s + \phi k_g$. Farrag et al. [247] shows experimentally that temperature has an effect on the effective thermal conductivity of the porous media. Thus, Farrag et al. [247] extends the definition of the effective thermal conductivity to a function of temperature. Convective flows will inevitably exist in the porous medium, nevertheless, it has generally been considered that they are sufficiently small to maintain a thermal equilibrium framework and therefore to account for them only a correction to the effective thermal conductivity is necessary. In a similar manner radiation between pores has been approximated by means of an effective thermal conductivity. Thus, the contribution of convection and radiation between the pores to the effective thermal conductivity is assumed to take an additive form ($k_{\text{eff}} = k_{\text{cond}} + k_{\text{conv}} + k_{\text{rad}}$).

In most experimental studies, the flow rates and heating rates are set in such a manner that these conditions are preserved and the evolution of the temperature during the ignition period can be described by means of a purely conductive approximation.

A complicating aspect of smouldering ignition is that it has an upper ignition bound defined by flaming. The upper bound of the ignition window is defined by a very different set of parameters and is very much dependent on the characteristics of the combustible material. Very few studies have explored this limit, therefore it is not possible to provide a general description of this upper bound; nevertheless, it is clear that in most cases as the heat flux increases, melting and/or gasification will be promoted leading to flaming as opposed to smouldering [218]. In the case of some solid porous fuels, melting eliminates the porous structure promoting flaming ignition. In a similar manner for CFIPM’s, a high heat flux accelerates gasification of the combustible material promoting ignition in the gas phase. Given that the processes that define the upper limits of radiative heating are material dependent, it is not possible to define bounds that apply in a universal...
manner. Nevertheless, the upper bounds for the ignition source for smouldering have been
explored by several authors [28, 60, 241, 248-253] mostly for polyurethane foams [241, 252, 253].

Practical approaches have been used to attain the conditions described above. In Fig. 13b, ignition
can be achieved by an embedded conduction source [47, 48, 50, 52, 56, 59, 62, 152, 246, 254,
255], placed between an inert porous bed and a bed of fuel that undergoes ignition. The objective
is to increase the temperature of the heater beyond the ignition temperature of the primary fuel
while preventing its flaming. Thermal equilibrium and an effective thermal conductivity remain
the basic assumptions used to analyze this ignition protocol. It is noted that when the bed is
comprised of a condensed fuel in an inert porous medium (where fuel is not exposed to the surface),
then flaming is not possible since the critical flame diameter is greater than the pore size.

To overcome the limitations of radiative ignition and to carry heat to greater bed depth, the air
supply can be heated [38, 49, 60, 61] (Fig. 13c). In this case, heat transfer relies on thermal non-
equilibrium and is strongly influenced by the characteristics of the porous medium. Some
experimental studies have used flames as a source of heat (Fig. 13c) [45, 256]. While ignition of
certain fuels can be achieved by impinging a flame, a flame increases the temperature at the
impingement point beyond the conditions that promote flaming of the combustible material.

Furthermore, the combustion products from the flame have low oxygen concentration, thus the
flame develops a region where the reduction of oxygen supply promotes pyrolysis over the onset
of smouldering reactions. Therefore, the generation of high temperatures and low oxygen
concentration regions make smouldering ignition by means of a flame very difficult to control and
not viable for most materials. A common procedure is to combine the heat of the flame with a
convective flow, but this, in essence, is the same process as igniting by heated air. No detailed
theoretical framework has been used to quantify these types of ignition protocols.

It is important to emphasize that the detailed characterization of heat and mass transfer processes
during the ignition period has not been fully achieved for any of these studies. Thus the need for
simplifications that make the analysis consistent with the detail of the experimental
characterization.
In summary, experimental ignition protocols for *self-sustained smouldering propagation* intuitively aim to achieve common objectives: (i) attain a critical condition that delivers a positive local energy balance (*self-sustained smouldering*); (ii) ensure this critical condition is achieved despite the influence of boundaries and global thermal conditions within the reactor (*positive global energy balance*); (iii) maintain temperature below characteristic values that promote homogeneous over heterogeneous combustion; (iv) deliver local conditions (i.e., temperature and oxygen concentrations) that favor exothermic oxidation over endothermic pyrolysis. Note that these points are defined by the characteristics of the ignition region. Therefore, the characteristics of *self-sustaining smouldering propagation* might, despite all efforts, be independent of the ignition method once the front is outside the distance of influence of the igniter and the oxidation reaction dominates the energy balance.

### 3.2. Extinction

As the uses of smouldering vary, critical conditions that govern self-sustained smouldering and propagation are becoming more relevant. For example, smouldering extinction, which was once of primary interest to characterize smouldering as a fire safety hazard, is now a key condition that defines the economic success of smouldering as a new technology for the destruction or conversion to energy of low calorific fuels. While smouldering ignition has received very little theoretical
attention, extinction has been more carefully addressed. In the following section, the fundamentals of extinction are explored through classical theories and additional insights are provided by experimental studies of extinction. Subsequently, Section 4.7 considers extinction from the perspective of a local and global energy balance.

3.2.1. Fundamental Principles of Extinction

To explain the state of smouldering extinction theory it is first useful to introduce key concepts developed for describing flaming extinction because many concepts are repurposed. The topic of flame extinction has been extensively studied [257-260] and providing a comprehensive review is beyond the scope of this study; only those studies relevant to smouldering will be presented here.

Ultimately, extinction results from a local energy imbalance, where energy is lost from the local reaction zone faster than the energy can be released from exothermic, chemical reactions. This causes the chemical processes driving combustion to cease. Extending from Semenov’s ignition criterion [224], extinction conditions can be attained when the Damköhler number decreases below a critical value. Liñán [179] and Fendell [261] first highlighted the use of Damköhler number to describe extinction and ignition in a counter-flow diffusion flame. Their theory draws heavily from the structure of diffusion flames and solutions obtained require the use of high-activation energy asymptotic methods [262, 263]. The same approach was used by Dosanjh et al. [75] to study smouldering extinction so it is helpful to briefly review the analysis by Liñán [179].

The analysis aims at obtaining a critical Damköhler number that serves to characterize ignition and extinction. Assuming a one-step Arrhenius reaction that is first-order with respect to the fuel and oxidizer, the dimensional temperature form of the steady-state energy equation is obtained:

\[ k \frac{d^2 T}{dz^2} - \rho C_p \frac{dT}{dz} = -\Delta H \rho A Y_{O_2} Y_F \exp \left( \frac{-E}{R_g T} \right) \]  

(22)

where \( T, z, Y_{O_2}, \) and \( Y_F \) are dimensional temperature, length, oxidizer mass fraction, and fuel mass fraction, respectively. \( E, R_g, A, \Delta H, C_p, \rho, k \) are the dimensional activation energy, ideal gas constant, pre-exponential factor, heat released per mass of fuel, the specific heat capacity, density, and thermal conductivity, respectively. Following derivations detailed in Chung et al. [264] and Fendell [261], and using the Schwab-Zeldovich procedure with equal diffusivities of mass and heat \((Le = 1)\), the non-dimensional temperature distribution becomes:
\[
\frac{d^2 \tilde{T}}{d \tilde{z}^2} + \tilde{z} \frac{d \tilde{T}}{d \tilde{z}} = -D \alpha Y_{O_2} \tilde{Y}_F \exp \left(-\frac{E}{\tilde{T}}\right)
\]  \hspace{1cm} (23)

where \( \tilde{T} \) is the non-dimensional temperature normalized by \( \Delta H/C_p Y_{F-\infty} \) and distance from the stagnation plane, \( \tilde{z} \), is made non-dimensional with the characteristic mixing length, \( \sqrt{D_g/a} \). \( D_g \) is the mass diffusion coefficient, \( a \) is the ratio between the velocity at the nozzle and the distance between the nozzle and the stagnation plane normal to the mixing layer (i.e., the strain rate). \( Y_{F-\infty} \) is the mass fraction of fuel in the fuel stream, \( v \) is the stoichiometric mass ratio of oxidizer to fuel, \( \tilde{E} \) is the non-dimensional activation energy, \( \tilde{Y}_{O_2} \) and \( \tilde{Y}_F \) are the oxidizer and fuel mass fractions divided by \( v Y_{F-\infty} \) and \( Y_{F-\infty} \), respectively. The Damköhler number is taken as:

\[
Da = A v Y_{F-\infty}/a
\]  \hspace{1cm} (24)

By taking the boundary conditions \( \tilde{T} = \tilde{T}_{\infty} \) at \( \tilde{z} \rightarrow \infty \) (oxidizer entrance), and \( \tilde{T} = \tilde{T}_{-\infty} \) at \( \tilde{z} \rightarrow -\infty \) (fuel entrance), and re-writing Eq. (23) as a function of the mixture fraction, \( x \), Liñán and Williams [265] derive the following distribution for the mixture fraction:

\[
\chi = \left(\frac{1}{2}\right) \text{erfc}(\tilde{z}/\sqrt{2})
\]  \hspace{1cm} (25)

where \( \text{erfc} \) is the complementary error function. This leads to Eq. (23) being re-written as:

\[
\frac{d^2 \tilde{T}}{d \chi^2} = -2\pi \exp \left(\tilde{z}^2\right)D \tilde{Y}_{O_2} \tilde{Y}_F \exp \left(-\tilde{E}/\tilde{T}\right)
\]  \hspace{1cm} (26)

where the new boundary conditions become \( \tilde{T} = \tilde{T}_{\infty} \) at \( x = 0 \) and \( \tilde{T} = \tilde{T}_{-\infty} - \theta \) at \( x = 1 \). Here, \( \theta \) is \( (\tilde{T}_{\infty} - \tilde{T}_{-\infty}) \). Liñán [179] then obtains the asymptotic solutions for four possible regimes: (i) nearly frozen ignition, (ii) unstable, partial burning where both reactants cross the reaction zone, (iii) premixed flame where only one reactant leaks through the reaction zone, and (iv) near equilibrium, diffusion controlled. Solutions from these regimes illustrate the characteristic S-curve [179] that explains extinction conditions in diffusion flames at a minimum Damköhler number and temperature.

A number of theoretical studies have built from this method to understand smouldering extinction starting with Dosanjh et al. [75]. These authors used a very similar analysis to describe an opposed smouldering front in one-dimension that is steady along the frame of reference travelling with the
reaction zone. This is just an extension of the analysis developed by Liñán [179] when describing a laminar premixed flame. Furthermore, it assumes the smoulder reaction can be described with a finite-rate, one-step reaction [262]. The conceptual form of the model is presented in Fig. 14, where the comparison to a premixed flame is quite clear, as the reactants are shown to enter the reaction zone from the bottom to the top (as the reaction is travelling downward). The parallel between a porous matrix and a premixed flame inevitably invokes the assumption of thermal equilibrium between phases.

![Conceptual model for the development of analytical solutions describing smouldering extinction (adapted from [75]).](image)

Note that the proposed reactant transport for this model does not address the diffusion of oxidant through the pore space and into the surface of the fuel. Therefore, the scale of the conceptual model proposed may be inappropriately large, and a global phenomenon (the extinction of self-sustained smouldering propagation) may be confused with the local phenomenon (extinction of self-sustained smouldering). Nevertheless, the analysis provides useful insight into extinction and lays the foundation for smouldering extinction theories.
By integrating the energy equation over the reaction zone and assuming all oxygen is consumed and diffusive heat and mass transport is negligible (i.e., convective transport dominates) the energy equation can be rearranged to express the smouldering velocity \( v_f \):

\[
 v_f = \frac{\Delta H \dot{m}_{O_2}''}{(1 - \phi)\rho_{s,0} C_{p,eff} (T_{\text{max}} - T_0)} - \frac{\phi \rho_{g,0} u_{g,0}}{(1 - \phi)\rho_{s,0}}
\]  

(27)

where \( \Delta H \) is the heat released per mass of oxygen consumed, \( \dot{m}_{O_2}'' \) is the incoming mass flux of oxygen, \( \phi \) is the porosity, \( C_{p,eff} \) is the effective specific heat capacity (a constant using the mass ratios of solid and gas), \( u_{g,0} \) is the initial gas velocity, \( \rho_{g,0} \) is the initial gas density, \( \rho_{s,0} \) is the initial solid density, \( T_{\text{max}} \) is the peak temperature, and \( T_0 \) is the ambient temperature, respectively. This expression can be made non-dimensional by defining a characteristic smouldering velocity as:

\[
 \frac{v_f}{\bar{v}_f} = \frac{\Delta H \dot{m}_{O_2}''}{(1 - \phi)\rho_{s,0} C_{p,eff} T_0}
\]  

(28)

The non-dimensional expression for smouldering velocity is now:

\[
 \bar{v}_f = \frac{1}{\theta} - \frac{1}{\Delta H}
\]  

(29)

where \( \theta \) is the non-dimensional temperature difference defined as:

\[
 \theta = \frac{(T_{\text{max}} - T_0)}{T_0}
\]  

(30)

and \( \Delta H \) is the non-dimensional measure of heat released in the reaction zone defined as:

\[
 \Delta H = \frac{\Delta H Y_{O_2,0}}{C_{p,eff} T_0}
\]  

(31)

where \( Y_{O_2,0} \) is the initial mass fraction of oxygen in the gas. For extinction, the smouldering velocity can be set to 0, which implies \( \theta = \Delta H \). This can be rearranged to obtain the extinction condition:

\[
 \{Decker, 2004 \#237\} Y_{O_2,0} \leq \frac{C_{p,eff} (T_{\text{max}} - T_0)}{\Delta H}
\]  

(32)
This implies that, at extinction, all the energy from the reaction is less than that necessary to heat the incoming reactants. This provides a reasonable criterion to describe extinction.

Schult et al. [64] extended this analysis, again using high-activation energy asymptotic methods, by including heterogeneous reaction rates and removing the assumptions regarding the small degree of conversion of solid and that the average heat capacity of the reactants remains constant. The physical condition for extinction here is again identified as the heat released being less than the heat necessary to bring the incoming reactants to a smouldering combustion temperature. Although these models are adiabatic, additional heat loss terms (e.g., into the environment, phase change of fuel, pyrolysis effects, etc.) could be included. It is also acknowledged that, as local thermal equilibrium is assumed, a multi-phase temperature description would also be helpful to improve the accuracy and provide deeper physical meaning. This analysis expanded the understanding of governing extinction mechanisms under solid and gas deficient cases and proposed additional key critical parameters: initial oxygen concentration, stoichiometric coefficient, gas heat capacity, activation energy, heat released per mass of oxygen reacted, initial temperature, and the product of initial heat capacity with density. The results from this analysis matched well with experiments performed by Ohlemiller and Lucca [180] but did not match extinction results from Torero et al. [144]. It is difficult to fully resolve the specific assumptions that may be responsible for this discrepancy, but it certainly suggests that conditions governing the smouldering extinction limits were not consistent between the experimental result and the mathematical representation. An important difference between the definition of extinction by Ohlemiller and Lucca [180] and that of Torero et al. [144] is that the latter considered extinction in the context of the spatial progression of the smouldering front within the reactor (self-sustained smouldering propagation). Ohlemiller and Lucca’s [180] approach is instead focused on a terminal condition (self-sustained smouldering). The analysis of Schult et al. [64] refers to the ultimate extinction of self-sustained smouldering thus is more suitable to the results of Ohlemiller and Lucca [180]. Decker and Schult [266] directly expand upon this work and further investigated the dynamic effects of a smoulder wave near extinction. Lozinski and Buckmaster [177] also revisited Dosanjh et al. [75]’s model and provides extra insight into the use of a temperature-dependent endothermic pyrolysis term, as well as the use of a classical heat loss term. However, the solutions still required many simplifications, in particular the condition of thermal equilibrium remains
throughout all these studies. Thus the differences between global and local energy balances cannot
be fully accounted in these analyses, thus comparison with experiments remains limited.

Repurposed homogeneous combustion theory has led to reasonable simplifications and valuable
solutions using high activation energy asymptotic techniques that provide adequate
phenomenological explanations for self-sustained smouldering extinction. Nevertheless, there
remains a significant discrepancy between smouldering extinction theory and results from
experiments. Importantly, the initial conceptual model and resulting set of governing equations
and assumptions appear to require more attention, as ad-hoc approaches that build from Dosanjh
et al. [75]’s original analysis still seem to exclude phenomena that govern the extinction of self-
sustained smouldering propagation. Therefore, there is still a gap in the literature and room for a
harmonized explanation for extinction.

3.2.2. Experimental Studies of Extinction

Only a few experimental studies have addressed smouldering extinction and in most cases the
extinction process has just been characterized as a necessary condition to avoid fire spread [144,
222, 223, 267, 268]. Earlier studies established air flow limits (oxygen-limited conditions) that
resulted in endothermic pyrolysis reactions becoming dominant over exothermic oxidation [268].
This results in smouldering sustained by the heat of the igniter, so as soon as the igniter is turned
off, extinction follows. While no detailed description of the sequence of events leading to
extinction was provided, these results provide evidence of the difference between self-sustained
smouldering and self-sustained smouldering propagation.

The progression towards extinction (limits of self-sustained smouldering propagation) was not
discussed until the solid porous fuel studies by Torero et al. [144] where smouldering fronts were
ignited, initiated propagation but eventually drifted towards extinction. In Torero et al. [144], the
effects of buoyancy in opposed smouldering under downward and upward configurations were
investigated. In downward opposed smouldering, air flows along the column’s cold walls towards
the reaction zone, reaching the virgin fuel region. Since the virgin fuel has relatively low
permeability, air returns and moves upward along the center-line with the forced air. This excess
of air enhances the reaction front providing more oxygen mass flux, but also can cool it, leading
to extinction if the reaction is already weak. In upwards opposed smouldering, extinction occurs
due to buoyant flows that oppose and partially cancel the air flux. After extinction, residual char
is still oxidized by the remaining oxygen in the system, especially near the igniter where
temperatures are high. These effects of buoyancy are relevant primarily to solid porous fuel
systems.

For forward smouldering of condensed fuels in inert porous systems, it has been shown that
progress towards extinction looks similar, regardless if caused by low air flux, low fuel
concentration, very low oxygen content, low fuel energy content, or high heat losses [81]. Each of
these either reduces the energy generated or increases the energy lost, such that the energy balance
becomes negative.

Experimental studies support these observations. For example, heat losses to the perimeter of the
reactor were studied and quantified by [38, 80, 223]. Bar-Ilan et al. [223] quantified the losses by
the identification of a minimum reactor size necessary to sustain one-dimensional smouldering
propagation. Zanoni et al. [80] found that 28-52% of the total energy in a laboratory column
smouldering system was lost to the surroundings, agreeing with [38, 129]. Such losses reduce the
amount of energy that can be transferred forward, potentially leading to extinction.

Studies have demonstrated that in CFIPM systems fuel concentrations less than approximately 3 -
5 g fuel per kg of inert porous media [53]. Studies have further shown that local Darcy air fluxes
less than approximately 0.5 cm s\(^{-1}\) in CFIPM systems can lead to extinction [47, 81, 151, 255,
269]. In opposed smouldering for PSF systems, extinction by convective cooling at high air fluxes
was found by [144, 222]. Under oxygen-limited conditions, additional oxygen supply by the high
air flux creates additional heat generation, which offsets the heat removed as the gas passes through
the reaction front. Under fuel-limited conditions, cold air passes through the hot sample, resulting
in partial consumption of the oxygen and resulting in a decrease of the peak temperature. The
reduced oxygen environment favored pyrolysis and lead to extinction [76, 123, 151]. In CFIPM
systems, convective cooling only occurs at extremely high air fluxes (e.g., above 30 cm s\(^{-1}\)) (further
detailed in Section 4.4).

Moisture content (MC) of the fuel is also a heat sink and thus affects the energy balance critical to
extinction. A “critical MC” is defined as a practical extinction limit in which self-sustaining
smouldering cannot be achieved. The concept of a critical MC is often discussed with respect to
the smouldering of peat [16, 108, 109, 201, 202, 270]. There remains an opportunity for further
research to provide a robust mechanism to fully explain the role of moisture content in smouldering propagation and smouldering extinction.

The study by Torero et al. [144] defined a methodology that enabled looking at the evolution of the smouldering reaction as it progresses through the reaction front. Only this new approach allowed to experimentally separate the effect of local and global energy balances in the extinction of a self-sustained smouldering reaction. Furthermore, this methodology allowed to differentiate extinction of self-sustained smouldering from the arrest of self-sustained smouldering propagation.

3.3. Transition to Flaming

Transition from smouldering to flaming combustion is a process that is relevant only to solid porous fuel systems. Systems containing condensed fuels in inert porous media cannot experience transition to flaming within the matrix. Flaming is possible under some circumstances when the reaction approaches an open boundary with a semi-volatile fuel present in the adjacent matrix. However, all transition to flaming research focuses on PSF systems, where this event poses a serious fire hazard, and thus is the focus of this section.

The basic principles behind this process were first discussed by Ohlemiller [222] and later reviewed by Santoso et al. [271]. The former study predates most of the studies that look at the evolution in space and time from smouldering towards flaming and the latter focuses on a phenomenological description focused on the transition from smouldering to flaming in wildfires. Santoso et al. [271] also provide a detailed review of other transition to flaming studies also discussed here. This paper discusses transition from smouldering to flaming for completeness and to establish existing evidence of the importance of the local and global energy balances. Nevertheless, for a detailed list of all studies devoted to this matter the reader should consult Santoso et al. [271].

In a similar manner to ignition and extinction, transition to flaming is a process that is influenced by the different thermal time scales; thus, it needs to be studied employing local thermal non-equilibrium conditions [161]. There are very few studies that systematically study transition to flaming [161, 222, 267, 272-275]. Tse et al. [272] established that transition to flaming is ultimately driven by an increase in the local energy supply that favours gasification over
heterogeneous combustion. Nevertheless, the conditions that lead to this increased energy release are dominated by changes in the nature of the porous matrix that affect the transport of oxidizer to the reaction zone. The observations by Tse et al. [272] therefore only apply to materials, such as polyurethane, where consumption of the fuel changes the morphology of the porous matrix.

Forward smouldering in porous solid fuels (i.e., reactive porous media) was considered a precursor of transition to flaming [272, 273]. Literature shows four possible factors affecting the transition to flaming under either natural or forced air forward smouldering: i) strong secondary char oxidation behind the front, ii) acceleration of the smouldering front velocity, iii) increase of oxygen supply, and iv) increase in sample size. Smouldering of reactive porous matrices typically leaves unburnt char (highly permeable matrix with large pore diameters) behind the front due to oxygen-limited conditions and heat losses. Residual char remains as an insulating material [180, 221, 222]. Under specific conditions, pyrolysis gases might circulate in convective currents inside the large pores within this residual char [272]. When air reaches the residual char region, char oxidation occurs, and if energetic enough it can ignite the pyrolysis gases (if flammability limits and sufficient heat are attained [274]) that might be circulating in the large pores, causing the transition to flaming [143, 180, 219, 222, 272-274, 276]. Note that the formation of large pores is a necessary but not a sufficient condition for transition to flaming, since large pores were found in flaming and non-flaming conditions [273].

Bar-Ilan et al. [276] suggested that high front velocities might cause transition to flaming. On the other hand, Tse et al. [272] and Putzeys et al. [273] showed that the front velocity sometimes decreases as transition to flaming is approaching, indicating that an increase in the front velocity is not the primary cause of transition to flaming. Furthermore, the front velocity is a function of multiple factors such as the location of oxygen consumption. Transition to flaming was observed to occur as the higher temperature char oxidation was enhanced. The enhanced char oxidation consumes a larger fraction of the oxygen, which in turn has the potential to slow down the smouldering reaction [272].

Large oxygen concentrations (>30%) are also suggested as a cause of transition to flaming [117, 273, 274]. The increase in oxygen concentration increases the reaction rate of the char oxidation, consequently increasing the heat release rate and local temperatures [142, 273, 276]. Note that high air fluxes may cause the same effect. However, although an increase in air flux will enhance
the oxygen mass flux, high air fluxes may decrease the front temperature by convective heat
transfer [274].

Finally, large samples were observed also as a condition necessary for transition to flaming. In
small samples, heat losses dominate and extinction occurs. However, small samples can transition
to flaming for high oxygen concentrations [272].

The limited literature on transition to flaming does not allow fully establishing all the variables
involved in this process. Nevertheless, it is clear that the interplay between a global energy balance
and local heat exchange determines whether the conditions necessary to shift from a heterogeneous
to a homogeneous reaction can be attained. As discussed for propagation, ignition and extinction,
the global energy balance provides an essential component of the local conditions at the reaction
zone. For transition to flaming, the reaction zone does not seem to be the smouldering front but
the char oxidation front. Given the importance of this phenomenon for fire safety, this is an issue
that needs to receive much greater attention.

4.0 General Conceptual Model of Smouldering Propagation

In this section, the goal is to provide a summary of key elements of a conceptual model of
smouldering propagation. Smouldering propagation, as outlined in Section 2.0, is the result of heat
and mass transfer processes integrated in space and time at the global (i.e., system, bed) scale. The
integral of these processes, in conjunction with boundary conditions, such as heat loss, provide a
net energy balance that evolves in time and enables the propagation of the reaction. The overall
energy balance serves to define a local energy balance at the reaction zone, so at any given time,
the smouldering reaction may be robust and self-sustaining, weak and self-sustaining, declining,
or extinguishing. Further details about such an analysis are given in Section 4.7.

The key parameters controlling the nature of the smouldering process are the fuel and the nature
of the heat and mass transfer processes to and away from the reaction. As indicated in Section 1.0
(Introduction), there are two systems of primary interest: porous solid fuels (e.g., polyurethane
foam, coal, and tobacco) and condensed-phase fuels (solid, liquid, sludge) embedded in an inert
porous matrix (e.g., oil shale, tar-contaminated soil, engineered mixtures of organic material and
sand). In the discussion below, key common elements between these two types of systems are
identified, as well as significant differences between them. Furthermore, these will be discussed in the context of specific characteristics of the heat transfer processes.

4.1 Fuel Bed Characteristics

Smouldering is a heterogeneous combustion reaction, with oxygen (gas) penetrating the surface of the combustible material (solid). Smouldering requires the fuel to exist either as a porous medium itself or to be embedded within a porous medium. Porous solid fuels (PSF) (e.g., polyurethane foam, coal, and tobacco) provide a reactive porous medium. In contrast, Condensed fuels in inert porous media (CFIPM) constitute inert media (e.g., sand, soil, rock, metal or ceramic beads) containing solid, liquid or semi-solid fuel distributed in its pores and pore throats. Fig. 15, with examples of these two systems, demonstrates some similarities and also some clear differences between the two. The differences are quantified in Table 5.
Fig. 15. (a) X-ray tomography image of a polyester urethane foam (reprinted from [277] with permission of Elsevier) and (b) X-ray tomography image of sand with 12% gravimetric liquid content (right), with additional images to illustrate the solid and liquid phases separately (left and middle). The liquid shown is water but oil in dry sand would look similar. Sample is 3 mm in each dimension, with average grain diameter of 0.65 mm, porosity = 0.44, saturation (i.e., fraction of porosity filled with liquid) = 0.41 (reprinted from [278] with permission of American Society of Civil Engineers).
Table 5. Contrasting macroscopic properties of porous solid fuels and condensed fuels in inert porous media

<table>
<thead>
<tr>
<th>Property</th>
<th>Porous Solid Fuels (PSF)</th>
<th>Condensed Fuels in Inert Porous Media (CFIPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>carbon-based, reactive</td>
<td>Carbon-free, inert</td>
</tr>
<tr>
<td>Fuel</td>
<td>Solid</td>
<td>Solid, liquid, or sludge</td>
</tr>
<tr>
<td>Porosity</td>
<td>92-98% [78, 108, 111, 153, 279]</td>
<td>38-50% [47, 50, 150]</td>
</tr>
<tr>
<td>Saturation (fraction of the porosity occupied by fuel)</td>
<td>0%</td>
<td>3-100%</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>80 – 900 kg m⁻³</td>
<td>1200 – 2000 kg m⁻³</td>
</tr>
<tr>
<td>Fuel concentration (fraction of the bulk density that is fuel)</td>
<td>100%</td>
<td>3-50%</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>O[10⁻² W m⁻¹ K⁻¹] [76, 111, 280]</td>
<td>O[10⁻¹ W m⁻¹ K⁻¹] [281]</td>
</tr>
<tr>
<td>Volumetric heat capacity</td>
<td>O[10⁴ J m⁻³ K⁻¹] [76, 111, 153]</td>
<td>O[10⁶ J m⁻³ K⁻¹] [281]</td>
</tr>
<tr>
<td>Intrinsic permeability</td>
<td>O[10⁻⁷ to 10⁻¹¹ m²]</td>
<td>O[10⁻⁷ to 10⁻¹⁴ m²]</td>
</tr>
<tr>
<td>Fuel surface area for reaction</td>
<td>Relatively high</td>
<td>Relatively low</td>
</tr>
<tr>
<td>Mobility</td>
<td>None</td>
<td>Liquids may mobilize upon heating</td>
</tr>
</tbody>
</table>

Porous solid fuels, in comparison to condensed fuels in inert porous media, are relatively reactive, immobile materials that contain large pores. The large pores result in high surface area to volume ratios favouring the transport of reactants and products in and out of the reaction zone (e.g., Fig. 15a). The macroscopic properties of the bulk material include high porosity, high pore connectivity, high effective permeability to air, low thermal conductivity, and low volumetric heat capacity. If it is an anthropogenic material (e.g., foam, tobacco product) then it is likely very homogeneous at the bed scale. Since the matrix is reactive, fuel shrinkage is common, which may damage the integrity of the smouldering front under certain conditions. Moreover, smouldering of porous solid fuels typically leaves un-oxidized char behind that insulates the front against heat losses. Complete consumption of the char is generally prevented by enhanced heat losses induced by the transformation of the porous matrix. For porous solid fuels, the void fraction is large and air supply by natural convection is common, thus the reaction can often propagate in the absence of any forced flow (i.e., air naturally enters the porous fuel induced by a density difference between hot gases inside and cold gases outside the system and boundary layer flows [122, 219, 282-284]). Fig. 16 illustrates several common examples of PSF.
Fig. 16. Examples of porous solid fuels: (a) Polyurethane foam, (b) peat (reprinted from [3] with permission of Elsevier), (c) charcoal (retrieved from [285]), (d) tobacco (retrieved from [286]).

Condensed fuels in inert porous media provide contrasting properties. The fuel may (i) be embedded within the microporosity of the inert porous medium (e.g., pyrolyzed sugar within alumina particles [269]), (ii) exist as a thin liquid or solid coating of the inert media grains at low fuel concentrations (e.g., oil sands), (iii) may occupy a fraction of the porosity at higher concentrations (e.g., oil-contaminated soil, as in Fig. 17c), (iv) may entirely fill the porosity (e.g., oil-soaked insulation), or (v) may be at concentrations so high that the porosity is exceeded, the inert grains are expanded from a typical packing structure – perhaps losing direct contact with each other – and the total volume of the mixture is larger than the volume of the inert medium alone. The latter is possible, for example, when artificially mixing organic wastes with inert or organic media for waste treatment (e.g., [57]). Fig. 17 provides examples of the wide range of materials that are CFIPM.
Fig. 17. Examples of condensed fuels in inert porous media: (a) oil sands (retrieved from [287]), (b) oil shale (reprinted from [38] with permission of Elsevier), (c) oil-contaminated soil (photo courtesy of Savron Ltd.), and (d) pyrolyzed sugar within activated alumina particles (reprinted from [269] with permission of American Chemical Society).

In all of these cases except the last, shrinkage of the bed during smouldering does not occur. If the inert medium is quartz and was dry when exposed to the organic material, then the quartz is likely hydrophobic; however, if the quartz was initially wet then it is likely hydrophilic, with a thin layer of water between the fuel and the grain [288]. Therefore, the portion of the porosity not occupied by fuel may be air-filled or water-filled. The macroscopic properties include a relatively low effective air permeability (this is the product of the inert media intrinsic permeability and the relative permeability reduction associated with the fraction of porosity that is occupied). These systems also exhibit relatively low porosity, smaller average pore size and potentially wider distribution of pore sizes (function of grain size and grain size distribution). Moreover, they exhibit relatively high thermal conductivity, high volumetric heat capacity, and higher dry bulk density. The surface area to volume ratio of the fuel is less than PSF systems and is a function of fuel saturation [38]. In addition, liquid fuels are potentially mobile due to liquid phase hydraulic gradients, influenced by gas phase pneumatic gradients, and affected by temperature-induced viscosity reductions [50].
The characteristics of the porous matrix and the fuel have important implications for the relevant mass transfer, heat transfer, heat generating, and heat loss processes. Fig. 18 illustrates the key mass and heat transfer processes for PSF and CFIPM systems. The two types of systems have many processes in common, albeit their relative magnitude and importance may differ. For example, in both cases the heated fuel, the char and any ash will transfer heat to the walls (items 4, 9 and 14 in Fig. 18), heat will be transferred perpendicular to propagation (item 10) and heat will be transferred by conduction and radiation through the pores (items 3 and 7, respectively). However, there are certain mechanisms that will be present in one type of system but not the other. For example, the inert matrix will retain heat, thus heat losses from the heated bed behind the front will be important for CFIPM but not for PSF. The energy retained in the inert bed can enable combustion to continue until fuel is fully consumed in CFIPM while, in the case of PSF, heat losses often extinguish the reaction before the fuel has been completely consumed. Thus, PSF systems are likely to result in chars that will rapidly cool down and remain after smouldering. While this is possible for CFIPM’s, it is uncommon because the inert porous medium is a major heat reservoir. For the same reason, radial heat losses through the wall (item 9) are more significant for CFIPM than for PSF systems.
Fig. 18. Heat and mass transfer processes in smouldering of PSF and CFIPM (adapted from [289] and [290]).

The implications of these pore- and macro-scale properties on smouldering behaviour are many and important. As a first illustrative example, a reasonable assumption for PSF smouldering studies is that local thermal equilibrium (LTE) exists between the fuel and the air [111]. However, this is
not the case for CFIPM systems due to 

(i) the high contrast in thermal properties between the matrix and the air, (ii) the higher local air flow velocities and (iii) the potentially smaller surface to volume ratio. Thus, accounting for local thermal non-equilibrium (LTNE) might not be necessary for PSF but essential for CFIPM [246]. Zanoni et al. [152], employing a new LTNE correlation function [246] for CFIPM systems using sand, demonstrated a normalized average temperature difference as great as 36% between the air and solid at typical air flow rates for smouldering of bitumen in sand.

The role of intrinsic permeability provides a second illustrative example. The intrinsic permeability to air can range over 7 orders of magnitude in CFIPM systems (Table 5), and the effective permeability (i.e. additionally accounting for fuel saturation) expands that several orders of magnitude further – always towards lower values. Therefore, for CFIPM systems natural convection is insufficient to support smouldering in most instances. Rather, significant pressure gradients are required to deliver forced air flow at a sufficient oxygen mass flux to sustain smouldering. Heuristic studies have suggested local, macroscopic values of \( \sim 0.5 \text{ cm s}^{-1} \) Darcy air flux (volume of air per unit total cross-sectional area perpendicular to flow) are required to sustain smouldering of organic liquid-embedded in coarse sand at a pilot treatment scale [291]. Many examples of PSF fuel matrices have shown that as the smouldering front progresses through the sample the permeability can increase several orders of magnitude due to the transformations occurring within the porous matrix [219, 282]. The increase in permeability can enable significant buoyancy induced flows that can sustain or extinguish a smouldering reaction [220]. Thus, while peat (PSF) will smoulder indefinitely fueled by natural convection, leading to catastrophic peat forest fires [204], smouldering of tar-contaminated soil (CFIPM) will stop immediately when injected air flow is terminated [48]. Moreover, CFIPM systems will typically have a threshold of effective permeability below which insufficient oxygen can be delivered and thus smouldering is not possible; therefore, smouldering is not possible in clay. While elevated air flows are predicted to provide convective cooling of the reaction in PSF systems, this is not observed for CFIPM systems for all practical values of air flux (e.g., \( 1 – 10 \text{ cm s}^{-1} \)) [59, 81].

Other effects, while different in nature, appear in both PSF and CFIPM systems. Mobility of the fuel is one such process. Mobility of fuel can be a benefit or a drawback that appears in both PSF and CFIPM systems. Oil mobilization ahead of the smouldering front is intentional in fire flooding.
for enhanced oil recovery. It can also be a benefit for waste destruction for oil-contaminated soil if the liquid cascades downwards into the front, feeding continuous smouldering. Kinsman et al. [50] demonstrates this effect and provides a method to calculate the upwards air flow rate that will counter downwards mobility of liquid fuel. However, migrating fuel can also cause unusual behaviour such as pseudo-super-adiabatic effects in which peak temperatures climb and front velocities decrease [45]. In the case of PSFs, melting can result in liquid fuel migrating or the collapse of the porous matrix. The ultimate impact of fuel migration is uncertain nevertheless, several studies have reported phenomena such as pore clogging due to melting leading to extinction [82, 122, 221].

As illustrated by the above examples, the nature of the fuel matrix can result in behaviour that is common or unique to the characteristics of each particular fuel. Therefore, when analyzing the available data, it is important to extrapolate behaviour with caution because specific phenomena can manifest itself in different ways whether smouldering is occurring in the context of a PSF or a CFIPM.

4.2 Classic Framework

The complexity of the heat transfer processes requires simplifying the problem for study. The main simplification is to idealize the processes within the framework of a one-dimensional smouldering wave which can be further separated into two configurations: i) flow transfers heat away from the reaction towards the unburnt fuel (forward), and ii) flow transfers heat from the reaction towards the burnt region (opposed) (Fig. 19). The direction of the smouldering front relative to the air flux defines the configuration [3, 143, 180, 282].

In opposed (also known as ‘reverse’) smouldering (Fig. 19a), the direction of the smouldering front is in the opposite direction to the air flux [180]. Opposed smouldering typically occurs in conjunction with natural convection, in which air generally travels upwards through the cold virgin fuel and reaches a reaction front that is travelling downwards. Smouldering of a coal pile, can occur in a similar manner even when ignited at the bottom. In this case the supply of oxygen is determined by air ingress at the top and sides of the pile [292]. Since the air is cold, the smouldering front is cooled down to heat up the gas [222]. Once the air is heated and passed through the front, convective heat transfer is towards the burnt region, resulting in less heat being transferred in support of propagation. Opposed smouldering is common for non-engineered PSF systems.
Forward smouldering (Fig. 19b) is when both the front and air flux travel in the same direction [180]. Cold air flows through the burnt region, a portion of which is still hot, heating up the air. Convective heat transfer in the gas phase delivers energy to the front where oxygen is depleted, and energy is further gained, from the oxidation reaction. Convective heat transfer then deposits energy in the cold fuel/matrix ahead of the front, where it is stored and contributes to pre-heating and fuel pyrolysis. In this way, forward smouldering stores and recycles energy in a manner that supports the propagation of the smouldering wave. This energy efficiency means it is the configuration of choice for applied smouldering and CFIPM system. In fact, opposed smouldering is often impossible in such systems due to the inherent thermal mass and chemical properties which require the benefit of energy storage and recycling to be self-sustaining. The focus in the rest of this review is on forward smouldering, but many of the concepts are still relevant to opposed smouldering. Moreover, it is acknowledged that most real-world smouldering scenarios are multi-dimensional and that, in the cases where buoyancy is relevant, the flow field could result in simultaneous forward and opposed propagation [220]. Thus, this framework is used mostly for clarity but it is likely that most cases will include a combination of both forward and opposed propagation [143, 282].
Fig. 19. (a) Forward and (b) opposed smouldering propagation. Within the colours are labelled the form of the fuel (PSF or CFIPM) in the system.

4.3 Distribution of Temperature in Space

Smouldering studies have regularly used temperature as the main indicator for the net energy balance in the system. Thus, it is useful to identify different regions and processes according to their spatial distribution with respect to temperature. Fig. 20 represents a conceptual model of the vertical spatial distribution of temperature for a forward smouldering combustion reaction, depicted at a single time. The figure contrasts PSF and CFIPM systems and the corresponding changes in oxygen concentration, fuel concentration, and fuel composition. The figures further identify key regions, which will form the basis for the conceptual model of smouldering referred to throughout the rest of this manuscript.
Fig. 20. Conceptual model of a forward upward smouldering front. Within the colours are labelled the form of the fuel and Inert Porous Media (IPM) in the system. Within the temperature and oxygen profiles (depicted at a particular moment in time) are labelled the heat transfer regions. This schematic highlights the two extreme cases, illustrating only the main differences in driving forces.

In Fig. 20, the uppermost “Virgin Fuel” region is well ahead of the smouldering front and since it receives only cold (less than ~80°C) gas flow, the fuel is unaffected by the smouldering reaction and the region exhibits near-ambient temperature ($T_0$). However, volatilized hydrocarbons and water vapour arriving by convection will condense in this region, altering the composition and moisture content of the fuel/matrix. Moreover, evaporation of water and liquid compounds can occur due to gas flow.

In the “Preheating” region, between the Smouldering region and the Virgin Fuel region, the fuel/matrix is exposed to elevated temperatures (between ~80°C and ~500°C, fuel-dependent) transferred forward by convection and conduction. The air flowing through this region exhibits a reduced oxygen fraction ($Y_{O_2,f} = x\%$ in Fig. 20b) due to partial consumption in the oxidation reaction that precedes it. At high fuel concentrations and low oxygen mass fluxes, oxygen can be entirely consumed before entering this region ($Y_{O_2,f} = 0\%$ in Fig. 20b). The upper part of this region (temperatures between ~80°C and 220°C) is characterized by inert heating, including the
volatilization and boiling of light hydrocarbons and water. The lower part of this region (temperatures between ~220°C and 550°C) is dominated by assisted thermal degradation (see Section 2.0 Nomenclature). Most importantly, the significant energy transferred forward from below supports the generation of a solid porous char by endothermic pyrolysis.

The boundary between the “Preheating region” and the “Smouldering region” is characterized by the temperature exceeding the smouldering ignition temperature (e.g., $T_{ig} \sim 550^\circ$C) and an increasing oxygen concentration. In this region the char has exceeded the activation energy for exothermic oxidation and there is sufficient oxygen for oxidation to proceed. Temperatures rise dramatically in this region, with the reaction “front” coincident with the location of the maximum rate of energy release and the peak temperature ($T_{max}$) (e.g., ~700 – 1200°C). $T_{max}$ is primarily dependent on the type (energy content) and concentration of the fuel. The majority of oxygen consumption occurs in this region. Generally, the smouldering region is quite thin, on the order of mm [38, 152] to cm [50] for CFIPM, whereas this region can be thicker for PSF [76, 111], for which the local rates of energy release and storage are lower and thus the energy is more widely distributed. The boundary between the “Smouldering region” occurs when oxidation reactions no longer occur, but the reasons are different for CFIPM systems and PSF systems. For inert porous media systems that exhibit smouldering propagation, in which the energy storage and recycling is so high, this occurs where the fuel is eliminated from the bed (Fig. 21a). However, for porous solid fuels, in which a much higher fraction of the generated heat is lost, this occurs where the temperature falls below that required for exothermic oxidation. Thus, in the latter, residual char with some (pyrolyzed) organic content typically remains behind the front (Fig. 21b).
Fig. 21. Examples of (a) CFIPM: (left) sand contaminated with a liquid hydrocarbon before smouldering and (right) clean sand after smouldering (fuel was eliminated from the sand) – photo courtesy of Savron Ltd.; (b) polyurethane foam showing residual char after smouldering extinction (reprinted from [13] with permission of Elsevier).

After the “Smouldering region”, CFIPM systems exhibit a “Heat Storage” region not observed in PSF systems. The storage of heat in CFIPM systems is associated with the high-volume fraction of inert (mineral) content which exhibits a high heat capacity. No reactions occur beyond the “Smouldering region” and therefore the oxygen remains constant at the initial concentration ($Y_{O_2,0}$) delivered from the lower boundary. In the “Heat Storage region”, the rate of change of temperature depends primarily on radial heat losses [150, 152]. Radial losses depend, in turn on the surface area to volume ratio of the system. In laboratory column reactors, temperature decreases here can be large, while in larger constructed or field systems, the “Heat Storage region” can exhibit a nearly constant temperature plateau extending for considerable distance behind the smouldering front. The heat storage region plays an important role in the significant energy recycling and high energy efficiency of CFIPM systems.

The “Cooling region” completes the profile extending to ambient temperature at its lower boundary. It is characterized by a relatively rapid temperature decay, dominated by convective heat transfer from the hot bed to the incoming cold air.
4.4 Evolution of the Reaction in Space and Time

The entire heated profile, from “Virgin Fuel region” to “Cooling region”, propagates in space and evolves in time, as the distribution of energy in the smouldering system evolves. Fig. 22 illustrates a sequence of these profiles for smouldering propagation that is initially self-sustaining and then experiences a transition to extinction conditions. The “Preheating region” exhibits a relatively consistent rate of temperature increase, associated with the rate of forward heat transfer. If water was present, a plateau at $\leq 100^\circ$C [56] would be observed at the front end of the thermal front until all the water was removed.

The self-sustaining reaction in the “Smouldering region” exhibits repeating, consistent peak temperatures that necessarily results in temperature profiles crossing each other; this is characteristic of energy gains (i.e. heat generation) exceeding energy losses in combination with forward heat transfer (Fig. 22). The leading edge of the “Smouldering region”, identified by the steepest temperature rise in time (Fig. 20b), maintains an approximately constant velocity as long as (i) bed conditions (fuel concentration, intrinsic permeability, air flux, etc.) are constant, and (ii) the boiling front for water or volatile compounds remains distinct and ahead of the smouldering front. Such conditions are common for self-sustaining smouldering systems that are robust (i.e., the degree to which the reaction resists extinction; see Section 4.7 for further details). It is not uncommon, at least in CFIPM systems, for the heated profile to thicken with time (particularly thickening the “Heat Storage region”), indicating increased cumulative energy in the system. In these cases, the energy extracted by the air from the inert media and radial energy losses are less than the energy produced by the propagating front (Fig. 22). It is important to note that this is not necessarily accompanied by an increase in the maximum reaction temperature. This is because the thickness of the heated profile is a function of a global energy balance, while the reaction temperature is the result of local energy exchanges.

The illustrated transition from self-sustaining to extinction (Fig. 22) is a dramatic example of an evolution in space and time that reflects a reduction in the net energy balance to below zero. This could be due to any parameters resulting in an increase of the energy loss (e.g., increased heat loss, for example due to loss of insulation, or increased water content) or a reduction in the energy generation (e.g., reduced fuel concentration or reduced air flow rate). After the transition, the temperature profiles lose many of the distinctive features articulated above, and instead are
dominated by diminishing peak temperatures, more gradual temperature increases in the “Preheating region”, and reduced cross-over of successive curves.

Fig. 22. Smouldering propagation in (a) space and (b) time. Temperatures are shown along the axial centreline of a reactor. The presented trends apply to both PSF and CFIPM systems.

The behaviour of smouldering propagation is sensitive to a number of key input and boundary parameters. These have been explored in both experimental [47, 56, 59, 75, 118, 142, 144, 255, 269, 293-296] and modelling [7, 16, 75, 76, 108, 118-120, 122, 123, 129, 141, 148, 150, 151, 153, 157, 177, 223, 297, 298] studies. Fig. 23 attempts to summarize some of the sensitivity trends for temperature in time and in space. The sensitivity analysis for all the variables presented in Fig. 23 reflect the underlying, dominating influence of the energy balance: the greater the net positive
energy, the higher the peak temperature and the higher the front velocity. The different plots show
the different manifestations on the energy balance induced by changes to these variables. Fig 23
is not intended to be specific to CFIPM or PSF systems, but instead to be a generalization of trends
appropriate to both systems.

The top panels of Fig. 23 illustrate that Darcy velocity in the direction of the front propagation (air
flow rate per unit cross-sectional area) has a strong effect. Higher air flux leads to increased
oxidation rates that exceed the capacity of forward heat transfer resulting in an increase in peak
temperature at the reaction front. It also results in more stored energy and a shorter “Cooling
region” due to enhanced convective heat transfer. A clear result of increased Darcy velocity is an
increased smouldering propagation velocity. Darcy and smouldering velocities can be linearly
related. This is because convection of heat from the reaction to the unburnt fuel in the “Preheating
region” dominates [7, 47, 59, 75, 76, 81, 118-120, 122, 123, 129, 144, 151, 153, 157, 177, 255,
269, 293, 297]; see example in Fig. 24 [59]. Fig. 24 demonstrates that at very high Darcy velocities
(i.e., greater than 30 cm s\(^{-1}\)), convective cooling will start to deliver a decrease in the peak
temperature. At these high velocities, the impact of LTNE between the air and solid phase is
significant. The cold air entering the hot reaction zone causes a cooling effect in the local energy
balance, thereby dropping the peak temperatures. Despite the drop in peak temperatures, forward
convective heat transfer continues to increase and therefore the front propagation velocity
continues to rise.

Moreover, a key factor is whether excess oxygen exists beyond the reaction zone or whether all
oxygen is consumed (i.e., \(Y_{O_2,f} = x\%\) or \(Y_{O_2,f} = 0\%\) in Fig. 20b). When excess oxygen exists (i.e.,
propagation is fuel-limited), all the energy that can be produced is produced for a set of heat
transfer conditions. However, if all the oxygen is consumed for the same heat transfer conditions
(i.e., propagation is oxygen-limited), less energy is produced and the temperature and front
velocity are negatively affected. This issue will be discussed in greater detail in following sections.
Fig. 23. Sensitivity of temperature profiles in time and space, peak temperature, and front velocity to five key variables: Injected air Darcy velocity, Fuel Saturation, O$_2$ enrichment, Heat Losses, and Heat of Combustion. Black is the lowest value of the variable, red is intermediate, and green is the highest value. All cases shown exhibit an excess of oxygen in the system. The presented trends apply to both PSF and CFIPM systems (adapted from [81]).
Fig. 24. Average smouldering velocity (left) and peak temperature (right) as a function of Darcy flux for feces mixed with sand in a laboratory column under forward smouldering (reprinted from [59] with permission of Taylor & Francis).

The sensitivity of smouldering to fuel concentration (saturation) illustrated in Fig. 23 is a prime example of this general phenomena. More fuel per unit volume always generates more total energy, with dramatic effects at low to intermediate fuel contents. However, as the fuel approaches 50% of the porosity in CFIPM systems, the amount of fuel requires more energy to heat and more time to fully consume so both smouldering and cooling fronts slow down. Moreover, beyond 50%, oxygen is fully depleted and peak temperature and velocities are impacted even further [81].

Similar, but less sensitive, effects are observed for O$_2$ mass fraction in the gas phase and the heat of combustion of the fuel, since increases in each produce more energy per unit mass of fuel oxidized. Moreover, the range of heat losses explored in Fig. 23 are insufficient to affect the peak temperatures resulting from a robust local energy balance, however the temperature profile reveals an impact on the energy stored in the “Heat Storage region” (Fig. 20).

A further effect that cannot be observed in Fig. 23 but that has been reported in the literature [47, 81, 151, 255, 269] is that in the case of CFIPM systems, there is a minimum air flux necessary to
support self-sustained smouldering (on the order of 0.5 cm s$^{-1}$). Altogether this reveals that for
applied smouldering, injected air flux is one of the most useful parameters manipulated by the
operator, allowing control of the mass rate of fuel destruction and terminating the reaction at will.
In PSF systems (e.g., underground coal seams), characterized by minimal heat losses, high
porosity, high permeability and other features of PSF systems (Table 5), the low Darcy velocities
of natural convection are sufficient to maintain self-sustaining propagation; this is one reason
extinction in such systems remains a key challenge [29, 30]. This issue will be discussed in greater
detail in following sections.

4.5 Governing Equations

The articulated conceptual model comes out of the complex interplay of heat and mass transfer
processes and chemical reactions that evolve in space and time. These are typically described via
coupled momentum, mass and energy conservation equations delineated at the macroscopic scale
with Representative Elementary Volume (REV, the minimum volume over which averaging is
meaningful) properties. The first comprehensive mathematical representation of a propagating
smouldering wave is due to Ohlemiller [7] and has been improved and reproduced by many others
[3], nevertheless, the essence of this framework remains the same.

A mathematical description of the relevant processes in one-dimensional smouldering is
summarized below. This applies to PSF systems and to CFIPM systems in which the fuel and the
solid are assumed to have effective properties of a single solid phase. The conservation of mass
[299] for the gas phase is defined:

$$\frac{\partial (\rho_g \phi_g)}{\partial t} + \frac{\partial (\rho_g u_g)}{\partial x} = Q_g$$  \hspace{1cm} (33)

which solves air pressures and velocities adopting Darcy’s Law [77] without gravity effects:

$$u_g = -\frac{k_g}{\mu_g} \left( \frac{\partial P_g}{\partial x} \right)$$  \hspace{1cm} (34)

with gas density ($\rho_g$):

$$\rho_g = \frac{P_g}{R_s T_g}$$  \hspace{1cm} (35)
following the ideal gas law [300]. The term $Q_g$ in Eq. (33) represents the generation (source) or removal (sink) of mass per unit volume per unit time for gas phase. It may include consumption or production of chemical species as well as evaporation and condensation. The bulk transport of oxygen and other species in the gas phase [77] is described by:

$$
\phi_g \left( \rho_g \frac{\partial (\rho_g Y_{O_2})}{\partial t} + \frac{\partial (\rho_g u_g Y_{O_2})}{\partial x} \right) = \phi_g \left( \rho_g D_g \frac{\partial Y_{O_2}}{\partial x} \right) + Q_{O_2}
$$

(36)

where $Q_{O_2}$ represents the mass per unit volume per unit time for oxygen consumption.

The conservation of energy follows one of two different approaches: Local Thermal Equilibrium (LTE) and Local Thermal Non-Equilibrium (LTNE). When assuming LTE, the temperatures of the gas and solid/fuel phases are locally the same [78, 79], and only one energy equation is required:

$$
\left( \rho C_p \right)_{eff} \frac{\partial T_g}{\partial t} + \rho_g C_{p_g} u_g \frac{\partial T_g}{\partial x} = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_g}{\partial x} \right) + Q_{gen} - Q_{loss}
$$

(37)

where assuming the pores are saturated with gas:

$$
\left( \rho C_p \right)_{eff} = (1 - \phi) \left( \rho_s C_{p_s} \right) + (\phi) \left( \rho_g C_{p_g} \right)
$$

$$
k_{eff} = (1 - \phi) (k_s + k_{rad}) + (\phi) (k_g)
$$

(38)

When considering LTNE, the solid temperature ($T_s$) differs from the gas temperature ($T_g$) [78, 79]:

$$
\left( \rho C_p \right)_{eff} \frac{\partial T_s}{\partial t} = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_s}{\partial x} \right) + \frac{A_{s,sp}}{V_{sp}} \left( T_g - T_s \right) + Q_{gen} - Q_{loss}
$$

(39)

$$
\phi_g \left( \rho_g C_{p_g} \right) \frac{\partial T_g}{\partial t} + \rho_g C_{p_g} u_g \frac{\partial T_g}{\partial x} = \phi_g \frac{\partial}{\partial x} \left( k_g \frac{\partial T_g}{\partial x} \right) + h_{sg} \left( A_{s,sp} \right) \left( T_s - T_g \right)
$$

(40)

Source/sink terms ($Q$) in Eq. (39) represent the net energy per unit volume per unit time for pyrolysis and oxidation reactions ($Q_{gen}$), and heat losses ($Q_{loss}$). The heat loss term ($Q_{loss}$) represents a means by which energy is extracted from the system [80, 81, 152, 223]. The means by which this term is quantified depends on the configuration that is being approximated by Eq. (39). For multicomponent systems where liquid and gas may occupy the pore space, effective thermal properties for the solid/liquid phases are considered.

85
\[ \left( \rho C_p \right)_{eff} = (1 - \phi) (\rho_s C_{ps}) + (\phi_t) (\rho_t C_{pt}) \]
\[ k_{eff} = (1 - \phi)(k_s + k_{rad}) + (\phi_t)(k_t) \]
\[ \phi = \phi_g + \phi_l \]  \hspace{1cm} (41)

The interfacial heat transfer coefficient \( (h_{sg}) \) is typically determined from an empirical Nusselt \( (Nu) \) versus Reynolds \( (Re) \) and Prandtl \( (Pr) \) correlation. The Wakao et al. [301] correlation has been widely used to quantify the interfacial heat transfer coefficient \( (h_{sg}) \) [151, 157], nevertheless, it has been shown to over-predict heat transfer between phases leading erroneously to conditions that tend to thermal equilibrium between phases in smouldering systems [246]. A validated correlation for CFIPM systems with quartz sand matrix is:

\[ Nu = \frac{h_{sg} d_p}{k_g} = 0.001 (Re^{1.97} Pr^{1/3}) \]  \hspace{1cm} (42)

valid for \( 0.5 \leq Re \leq 31 \) [246]. This correlation shows that LTNE results for a much wider range of conditions than previously believed. Nevertheless, there is still a wide range of scenarios where within the REV the difference between the solid and gas temperature is negligible \( (T_g = T_s = T) \). In this cases, the hypothesis of LTE can still be made.

Eq. (36) considers that all of the bulk oxygen is available for the oxidation reaction. Nevertheless, Leach et al. [76] suggested that diffusion of oxygen into the surface of the fuel (here, fuel is the porous solid) might limit the reaction rate:

\[ \phi_{bk} \frac{\partial}{\partial t} (\rho_{g,bk} Y_{O_2,bk}) + \frac{\partial}{\partial x} (\rho_{g,bk} u_{g,bk} Y_{O_2,bk}) \]
\[ = \phi_{bk} \frac{\partial}{\partial x} \left( \rho_{g,bk} Y_{O_2,bk} D_{g,bk} \frac{\partial Y_{O_2,bk}}{\partial x} \right) + h_m \left( \frac{A_{ssp}}{V_{sp}} \right) (Y_{O_2,sf} - Y_{O_2,bk}) \]  \hspace{1cm} (43)

\[ \phi_{sf} \frac{\partial}{\partial t} (\rho_{g,sf} Y_{O_2,sf}) \]
\[ = \phi_{sf} \frac{\partial}{\partial x} \left( \rho_{g,sf} Y_{O_2,sf} D_{g,sf} \frac{\partial Y_{O_2,sf}}{\partial x} \right) + h_m \left( \frac{A_{ssp}}{V_{sp}} \right) (Y_{O_2,bk} - Y_{O_2,sf}) + Q_{O_2} \]  \hspace{1cm} (44)

where \( \phi_g = \phi_{bk} + \phi_{sf} \) and \( u_{g,sf} = 0 \). Eq. (43) describes the transport of \( O_2 \) in the bulk gas \( (Y_{O_2,bk}) \), and Eq. (44) describes the transport of \( O_2 \) at the surface of the solid \( (Y_{O_2,sf}) \). The sink term \( (Q_{O_2}) \) indicates the depletion of oxygen by oxidation reactions on the fuel surface. Eqs. (43) and (44) are also linked by a mass transfer coefficient \( (h_m) \) [302]. Beyond conventional textbook values the
mass transfer coefficient \( (h_m) \) has not been studied and its determination still poses complex practical problems that have not been resolved. Thus, proper quantification of the mass transfer coefficient \( (h_m) \) remains a limitation to all existing mathematical models. Even the most recent studies use approximations for forward diffusion through the porous bed by modifying the gas phase diffusivity by a simple constant labelled the tortuosity factor \([303]\) but do not model diffusion of oxygen to the pore surface in an explicit manner \([304]\). Given that diffusion of oxidizer to the surface could be the rate limiting mechanism, this limitation disables the use of numerical models for the purpose of assessing the adequacy of different reaction mechanisms and their respective kinetic constants.

When certain assumptions are made (e.g., one-dimensional configuration, simple reaction models, LTE, simplified source and neglecting sink terms, etc. \([64, 75, 147]\)), the above equations can be solved analytically. Approximate analytical expressions are used for determining the structure of the smouldering front, the front propagation velocity, and the maximum (adiabatic) temperature at the combustion front \([64, 75, 125, 143, 147-149, 305]\).

Solution of these equations needs to address (and many times simplify) a comprehensive system of chemical kinetics; this is reviewed in Section 2.4 Chemistry. The complexity of the system of equations solved must be commensurate with the problem under consideration. The above equations may be sufficient for robust smouldering in one-dimension in a bed of fixed bulk density. For many cases of smouldering in natural and applied contexts, they will need to be solved numerically to access a more detailed interplay of heat and mass transfer with chemical reactions in space and time. Explicit study of radial heat loss, front geometry, and fuel/bed heterogeneity require multidimensional equations and models. Considering a bed that changes under smouldering (e.g., where the bulk of the system mass is carbon-based) requires an explicit analysis of the evolution of the porous medium, e.g., permeability and porosity changes. However, relatively straightforward cases, such as those involving steady-state systems, can be investigated with analytical solutions.

4.6 Analytic Solutions

Analytical descriptions of different aspects of smouldering propagation have been provided by many authors \([64, 117, 122, 123, 125, 146-149, 306-308]\). Three distinct structures have been
described: reaction leading, reaction trailing, and super-adiabatic (Fig. 25). The definition of each structure is based on simple analytical assumptions, and the conditions that lead to structure change are still not well understood. However, since it is present in the smouldering literature, a brief summary will be described here for completeness. In the reaction leading structure (Fig. 25a), the chemical reaction front propagates faster than the heat transfer front, whereas in the reaction trailing structure (Fig. 25b), the opposite occurs. In the super-adiabatic structure (Fig. 25c), the velocity of the reaction front overlaps the velocity of the heat transfer front, causing a steep increase in the combustion temperature ($T_{max}$); in theory, it approaches infinity. In practice, the reaction leading structure has been observed virtually for almost the integrity of the experimental research on smouldering of PSF and CFIPM systems; this appears to be the dominant structure for the practical conditions of interest to these systems.

Fig. 25. Forward smouldering front: (a) reaction leading (process dominated by the reaction layer, i.e., the reaction layer travels faster than the heat transfer layer); (b) reaction trailing (process dominated by the heat exchange layer, i.e., the heat transfer layer travels faster than the reaction layer); (c) super-adiabatic (the heat transfer later and reaction layer travel at the same velocity leading to a singularity in the peak temperature) (adapted from [125, 147]).
From the analysis, a non-dimensional propagation velocity (Δ) for the smouldering front structure emerges [64, 75, 125, 147, 305]:

\[
\Delta = \frac{\phi_g \rho_g u_g}{(\phi_g \rho_g C_{pg} + (1 - \phi_g) \rho_s C_{ps}) v_f} = \frac{(1 - \phi_g) \rho_s C_{ps}}{\phi_g \rho_g C_{pg} + (1 - \phi_g) \rho_s C_{ps} ([Fuel]_{in} - [Fuel]_{out})} ([O_2]_{in} - [O_2]_{out})
\]

where \([O_2]_{in}\) and \([O_2]_{out}\), \([Fuel]_{in}\) and \([Fuel]_{out}\), are the oxygen and fuel concentrations upstream and downstream from the combustion front, respectively. The value of Δ determines whether the smouldering front structure is reaction leading (Δ < 1), reaction trailing (Δ > 1), and super-adiabatic (Δ = 1). Thus, following the assumptions above, an analytical expression for the smouldering front velocity \(v_f\) and the combustion temperature \(T_{max}\) were obtained:

\[
v_f = \frac{\phi_g}{1 - \phi_g ([Fuel]_{in} - [Fuel]_{out})} u_g
\]

\[
T_{max} = \frac{(1 - \phi_g) ([Fuel]_{in} - [Fuel]_{out}) \Delta H_{oxid}}{\phi_g \rho_g C_{pg} + (1 - \phi_g) \rho_s C_{ps}}
\]

Eq. (46) can be reformulated based on a single carbon oxidation reaction [269] and becomes:

\[
v_f = \frac{u_g \rho_g Y_{O_2} f r_{O_2oxid} M_C}{M_g \rho_{bed} X_C f r_{Coixd} (1 - f_{iCO}/2)}
\]

Eq. (48) provides physical insight into the parameters controlling the front velocity, which is one of the most significant parameters in smouldering research. A fast front velocity may represent a significant fire hazard or a desirable industrial process depending on the context. The earliest front velocity models were empirical relationships fitted to experimental data from smouldering dust trains and board strips at various air velocities by Palmer [4]. These first models postulated smouldering spread was limited by the oxygen supply to the smouldering surface and thus fitted the experimental data to a linear function of the airflow. Ohlemiller [7] later proposed the necessary equations to comprehensively model smouldering but resorted to a numerical solution. It is Dosanjh et al. [75] who provided the first analytical solution for the front velocity (see Eq. (27)). Torero et al. [143, 144, 219, 223] extended the theory from Dosanjh et al. [75] and developed a
similar analytical expression for the front velocity based on an energy balance at the oxygen-limited reaction front, local thermal equilibrium, and two-step reactions (pyrolysis and oxidation):

\[
v_f = \frac{Y_{O_2} \rho_g u_g \Delta H_{oxid} + (\dot{Q}_{ig} - \dot{Q}_{loss})(A_s/V)}{[(1 - \phi_g)\rho_s C_p_s + \phi_g \rho_g C_p_g](T_{max} - T_0) - (1 - \phi_g)\rho_s \Delta H_{pyr} + Y_{O_2} \rho_g \Delta H_{oxid}} \tag{49}
\]

Although analytical expressions are useful for general understanding of the process, in complex cases in which many chemical reactions take place, local thermal equilibrium is not valid, or further understanding is necessary, evaluating smouldering with simple analytical expressions provides insufficient information. Numerical models have been used to release some of the assumptions necessary to obtain an analytical solution and to expand the exploration of parameters that cannot be varied within these models.

4.7 Global Energy Balance

As introduced in Section 2.0, the ultimate characteristics of the smouldering front are the result of a local energy balance at the reaction zone; this is well described by Dosanjh et al. [75, 122]. However, to fully describe the local energy balance, a global (system, bed) energy balance is needed. Fig. 26 illustrates the difference between the local and global energy balance concepts; while a CFIPM system is illustrated as an example, the concepts and energy components apply equally to both CFIPM and PSF systems. As shown, the global energy balance considers all the major sources and sinks in the system: the energy absorbed by pyrolysis, released by oxidation at different locations in the system, lost radially, entering the system (heater during ignition) and leaving the system (gas convection) (see equations in Table 6). This allows an individual and cumulative treatment of all heat transfer time scales and links them to local heat transfer in the proximity of the reaction front. When the Net Energy Rate \((\dot{E}_{net})\) is positive, then the smouldering propagation is self-sustaining and the greater its magnitude, the more robust the smouldering. When \(\dot{E}_{net}\) falls below zero, the system predicts, in advance, that unless a parameter changes (e.g., increase in air flow) the smouldering will inevitably go extinct [80, 81].
Fig. 26. (a) Conceptual model showing a smouldering front (red) propagating through the contaminant region (gray), leaving only clean sand (orange) behind. (b) Temperature profile at a specific time. (c) Local and (d) global energy balance. Energy rate components ($\dot{E}$) accounts for (red) energy rate added into and (black) removed from the system (reprinted from [81] with permission of Elsevier). While a CFIPM system is shown, the concepts and energy components apply equally to a PSF system.
Table 6. Global and local energy balance equations (reprinted from [81] with permission of Elsevier).

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<thead>
<tr>
<th>Energy Rate [J s⁻¹]</th>
<th>Global Energy Balance</th>
<th>Local Energy Balance</th>
</tr>
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<tbody>
<tr>
<td>In</td>
<td>( \dot{E}<em>{\text{in}} = q^n</em>{\text{in}}A_{cs} \bigg</td>
<td>_{x=0.1} )</td>
</tr>
<tr>
<td>Oxidation</td>
<td>( \dot{E}<em>{\text{oxid}} = \int \left( -\Delta H</em>{\text{Ch}}R_{\text{Ch}}A_{cs} \right)_d )</td>
<td>( \dot{E}<em>{\text{oxid}} = \int \left( -\Delta H</em>{\text{Ch}}R_{\text{Ch}}A_{cs} \right)_d )</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>( \dot{E}<em>{\text{pyr}} = \int \left( -\Delta H_pR_pA</em>{cs} \right)_d )</td>
<td>( \dot{E}<em>{\text{pyr}} = \int \left( -\Delta H_pR_pA</em>{cs} \right)_d )</td>
</tr>
<tr>
<td>Radial Heat Loss</td>
<td>( \dot{E}_{\text{loss}} = \int \left( -U(2\pi r) (T_s - T_0) \right)_d )</td>
<td>( \dot{E}_{\text{loss}} = \int \left( -U(2\pi r) (T_s - T_0) \right)_d )</td>
</tr>
<tr>
<td>Out</td>
<td>( \dot{E}<em>{\text{out}} = (\rho_g u_g A</em>{cs})C_{pg}(T_g - T_0) \bigg</td>
<td>_{x=0.45} )</td>
</tr>
<tr>
<td>Net</td>
<td>( \dot{E}<em>{\text{net}} = \dot{E}</em>{\text{in}} + \dot{E}<em>{\text{oxid}} + \dot{E}</em>{\text{pyr}} + \dot{E}<em>{\text{loss}} + \dot{E}</em>{\text{out}} \bigg</td>
<td>_{x=0.45} )</td>
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<tr>
<td>Net</td>
<td>( \dot{E}<em>{\text{net}} = \int</em>{\text{f}}^{\text{i}} (\dot{E}_{\text{net}})_d )</td>
<td>( \dot{E}<em>{\text{net}} = \int</em>{\text{f}}^{\text{i}} (\dot{E}_{\text{net}})_d )</td>
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</tbody>
</table>

Using a numerical model, Zanoni et al. [152] described the role of the global energy balance to predict ignition and extinction for smouldering bitumen/sand mixtures. Details on the model and a sensitivity analysis can be found in [80, 81, 152]. Here a few published results are presented along with a suite of new results in order to illustrate the value of a global energy balance analysis in describing and explaining smouldering propagation, ignition, and extinction. While a CFIPM case is used for example, this type of analysis is applicable to all smouldering systems including PSF scenarios.

Figs. 27a-c describe the global energy balance for Case 1 (a robust smouldering propagation case): air flux \((u_g)=0.058 \text{ m s}^{-1}\), bitumen saturation \((S_b)=0.15\), oxygen concentration \((O_2)=0.204\). Smouldering is self-sustaining as indicated by the positive \( \dot{E}_{\text{net}} \) (black line, Fig. 27c), which is dominated by the energy added from oxidation (red line, Fig. 27b). Energy is lost radially \( \dot{E}_{\text{loss}} \) but this is only ever 50% of the oxidation energy (magenta line, Fig. 27b). This continuing positive energy balance causes energy accumulation \( \dot{E}_{\text{net}} \) in the porous medium (red line, Fig. 27c). As the reaction approaches the end of the domain (DT=1), energy leaves the system via hot air convection \( \dot{E}_{\text{out}} \) (green line, Fig. 27b). After this, all fuel is eliminated (i.e., \( \dot{E}_{\text{oxid}} = \dot{E}_{\text{pyr}} = \)).
0 and only clean, hot sand remains) and only $\dot{E}_{\text{loss}}$ and $\dot{E}_{\text{out}}$ are observed as the system cools (Fig. 27b).

Figs. 27e-g present Case 2, which is the same Case 1 but with lower air flow ($u_g=0.014 \text{ m s}^{-1}$) [81]. In this case, the reaction successfully ignites but quickly diminishes and proceeds to extinction. Fig. 27g reveals that $\dot{E}_{\text{net}}$ becomes negative at early time due to radial energy losses exceeding oxidation energy gains (Fig. 27f). Here it is observed that the global energy balance predicts extinction will occur even when temperatures are high at the reaction front and oxidation is active (Fig. 27e). In other words, when the cumulative energy in the system, $E_{\text{net}}$, starts decreasing while much fuel remains, failure is predicted (Fig. 27f). This is consistent with the transient extinction observations of Torero and Fernandez-Pello [143, 219] and explains the discrepancies between these observation and previous theoretical models.

The global energy balance for Cases 1 and 2 were compared with the local energy balance (Figs. 27d and 27h) at a single representative time (DT=0.2; i.e., dimensionless time of 0.2, or when the smouldering reaction propagated 20% of the length of the reactor) following the methodology presented in Zanoni et al. [81]. In Case 1 (self-sustaining propagation), the local energy balance is dominated by the rate by which oxidation ($\text{oxid}$) delivers energy to the front (Fig. 27d). The convective rate by which energy enters the front ($\text{in}$) exceeds the rate by which energy leaves the front ($\text{out}$). In addition to the energy $\text{out}$, it is necessary to add the rate of energy supply needed to sustain pyrolysis ($\text{pyr}$). It is important to note that for the conditions studied in this example the energy loss to pyrolysis is consistently low [80, 81]. The radial heat losses ($\text{loss}$) is negligible in the local analysis due to a very thin front. In the global energy balance (Fig. 27d), there is no energy entering ($\text{in}$) or leaving ($\text{out}$) the system. Moreover, global energy losses are not negligible, exceeding by 10 to 20 times the local heat loss. For the global system, the net energy balance leads to less energy than the local balance, nevertheless, it still remains positive therefore the smouldering propagation is self-sustained (Fig. 27d). In this case, local and global energy analyses describe a scenario that is self-sustaining.

Fig. 27h describes the local and global energy balances for Case 2 (extinction-after-ignition). It is clear that the oxidation energy rate is less than previous case due to the lower oxygen mass flux. In the local analysis, energy $\text{in}$ and energy $\text{out}$ of the front are essentially equal. At this time (DT=0.2), oxidation is still occurring, while pyrolysis and heat losses are minor, which means the
local net energy rate is positive. However, in the global energy balance, radial losses are much higher due to the heated length.
Fig. 27. (a,e) Numerical sand/bitumen temperature versus DT. Colours describe thermocouple positions (x) from 0.12 to 0.40 m with 0.07 m intervals; (b,f) energy rate for each component versus DT: (black) heater, (red) oxidation, (blue) pyrolysis, (magenta) radial loss, and (green) convection out; (c,g) (black) net energy rate and (red) cumulative net energy versus DT, and (d,h) local and global energy balance with energy rates depicted at DT=0.5. Dashed grey line marks when $\dot{E}_{\text{net}} = 0$ while dashed blue line marks when a constant velocity front would have reached the end of the column (DT=1) (adapted from [80, 81]).
When radial losses are combined with the pyrolysis energy consumption rate, sinks exceed sources and the global net energy rate is negative, in contrast to the positive local energy balance. This illustrates how the smouldering reaction can still be active while the global energy balance predicts that extinction is approaching. At this time, conditions could be altered (e.g., more heat added, heat losses reduced, air flux increased) such that the global energy balance returns to positive and the smouldering propagation would switch to self-sustaining.

The same approach was used to study ignition, presented here for the first time. Figs. 28a-c show Case 3, a failure-to-ignite scenario \( \left( u_g=0.025 \text{ m s}^{-1}, S_b=0.15, O_2=0.204 \right) \) in which the heater was turned on at \( t=0 \text{ s} \) and turned off at \( DT = -0.15 \) (\( t=3049.5 \text{ s} \)). At the moment that the heater is turned off, the temperature at the first thermocouple starts decreasing (Fig. 28a) and only increases again when the air is turned on, at \( DT=0 \) (\( t=4926 \text{ s} \)). However, this increase in temperature is not enough to create self-sustaining conditions, i.e., oxidation is weak, decreasing with time and losses are high, increasing with time (Fig. 28b). This results in an energy balance that leads to a negative net energy rate at \( DT=0.237 \) (\( t=7070 \text{ s} \)), causing a rapid extinction due to insufficient heat supply for self-sustained smouldering propagation. These results have similar qualitative features to the observations that have led to most smouldering ignition protocols.

Studies conducted to develop ignition protocols demonstrated that it was not sufficient to bring the reaction to a critical ignition temperature (or Damköhler number) but that it was necessary to have a positive global heat transfer environment for the reaction to continue to propagate. As evidence for this, this simulation was rerun (Case 4) except, this time, the heater was turned back on at \( DT=0.237 \) (\( t=7070 \text{ s} \)) and kept on until \( DT=0.94 \) (\( t=13460 \text{ s} \)), which resulted in an increase in the temperature (Fig. 28d) sufficient to fully re-activate oxidation (Fig. 28e). This created an energy balance that leads to a positive global net energy rate (Fig. 28f) and achieved self-sustaining smouldering propagation.
Fig. 28 (a,d) Numerical sand/bitumen temperature versus DT. Colours describe thermocouple positions (x) from 0.12 to 0.40 m with 0.07 m intervals; (b,e) energy rate for each component versus DT: (black) heater, (red) oxidation, (blue) pyrolysis, (magenta) radial loss, and (green) convection out; and (c,f) (black) net energy rate and (red) cumulative net energy versus DT. Dashed grey line marks when $\dot{E}_{\text{net}} = 0$. See Fig. 29 for information on the four circled times.

The four circled times shown in Fig. 28c and 28f were used to compare the global with local energy balances for these two cases. Figs. 29a and 29b describe regions (1) and (2), respectively, for the Case 3 (Failure to Ignite); Figs. 29c and 29d describe regions (3) and (4), respectively, for the repeat with re-ignition (Case 4). Fig. 29a (DT=0.237, t=7070 s) reveals that although the global net energy rate is zero, the local net energy rate is positive because oxidation is still active and local radial losses are small. At 7510 s (DT=0.28, Fig. 29b), the non-self-sustaining fate of the reaction (due to insufficient ignition) is indicated by a negative net energy rate, whereas the local
energy balance is still describing a positive net energy rate. This confirms, now also for an ignition case, that the global energy balance predicts in advance the extinction (or non-ignition) of the front, as long as no conditions are changed [80, 81]. Moments after the heater is turned back on (Fig. 29c), there is a sudden increase in the global net energy rate, which is entirely dominated by the input of energy from the heater (note that all the other components either for the local or global energy balances are unchanged, Fig. 29c). This will provide the energy necessary to strengthen oxidation, consequently creating a self-sustaining front with positive net energy rates locally and globally (Fig. 29d).

![Figure 29. Energy rates for the local and global energy balances. (a,b) Case 3, Failure to Ignite (heater-OFF=3049.5 s), (c,d) Case 4, Failure to Ignite followed by Ignition (heater-OFF=3049.5 s, heater-ON=7070 s, and heater-OFF=13460 s). Both simulations used \( u_s = 0.025 \) m s\(^{-1} \), \( S_o = 0.15 \), \( O_2 = 0.204 \).](image)

The global energy balance is valuable not only to distinguish self-sustaining versus extinguishing cases, but also the robustness of the smouldering system. Robustness ultimately describes how far the system is from extinction. In these simulations, robustness is measured by the positive magnitude of the net energy rate at a given time, i.e., how rapidly excess energy is being generated and stored. A robust system can suffer mild or temporary negative circumstances (e.g., temporary loss of air flow, reaction reaching limited zone of low fuel content) and survive to propagate in a
self-sustaining manner. Fig. 30 illustrates this for a series of cases of varying operating conditions, including varying saturation, air flux, oxygen content, heat of combustion, and radial heat losses. The figure reveals that robustness of the system increases with increasing fuel saturation, air flux, oxygen content of the air, and heat of combustion. It further illustrates that a minimum value in all of these parameters is needed to avoid extinction. Robustness decreases with increases in heat losses and a maximum value must not be exceeded to avoid extinction. The specific net energy rate values shown are specific to the cases examined, but the concepts and procedures are expected to be generally applicable across smouldering scenarios. The use of the global energy balance concept, in combination with traditional local energy balance metrics, to better understand and control smouldering has significant potential.

![Global net energy rate at DT=0.5 versus normalized independent variable](image)

Fig. 30. Global net energy rate at DT=0.5 versus normalized independent variable (reprinted from [81] with permission of Elsevier).

The introduction of the global energy balance allows full descriptions of the seven distinct processes identified in Section 2.0. In the case of inert heating the local energy balance is negative but the global energy balance is positive. Temperatures have not yet attained conditions that introduce significant heat generation or pyrolysis reactions. In the case of endothermic pyrolysis the local energy balance is negative. The global energy balance is negative and the temperature has only increased to a magnitude where endothermic pyrolysis reactions proceed but oxidation reactions are yet not evident. In the case of exothermic degradation, the non-oxidative degradation
chemistry can have exothermic components, therefore the local energy balance can be positive with no assistance from the global energy balance. In \textit{assisted thermal degradation}, endothermic components are stronger than exothermic reactions and therefore the local energy balance needs assistance from the global energy balance for the reactions to proceed. In \textit{self-sustaining thermal degradation} that assistance is not necessary. In a similar manner, in \textit{self-sustaining smouldering} the local energy balance is positive but the exothermic reactions are oxidative. The global energy balance can be positive or negative. As explained above, if the global energy balance is negative the reaction will not propagate and eventually extinguish. If the global energy balance is positive, then \textit{smouldering propagation} will follow. Furthermore, the relationship between the local and global energy balance can also serve to describe in a more comprehensive way ignition, extinction and transition to flaming. And in all cases these apply to both PSF and CFIPM systems.

Overall, the conceptual model of smouldering presented in this section integrates concepts developed over 50 years of smouldering research. Moreover, it provides fresh perspectives on the continuum of behaviour exhibited by porous solid fuels and condensed fuels in inert porous matrices. Finally, it posits this conceptual framework in the language of local versus global energy balances, which can – for the first time – explain the wide range of smouldering behaviours observed.

\textbf{5.0 Emissions}

\textit{5.1 Introduction}

The species associated emissions from smouldering combustion are often far more numerous and complex with many species exhibiting much greater yields than for flaming combustion [309-312]. The spatial resolution of the different regions associated with smouldering propagation (see Section 4.0) allows for a complex combination of compounds transferred with the flow from each stage of the degradation process. Furthermore, the heterogeneous oxidation steps are oxygen-limited [133, 180], since oxygen penetrating the surface is diffusion-limited despite a potential excess in bulk-phase oxygen, and therefore combustion is necessarily incomplete. The inert heating, pyrolysis and exothermic degradation processes are well known to generate many complex gaseous compounds [3, 313].
The basics of the processes (Section 2.0) has been detailed above and the spatial distribution and
temporal evolution of temperature regions will be detailed in Section 4.0. In this section, our goal
is to explicitly link these processes and regions with expected types of emissions. For example,
the inert heating region, volatile and semi-volatile non-water compounds can be distilled from the
fuel as it is heated ahead of the front causing these substances to change to the vapour state while
experiencing negligible pyrolytic degradation [313-315]. These compounds will continuously
condense in the cold regions ahead of the front and re-volatilize as the self-sustained smouldering
reaction progresses [142, 316].

The assisted thermal degradation processes, comprising endothermic pyrolysis and exothermic
degradation, exist in the hotter portion of the preheating region and thus precede the smouldering
front. Pyrolysis of a fuel causes it to reduce to a solid, carbon-rich char while also degrading into
condensable, semi-volatile components ubiquitously defined as tars [313, 317]. Gas phase
compounds may also be formed by high temperature, oxygen-limited pyrolysis of the fuel or
residual char which may be referred to as gasification [15, 180]. The condensed phase fuel often
produced, in part, from assisted thermal degradation is the fuel which undergoes smouldering
combustion [110, 313]. The tars formed through this process can either undergo further
degradation themselves or be emitted as condensable gaseous vapours. Assisted thermal
degradation of a single species fuel can therefore create many different emission products which
are not formed from the oxidative combustion process but rather the high temperature, reduced
conditions ahead of the self-sustained smouldering reaction. However, most fuels contain
numerous species and their co-pyrolysis can result in pyrosynthetic reactions where-by formation
of new species can be created heterogeneously and homogenously from the interaction of the
different pyrolysis products (e.g., [318]). The assisted thermal degradation processes dominate
emissions formation and the preheating region is the dominant emissions forming location
associated with smouldering [313, 319].

As indicated above, inert heating will produce emissions that will most likely re-condense within
the porous media and will not appear unless the reaction front is reaching the end of the reactor
[50]. The thermally assisted region will also deliver many species that will re-condense and follow
the same pattern as the products of inert heating. Nevertheless, several highly volatile products
will inevitably emerge through the integrity of the process [143].
In smouldering combustion, the ratio of CO/CO$_2$ is much higher than in conventional flaming combustion. The exact ratio will vary depending on oxidant flux to the reaction zoned and fuel chemistry. CO and CO$_2$ are predominantly produced from the oxidation of the fuel but both can also be emitted during exothermic degradation, in particular for biological fuels, with CO$_2$ dominating the pair below 550°C and CO dominating above 550°C [320].

There is no clear agreement in the literature as to whether smouldering or flaming combustion of the same fuel produces more particulate matter with some finding smouldering generates more [321], while others indicating flaming produces more [322-324]. However, it is clear that the particulate emissions from smouldering and flaming the same fuel will be different.

5.2 Links to Fuel Types

The emissions from smouldering are most strongly correlated to the chemical composition of the fuel. The chemistry of the fuel will be the strongest determinant of the possible gaseous and condensable thermal degradation products as well as the extent of fixed carbon remaining for combustion thereby also influencing combustion temperatures. The temperature affects the type of emissions produced but, in the case of smouldering, it is secondary to the importance of chemical structure. Table 7 catalogues general emission products as a function of the starting fuel, relevant process (Section 2.0), and spatial temperature region (Section 4.0).
### Table 7. Typical emissions for major fuel types categorized by spatial temperature region, process type, and temperature range

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Preheating Region</th>
<th>Smouldering Region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inert Heating (Boiling)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inert Heating (Distillation/Volatilization)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low Temperature Assisted Thermal Degradation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High Temperature Assisted Thermal Degradation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Self-Sustained Smouldering</td>
<td></td>
</tr>
<tr>
<td><strong>Biological Fuels (Biomass, Peat, etc.)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bound Water</td>
<td>Steam</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Terpenes [330], Light Hydrocarbons, Semi-Volatile Molecules [314]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;95% transmission through system [314]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cellulose [315], Hemicellulose [325], Lignin [325], Sugars [313], Pectin [313, 326], Organic Acids, Long-Chain Hydrocarbons [315]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO and CO$_2$ [309, 320, 331, 332], C$_x$-C$_y$ Alkanes/Alkenes [313, 325, 331, 332], Small Alcohols Ketones/Aldehydes (Formaldehyde) [15, 313, 319, 329, 333], HCN [276], NH$_3$ [333]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cellulose, Lignin [15], Amino Acids [313, 327], Esters [313], Plant Steroids [328]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO/CO$_2$ [309, 311, 332], &gt;C4 Alkanes/Alkenes [15, 315, 332], Aromatic Hydrocarbons [315, 329], PAHs [315, 328, 334], NH$_3$, H$_2$ [333]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fixed Carbon Chars, O$_2$, Bound Inorganics</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO$_2$, CO, PAHs [318, 335], NO$_x$, PCCD/F [335], H$_2$O, HCN, (Alcohols and Ketones)</td>
<td></td>
</tr>
<tr>
<td><strong>Heavy Hydrocarbon Tars/Sludges/Shale</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bound Water</td>
<td>Steam</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Volatile aliphatic and aromatic compounds, Saturates [172]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Long-Chain Saturated and Unsaturated Hydrocarbons [336], Aromatic and Naphthlenes, Asphaltenes, Bitumen, Kerogen</td>
<td></td>
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<tr>
<td></td>
<td>CO/CO$_2$, C$_x$-C$_y$ Alkanes/Alkenes/Alkenes [336, 337, 339], Aromatic Hydrocarbons [172, 336, 339], PAHs, SO$_2$ [38], H$_2$O [61, 340]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fixed Carbon Chars, O$_2$, Bound Inorganics</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO$_2$, CO, PAHs, NO$_x$, PCCD/F, H$_2$O, Formic/ Naphthenic Acids, Aromatic Hydrocarbons [172]</td>
<td></td>
</tr>
<tr>
<td><strong>Polyurethane Foam</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bound Water</td>
<td>Steam</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyurethane</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isocyanates, Polyols, H$_2$O [110, 343]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isocyanates, Polyols</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO$_2$ [343], C$_x$-C$_y$ Alkanes/alkenes [342, 343], ethers [343], HCN [342], NH$_3$ [342]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fixed Carbon Chars, O$_2$, Bound Inorganics</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO$_2$, CO, H$_2$O,</td>
<td></td>
</tr>
</tbody>
</table>

1. This temperature region overlaps with the combustion region and can typically only occur in oxygen devoid regions around the combustion zone
2. Only possible with chlorinated species in the system
3. Hydrocarbon emissions emit broadly with little work exploring high temperature pyrolysis because it is either dominated by combustion or mineral decomposition
4. Decreasing yield with increasing chain length
5. Wide variety in peak temperature depending on fuel type, inherent moisture content, oxygen flux, and heat losses
6. Unlikely to initially have moisture content but some could form from combustion and condense in the system
It is beyond the scope of this work to explore the minutia of emission formation mechanisms, however, the major compounds and trends are summarized.

Biological fuels including peat, biomass, tobacco, etc. are all chemically similar in that they are formed from mixtures of cellulose, lignin, saccharides, organic acids, proteins and steroids, as well as long chain hydrocarbons in the form of fats or waxes. These fuels all contain oxygen bearing molecules which gives them characteristically low-temperature pyrolysis products that are relatively unique. Many low molecular weight oxygenated groups are evolved through pyrolysis of these fuels below 300°C creating a highly aliphatic char [15, 319, 329, 333, 344]. Increasing temperatures results in the char becoming more aromatic in content and the evolution of gas phase alkanes [15].

If temperatures are able to rise above 600°C, some polycyclic aromatic hydrocarbons (PAHs) may begin to form and will increase in concentration with increasing temperatures [318, 328, 334]. PAH formation can occur in the absence of oxygen, and are therefore pyrolysis products. However, PAHs have been shown to yield equal or higher concentrations under oxidative conditions and thus can also be considered a combustion product [318, 335].

Heavy hydrocarbons are capable of undergoing smouldering combustion so long as they are suspended in a porous matrix allowing adequate air flux, heat storage, and surface area for reaction [48, 50, 80, 81, 152, 255, 296]. Smoulderable hydrocarbons are a complex mixture of numerous aliphatic and aromatic groups often containing oxygen, nitrogen and sulfur impurities. Emissions from these combustible materials have not been characterized in detail, nevertheless, these fuels have been shown to deliver smouldering temperatures that exceed 800°C with the subsequent potential for the production of species more common to gas phase combustion.

Polyurethane foam has been extensively studied and has been shown to thermally breakdown in two steps staring with the scission of the polyol-isocyanate bond between 250-300°C [110, 143, 194, 343]. Both compounds can further degrade at higher temperatures with polyol decomposing to contribute a secondary char [343]. Additional details, in particular with respect to agricultural fuels, are presented in Section 2.0.
5.3 Metals

Metal emissions are affected by metal content of the combustible material, fuel bed temperature, and the level of particulate matter control. Metals are volatilized in the preheating or smouldering regions (depending on compound boiling temperatures) and then condense in the cooler portions of the fuel bed ahead of the front or in the exhaust gas stream. Most metals (except mercury) are associated with fine particulate and are removed as the fine particulates are removed. Therefore, an effective technique to control the metals emissions in the flue gas is to employ an ash removal device. However, due to the instability of the mercury compounds in the gaseous form at higher temperatures, more often above 700°C, the compounds decompose to form elementary mercury. The elementary mercury is not readily soluble and thus, unlike other heavy metals, is not removed with the ash during post-combustion flue gas treatments.

Additionally, some flue gas components may react with the dissolved mercury compounds and release elementary mercury. To reduce this effect, additives may be added to scrubbing water or the flue gas, which would react with the mercury compounds and form precipitates. Some of the additives in the market include trimercapto-S-triazin (TMT 15) from Degussa AG and Nalmet A1 from Nalco Chemie GmbH [345].

Different types of emission control systems have been used on incinerators. In general, old installations included only electrostatic precipitators (ESP) for control of particulates. Some of these installations achieved low emissions for some metals. However, ESP may be problematic because they can produce dioxins and furans. Many installations include a semi-dry scrubber where an alkaline reactant (e.g., lime) is injected to absorb acid gases. An ESP or a fabric filter that removes the particulate matter follows the scrubber. In general, the dry scrubber-equipped facilities have shown lower heavy metal emissions in the stack gases.

Flue gas temperature and particulate matter size are major factors in the control of heavy metals emissions. The metals and their compounds carried by the furnace exhaust flue gas enter the emission control system as solids, liquids and vapours. In the semi-dry scrubber, some of the vapours convert to solids or liquids (depending on the vapour pressure/temperature relationship) which are then removed from the flue gas. Based on theoretical vapour pressure considerations, it should be possible to remove 99% of the heavy metals by lowering the flue gas temperature to below 200°C [346].
During smouldering, particulate matter most likely is only emitted if the reaction front is allowed to progress to the end of the reactor; therefore, the metals in the combustible material are expected to remain primarily in the ash and/or within the pores of the inert porous matrix. With the exception of some scenarios in surface smouldering, as the energy from combustion is mostly accumulated within the reactor, the temperature of the flue gas is usually below 200°C \[50\]. Furthermore, controlling smouldering temperatures below 700°C is possible \[56\], avoiding the formation of elementary mercury. In this way, all the metals should be present in the ash and/or within the porous matrix. Importantly, this represents a potential source for metals recovery.

5.4 NOx Formation

NOx is the general term which encapsulates the seven oxides of nitrogen (NO, NO2, NO3, N2O, N2O3, N2O4, N2O5); however, in combustion, NOx generally only pertains to the production of NO and NO2. Though NOx formation has been extensively studied, particularly in the relation to boilers, incinerators, and fluidised bed reactors, very little focus has been given to NOx formation during smouldering.

There are generally three pathways for NOx production: Thermal NOx, Prompt NOx and Fuel NOx. Prompt NOx is the formation of NOx from the reaction of atmospheric nitrogen in hydrocarbon-rich flame zones and is therefore inapplicable to smouldering combustion and will not be discussed further.

Thermal NOx is formed during the high temperature oxidation of atmospheric nitrogen following the two-step Zeldvich mechanism \[347\]. Under the Zeldvich model, thermal NOx formation is highly sensitive to temperature with NOx formation being significantly reduced at temperatures less than 1300-1600°C \[348, 349\]. It is possible that smouldering combustion of biomass reaches levels beyond the onset of thermal NOx production but these temperatures have not been commonly attained with biomass or sludge \[18, 56, 293\] and may be more practical with materials such coal tar \[50\]. Most acceptable operating conditions will not exceed 700°C, thus self-sustained smouldering propagation can be maintained at temperatures below those that result in significant production of thermal NOx.
Many fuels contain a small percentage of organically bound nitrogen which can contribute significantly to the total NO\textsubscript{x} production. Table 8 shows the typical nitrogen contents within a variety of fuels.

Table 8. Typical fuel-nitrogen content (reprinted from [349] with permission of Elsevier).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>N content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straw</td>
<td>0.3-1.5</td>
</tr>
<tr>
<td>Other agricultural residues</td>
<td>0.4-3.5</td>
</tr>
<tr>
<td>Wood</td>
<td>0.03-1.0</td>
</tr>
<tr>
<td>Peat</td>
<td>0.5-2.5</td>
</tr>
<tr>
<td>Coal</td>
<td>0.5-2.5</td>
</tr>
<tr>
<td>Paper</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>RDF</td>
<td>0.8</td>
</tr>
<tr>
<td>Tires</td>
<td>0.3</td>
</tr>
<tr>
<td>Household waste</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Plastic waste</td>
<td>0.0</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>2.5-6.5</td>
</tr>
</tbody>
</table>

Fuel nitrogen is typically bound to the fuel by C-N or H-N bonds which are substantially weaker than the triple bond of molecular nitrogen [350]. Unsurprisingly, it is easier to break these bonds allowing for the formation of fuel NO\textsubscript{x} far more readily than thermal NO\textsubscript{x} and at relatively lower temperatures. Fuel-bound nitrogen is the dominant NO\textsubscript{x} formation pathway accounting for 50%-80% of the NO\textsubscript{x} in these systems [348, 351, 352]. Despite the significant contribution of fuel nitrogen to the total NO\textsubscript{x} production, only 10%-60% [353] is converted to NO\textsubscript{x} due to competing oxidation and reduction mechanisms.

Fuel nitrogen has been found to split between volatile species and the residual char during thermal degradation; both of which can be oxidized to form either Volatile NO\textsubscript{x} or Char NO\textsubscript{x} or be reduced to N\textsubscript{2}. Nitrogen-bearing fuels have also been found to produce appreciable levels NH\textsubscript{3} and HCN during combustion [354, 355] with the ratio between NH\textsubscript{3}/NO\textsubscript{x} generally increasing as the combustion reaction becomes more dominated by smouldering than flaming [356].

Volatile NO\textsubscript{x} is generally considered to form through the oxidation of HCN, NH\textsubscript{3}, and HNCO volatiles and is typically responsible for 60%-80% of the total Fuel NO\textsubscript{x} [348, 349, 351]. Volatile NO\textsubscript{x} formation is a homogenous process and is therefore highly dependent on contact with free
oxygen. Local conditions beyond the combustion front therefore determine the extent to which volatile nitrogen is oxidized or reduced. Smouldering can be controlled such that it operates near a stoichiometric oxidant flux, which would result in reducing conditions beyond the combustion front, but typically the reaction has excess air. NO\textsubscript{x} produced from volatile nitrogen can also be reduced by heterogeneous reactions with the char.

The quantity of fuel nitrogen which remains in the char is variable and depends on the fuel composition as well as the extent of heating it experiences [351, 357]. Studies on the combustion of char at single char particle conditions (i.e., approaching the limit of zero char mass) have shown that char nitrogen can be oxidized to NO with a net conversion of 65-100\% [358]. As char NO\textsubscript{x} yields are substantially lower than this in practice, the produced NO\textsubscript{x} is believed to undergo heterogeneous reduction by reaction with other, active char particles which has been thoroughly reviewed by [359]. NO yields as a function of increasing coal char masses is shown in Fig. 31 which clearly demonstrates that as more char is in the system, the efficiency of the conversion of char nitrogen to NO rapidly decreases due to the reduction of NO by reaction with the excess char. Char NO\textsubscript{x} therefore only accounts for a small portion of Fuel NO\textsubscript{x}. Char formation is integral to smouldering combustion. The extent to which its formation affects NO\textsubscript{x} yields is likely significant but unexplored.

Fig. 31. NO yields as a function of char mass (reprinted from [358] with permission of Elsevier).
As discussed previously, there is very little in the literature which specifically explores NO\(_x\) formation in a smouldering regime. Studies which have been conducted do show agreement with volatile NO\(_x\) accounting for the majority of total NO\(_x\) with some contribution from char NO\(_x\) and no thermal NO\(_x\) (Fig. 32).

The early-time peaking of NO\(_x\) in Fig. 32 is the formation of volatile NO\(_x\) from volatile nitrogen species. After all volatiles have been emitted, a constant production of NO\(_x\) from the oxidation of char nitrogen occurs until the fuel is completely consumed.

The spatial variability of smouldering has the potential to affect NO\(_x\) formation in a number of ways. The chemical and physical characteristics of a fuel will constantly be changing in time and space as the smouldering front progresses. The fuel will thermally degrade as it undergoes pyrolysis producing volatiles and char. The characteristic of the char can change with time as the oxidation front approaches and temperatures increase. Likewise, the emitted species will change in the same space over different times. The formation of volatile NO\(_x\) and char NO\(_x\) from fuel nitrogen will therefore be a complicated matter. It is unclear what effect the abundance of evolved volatiles and tars generated from smouldering or the role that the porous media will have on the volatile nitrogen and its competition for free oxygen. The spatial temperature distribution and thermal non-equilibrium ahead of the combustion front is much different for smouldering and could have a profound effect on the formation potential of NO\(_x\). Similarly, the characteristics of the evolving char produced during pyrolysis and its effect on char NO\(_x\) formation/reduction are unexplored. Finally, fuels such as sludges, with significantly higher fuel nitrogen content which cannot be conventionally treated by incineration, can be destroyed by smouldering. The effect of this fuel stoichiometry on NO\(_x\) formation has yet to be seen.
5.5 Summary

It is important to reiterate that the spatial and temporal evolution of the smouldering front within the porous bed will determine the overall emissions of a reactor. Though it is well established that emissions from smouldering have multiple formation pathways, many smouldering experimental studies look at the bulk emissions for the global smouldering process and do not distinguish how or when they were formed. In contrast, extensive research has been carried out (primarily via TGA or Pyrolyser) to determine pyrolytic and oxidative thermal processes for many different chemical species with various reaction mechanisms proposed for the detected gaseous emissions. Important physical and chemical information can be elucidated from these studies, however, care must be taken when extrapolating these results to smouldering. Smouldering is a dynamic process where temperature and species concentrations can vary sharply over very small distances. Furthermore, heating rates in smouldering are dependent on the gaseous flux through the system and can also vary in space and time. Often, thermal degradation studies do not mimic the conditions as experienced in actual smouldering combustion by using unrepresentative heating rates and atmospheres [313]. H₂, for example, is often a main pyrolytic decomposition product found in thermal degradation studies but is generally negligible in true smouldering because heating rates favours the formation of H₂O. While it is not possible to generalize the production of different species during smouldering, it is important to emphasize the nature of the reactions present during smouldering and the temperatures at which they occur. The specific operating conditions will determine the species produced and their quantities. There is very little data available on the production of different pollutants under the specific conditions of smouldering, thus it is very important to evaluate this experimentally.
6.0 Research Gaps and Opportunities

Smouldering combustion is a growing research field of critical value to society. Innovative experimental and numerical work has brought our understanding of smouldering science to levels where solutions to long-standing fire safety challenges are within reach and novel applications to solve a wide range of safety, waste and energy problems are emerging. Integrating the existing research into a unified conceptual model and emphasizing the key role of local and global energy balances reveals a framework upon which predicting are realistic and thus, proactive manipulation of complex smouldering systems is possible for productive purposes. Moreover, this exercise reveals some remaining research gaps and thus opportunities for future research directions; a selection of these are summarized below.

Beyond conventional textbook values, the mass transfer coefficient between solid and gas phases in the porous medium \( (h_m) \) has not been studied and its determination still poses complex practical problems that have not been resolved. Thus, proper quantification of the mass transfer coefficient \( (h_m) \) remains a limitation to all existing mathematical models.

There exists very little data available on the production of different pollutants under the specific conditions of smouldering, thus it is very important to evaluate this experimentally. Moreover, emissions control technologies optimized for smouldering applications have not received attention but will be critical for upscaling and commercialization of smouldering applications.

The identification of the roles of global and local energy balances on the onset of self-sustained smouldering propagation makes evident the need for a much more precise understanding of heat and mass transfer processes within porous media. Existing ignition criteria presented in Table 4 remain valid for the ignition of self-sustained smouldering, nevertheless these criteria are only relevant to self-sustained smouldering propagation if heat and mass transfer processes pertaining the global energy balance are properly quantified.

The conceptual model and resulting set of governing equations and assumptions in ad-hoc approaches to extinction that build from Dosanjh et al. [75]’s original analysis still seem to exclude phenomena that govern the extinction of self-sustained smouldering propagation. Therefore, there is still a gap in the literature and room for a harmonized explanation for extinction.
The limited literature on transition to flaming does not yet allow establishing all the variables involved in this process. Nevertheless, it is clear that the interplay between a global energy balance and local heat exchange determines whether the conditions necessary to shift from a heterogeneous to a homogeneous reaction can be attained. Characterization of the evolution of the porous media as thermal conditions progress towards transition to flaming appears essential. Given the importance of this phenomenon for fire safety, this is an issue that needs to receive much greater attention.

It is an open question as to the appropriateness of the existing mathematical representations of chemical schemes for the full description of all stages of smouldering and the degree of simplification that can be employed while still producing meaningful predictions. Currently, this question cannot be addressed because mass transfer effects between the different phases have not been studied in detail. The reaction rates depend on the supply of reactants to the reaction zone (Eq. (19)) and the reaction occurs in the solid phase. Therefore, without detailed quantification of mass transfer between phases it is not possible to ascertain if the mathematical expression and embedded parameters properly quantify the reaction rates. As a simple example, water evaporation/condensation – which are critical to applications of smouldering destruction of high moisture content wastes – are currently treated as chemical reactions. However, to simulate this process with correct predictions of the energy balance, water evaporation/condensation must be integrated as a phase-change process; resolving this challenge is a significant opportunity, as are many related aspects within this sub-discipline.

In general, there exists a much larger body of information on porous solid fuels than on condensed fuels in inert porous media. Nevertheless, in the context of the former, effective means of extinguishing large smouldering hazards remains elusive. Moreover, for the latter, a wide array of thermodynamic parameters remain to be quantified. Little research exists on effectively managing organic wastes with smouldering and the potential to thereby recover materials and energy as part of the drive towards a fully circular economy. There is substantial opportunity to use smouldering to destroy a long list of legacy organic contaminants as well as the many emerging contaminants being revealed as extensive in the environment. Smouldering applications all share the promise of providing well controlled engineering processes that are technically effective while also low energy, low carbon footprint, and therefore more sustainable than alternatives (e.g.,
incineration). However, such research is in its early stages and the myriad of potential applications and process optimizations reveals a research landscape rich in opportunities.

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References


[300] Clapeyron É. Mémoire sur la puissance motrice de la chaleur: Jacques Gabay; 1834.


[315] Baker RR. Smoke generation inside a burning cigarette: Modifying combustion to develop cigarettes that may be less hazardous to health. Prog Energy Combust Sci. 2006;32:373-85.


