Study of Multi-dimensional Transfer Effects in Applied Smouldering Systems

Seyed Ziaedin Miry Mr, Western University

Supervisor: Jason I. Gerhard (Passed away), The University of Western Ontario
Co-Supervisor: Christopher Power, The University of Western Ontario
Co-Supervisor: Marco A.B. Zanoni, The University of Western Ontario

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Abstract

Smouldering is a flameless form of combustion that is driven by oxygen directly diffusing into the surface of condensed phase fuel (liquid or solid) and involves a complex interplay between heat and mass transfer through porous media, chemical reactions, and multiphase flow. Applied smouldering systems have been gaining popularity for a variety of applications including (i) energy and resource recovery, (ii) waste-to-energy, (iii) pyrolysis and gasification, and (iv) applied smouldering of organic liquids/solids for environmental benefits. In all contexts, smouldering is a complicated oxygen-limited phenomenon where multi-dimensional transfer effects (i.e., non-uniformities in temperature, airflow, and chemical reactions) control system operation limits and performance. Therefore, a robust numerical model can be a highly efficient tool to better understand applied smouldering characteristics and these multi-dimensional transfer effects.

For the first objective, a 2D smouldering model was developed, calibrated, and validated for a quantitative and qualitative investigation of multi-dimensional transfer effects. Numerical results confirmed that radial heat losses extracted approximately 52 and 70% of the energy added into systems for granular activated (i.e., fuel) concentrations of 0.02 and 0.03 kg\textsubscript{GAC} kg\textsubscript{sand}\textsuperscript{-1}, respectively. The modelled results closely matched experimental observations and the model elucidated the non-uniformities that could not be measured from experiments, e.g., in air flow. For the second objective, the 2D model was used to explore the effects of oxygen mass flux on smouldering robustness and clarify the role of quasi super-adiabatic effects in applied smouldering systems. By diluting the oxygen mass fraction from 0.230 to 0.115 and 0.057, the smouldering condition changed from robust oxygen-rich to robust fuel-rich and weak fuel-rich, respectively. While the peak temperature remained almost uniform at oxygen fractions of 0.230 and 0.115 (i.e., near 930 °C) due to quasi super-adiabatic effects, it decreased to 700 °C at the lowest oxygen fraction of 0.057. The third objective investigated the effects of fuel mobility on applied smouldering systems using a validated 1D model. Sensitivity analyses confirmed that smouldering robustness increased with decreasing Darcy air flux and increasing fuel viscosity, as higher fuel saturation was deposited in the reaction zone. The numerical
results compared well with experimental observations from the literature. Overall, this thesis explored these three important aspects of applied smouldering systems to provide a deeper understanding that enables scientists and engineers to design and optimize future smouldering reactors for a wide range of applications.

Keywords

Smouldering combustion; thermal treatment; multi-dimensional transfer effects; 1D and 2D numerical modelling; heat losses; energy analysis; oxygen mass flux; super-adiabatic effects; fuel mobility; multiphase flow.
Summary for Lay Audience

Flaming combustion involves a system of rapid chemical reactions in the presence of oxygen that results in the generation of heat and light in the form of flames. Smouldering combustion, on the other hand, is non-flaming combustion that occurs within a porous medium. A classic example is a glowing, hot charcoal briquette. Traditionally, smouldering has been associated with fire safety concerns due to its hidden nature, release of toxic gases, re-ignition risks, and resilience to quenching. However, in recent years smouldering has been used in various environmental engineering applications, such as waste-to-energy, due to its high energy and cost efficiencies. For these applications, organic contaminants are combined with a porous medium (e.g., sand) and placed in a system where applied smouldering effectively can be used to burn the contaminants to leave behind a clean porous medium and ash. Smouldering systems are complex, where the presence of energy losses to the environment adds a key layer of complexity, leading to non-uniform temperature, air mass flux, and chemical reactions distribution across the system. Moreover, oxygen mass flux plays a crucial role, as these systems typically operate in oxygen-limited conditions. Last, because smouldering is well-suited to treating hazardous liquid wastes (like crude oil sludge), liquid fuel movement must also be understood alongside smouldering dynamics. Altogether, these compounding effects lead to a highly complex system, and numerical modelling is therefore an appropriate tool to untangle these complexities. In this thesis, a smouldering numerical model was developed to better understand applied smouldering under varying conditions. The findings from this thesis will provide engineers and researchers with valuable insights into applied smouldering systems that can be used to enhance the design and optimization of these systems for a wide range of environmental engineering applications.
Co-Authorship Statement (where applicable)

The thesis was written in accordance with the guidelines and regulations for an integrated-article format stipulated by the School of Graduate and Postdoctoral Studies at The University of Western Ontario, Canada. The candidate designed and conducted all the simulations and laboratory experiments presented in this thesis (unless otherwise stated), analyzed all data, and formed the conclusions presented. The work was conducted at Western University under the supervision of Drs. Jason I. Gerhard, Marco A.B. Zanoni, Tarek L. Rashwan, Jose L. Torero, and Christopher Power. The candidate wrote the thesis and was the lead author on the manuscript drafts of the following chapters:

Chapter 3: Investigation of multi-dimensional transfer effects in applied smouldering Systems: A 2D numerical modelling approach


Chapter 4: Investigation of applied smouldering in different conditions: The effect of oxygen mass flux


Chapter 5: Delineating the role of fuel mobility in applied smouldering systems

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Contributions:

Seyed Ziaedin Miry: Conceptualization; Formal analysis; Data curation; Formal Analysis; Investigation; Methodology; Project administration; Visualization; Validation; Writing - original draft.

Marco A.B. Zanoni: Conceptualization; Project administration; Formal analysis; Investigation; Methodology; Software; Supervision; Writing - review & editing.

Tarek L. Rashwan: Conceptualization; Data curation; Investigation; Methodology; Supervision; Writing - review & editing.

Jason I. Gerhard: Conceptualization; Fund acquisition; Formal analysis; Investigation; Project administration; Supervision; Validation; Writing - review & editing.

Jose L. Torero: Conceptualization; Project administration; Resources; Supervision; Validation; Writing - review & editing.

Christopher Power: Supervision; Resources; Software; Thesis Writing - review & editing.
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### Nomenclature

#### Abbreviations
- **GAC**: Granular Activated Carbon
- **Dt**: Dimensionless time
- **DTG**: Derivative Thermogravimetry
- **DRUM**: Oil-drum sized reactor
- **DSC**: Differential Scanning Calorimetry
- **LTE**: Local thermal equilibrium
- **LTNE**: Local thermal non-equilibrium
- **REV**: Representative elementary volume
- **TC**: Thermocouple
- **TCE**: Trichloroethylene
- **TG**: Thermogravimetry
- **PCE**: Tetrachloroethylene

#### Latin Letters
- **A**: Pre-exponential factor, s\(^{-1}\)
- **A\(_s\)**: Surface area per unit volume of the porous medium, m\(^{-1}\)
- **C**: Fuel concentration
- **C\(_p\)**: Specific heat capacity, J kg\(^{-1}\) K\(^{-1}\)
- **d\(_p\)**: Particle diameter, m
- **D\(_g\)**: Diffusion coefficient, m\(^2\) s\(^{-1}\)
- **E**: Activation energy, kJ mol\(^{-1}\)
- **Fr**: Mole Fraction
- **G**: Gravity, m s\(^{-2}\)
- **H**: Radial heat transfer coefficient, W m\(^2\) K\(^{-1}\)
- **h**: Metal sheet thickness, m
- **h\(_{sg}\)**: Interfacial heat transfer coefficient, W m\(^{-2}\) K\(^{-1}\)
- **K**: Thermal conductivity, W m\(^{-1}\) K\(^{-1}\)
- **k\(_i\)**: Intrinsic permeability, m\(^2\)
- **k\(_r\)**: Relative permeability, m\(^2\)
- **L**: Fuel bed length, m
- **M\(_g\)**: Molar weight, g mol\(^{-1}\)
- **M**: Total mass, kg
- **Nu**: Nusselt number
- **P**: Pressure, Pa
- **P\(_d\)**: Displacement pressure, Pa
- **Pr**: Prandtl number
- **Q**: Darcy Flux, m s\(^{-1}\)
- **q\(_\dot{}\)**: Heat flux, W m\(^2\)
- **R**: Reaction rate, s\(^{-1}\)
- **Re**: Reynolds number
<table>
<thead>
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<tr>
<td>$R_g$</td>
<td>Ideal gas constant, J mol$^{-1}$ K$^{-1}$</td>
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<tr>
<td>$S$</td>
<td>Saturation</td>
</tr>
<tr>
<td>$S_e$</td>
<td>Effective saturation</td>
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<tr>
<td>$T$</td>
<td>Temperature, °C</td>
</tr>
<tr>
<td>$\nu_c$</td>
<td>Cooling front velocity, cm min$^{-1}$</td>
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<td>$\nu_f$</td>
<td>Smouldering front velocity, cm min$^{-1}$</td>
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<tr>
<td>$\nu_{O_2}$</td>
<td>Oxygen mass yield, kg.O$_2$ kg.Char$^{-1}$</td>
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<td>$Y$</td>
<td>Mass fraction</td>
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**Greek Symbols**

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<td>$\Delta H$</td>
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<td>$\mu$</td>
<td>Dynamic viscosity, Pa s</td>
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<tr>
<td>$\rho$</td>
<td>Density, kg m$^{-3}$</td>
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<tr>
<td>$\phi$</td>
<td>Porosity</td>
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<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant, W m$^{-2}$ K$^{-4}$</td>
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<tr>
<td>$\tau$</td>
<td>Time scale</td>
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<tr>
<td>$\lambda$</td>
<td>Pore size distribution</td>
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**Subscripts/Superscripts**

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<td>Gas</td>
</tr>
<tr>
<td>In</td>
<td>Inlet</td>
</tr>
<tr>
<td>N</td>
<td>Non-wetting phase (i.e., Air)</td>
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<td>P</td>
<td>Pyrolysis</td>
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<tr>
<td>Peak</td>
<td>Peak</td>
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<tr>
<td>Rad</td>
<td>Radiation</td>
</tr>
<tr>
<td>S</td>
<td>Solid</td>
</tr>
<tr>
<td>sp</td>
<td>Spherical</td>
</tr>
<tr>
<td>W</td>
<td>Wetting phase (i.e., Canola Oil, Canola Oil with VI improver, VI Improver)</td>
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<tr>
<td>0</td>
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Chapter 1

1 Introduction

1.1 Background

Applied smouldering has been employed recently as an engineering technology for various environmentally-beneficial applications including (i) destruction of organic liquid/solid contamination (e.g., non-aqueous phase liquids (NAPLs), faeces [1], wastewater sludge [2]), (ii) resource recovery [3], (iii) waste-to-energy conversion [4, 5], and (iv) pyrolysis and gasification (e.g., for carbon monoxide (CO) and hydrogen (H₂) production) [6-9]. NAPLs constitute a large class of industrial organic compounds that are among the most hazardous contaminants in soil and groundwater. NAPLs are generally categorized into (i) LNAPLs (e.g., hydrocarbon fuels with a density lower than water) and (ii) DNAPLs (e.g., coal tar [10] and bitumen [11] with a density higher than water) [12]. DNAPLs can migrate underground in the vadose zone, penetrate the water table and distribute heterogeneously, providing complex, long-term sources of soil and groundwater contamination that pose a significant threat to the environment and human health. To eliminate these threats, effective remediation technologies are required [13].

Effective remediation technologies for contaminated soil and groundwater treatment can be ex-situ (e.g., pump-and-treat [14]) or in-situ (e.g., steam injection [15]), or both (e.g., applied smouldering [16]). Applied Smouldering can be performed as a thermal remediation technique, in-situ with several successful field-scale treatments [16], and ex-situ in the reactors with different scales ranging from the laboratory to intermediate and pilot field-scale [17-20].

Smouldering is defined as a flameless form of combustion governed by heterogeneous reactions where oxygen directly diffuses to the surface of the condensed phase, such as an organic solid or liquid embedded in an inert porous medium [21]. A classic example to describe the smouldering phenomenon is a charcoal barbecue [22]. Smouldering is governed by heat and mass transfer through the porous medium, chemical reactions, and multiphase flow. As a result, smouldering is a complex phenomenon and challenging to
understand solely through laboratory experiments; therefore, numerical modelling is an efficient smouldering research tool [23, 24].

Most smouldering numerical models have been developed in one-dimension (1D). These are powerful tools to investigate smouldering chemical kinetic reactions [25-27] and the interaction between local and global effects [11, 23, 28-30]. However, 1D models have some restrictions, e.g., they cannot (i) simulate the multi-dimensional transfer effects and heterogeneities across the radial direction, which is a limitation in extending model results to field smouldering systems; (ii) energy redistribution in the weak smouldering systems [30]; and (iii) multi-dimensional smouldering propagation, which could result due to the intrinsic permeability and/or fuel concentration heterogeneities. Therefore, a two-dimensional (2D) smouldering model was developed in this thesis and validated with experimental results qualitatively and quantitatively to investigate notable knowledge gaps in this area.

Radial heat losses from smouldering reactors, or heterogeneities (e.g., which are widely present in the field) cause multi-dimensional transfer effects (i.e., non-uniformities in temperature, air mass flux, oxygen concentration, and chemical reactions), which are not well-understood. These effects control system operation limits and performance; therefore, a robust understanding is crucial for researchers and design engineers. A validated 2D smouldering numerical model is required to obtain a qualitative investigation of multi-dimensional effects and quantitative analysis of the energy balance that dictates the limits of the self-sustaining process [31-33]. The results provide insight into the interconnected nature of key physical (e.g., temperature, air flow, porous beds) and chemical (e.g., oxygen concentration, reaction intensity) qualities.

In all mentioned applications, smouldering is an oxygen-limited phenomenon and therefore oxygen mass flux plays a major role in these systems; however, the effects of oxygen limitations on smouldering robustness remain a challenging area that needs more investigation. Oxygen supply can be varied by diluting oxygen mass fraction, which decreases smouldering robustness – as quantified by local and global energy balances [34]. However, oxygen supply variations may increase heat transfer efficiencies and drive
smouldering towards super-adiabatic conditions [35]. Under these conditions, key multidimensional heat and mass transfer effects should also be explored systematically, as the displacement of air towards the periphery of the reactor can lead to lower peak temperatures and eventually localized quenching. The visual manifestation of localized quenching is an unburnt crust near the reactor wall [30].

In many environmentally beneficial applications of smouldering (e.g., contaminated soil remediation, treating organic liquid waste), organic liquid fuels have been combined in an inert porous media (e.g., coarse grain sand). Therefore, organic liquid mobilization affects smouldering performance (e.g., peak temperature and smouldering front velocity) and remediation efficiency – e.g., mobilization can introduce contamination to previously clean regions. However, the dynamics of fuel mobility in smouldering systems are poorly understood [17, 36, 37]. This is a key knowledge gap that hinders the optimization of applied smouldering, especially in large scale systems. As liquid mobilization in porous media cannot be measured directly, numerical modelling can be used to improve the fundamental understanding and clarify the effects and dynamics of fuel mobilization in the context of applied smouldering remediation.

The findings from this thesis shed light on the complicated interplay between multiphase flow, chemistry, and heat and mass transfer common to many applied smouldering systems. These findings are critical for both engineers and researchers to better understand the effects of various operational parameters (e.g., Darcy air flux and fuel saturation) on key fundamental and practical aspects of applied smouldering systems (e.g., robustness and energy efficiency of the system). The improved understanding generated from this research will improve the design, implementation, and optimization of smouldering-based technologies for environmentally beneficial applications worldwide.

1.2 Research Objectives

The goal of this thesis is to improve our understanding of applied smouldering by clarifying the effects of major parameters including radial heat losses, oxygen limiting conditions, and liquid fuel mobility. To achieve this goal, three main objectives were accomplished:
1. Develop and validate a 2D numerical model to investigate multi-dimensional transfer effects associated with radial heat losses.

2. Determine the role of oxygen mass flux on the robustness of applied smouldering systems.

3. Delineate the effects of liquid fuel mobility in applied smouldering systems using a 1D numerical model.

It is noted that, even though applied smouldering for environmental studies was the focus of this thesis, the findings will also provide valuable insights into fire safety and other similar technologies in packed bed reactors (e.g., enhanced oil recovery and energy storage systems). Moreover, the methodology and results of this thesis are applicable to researchers and practitioners in all fields associated with heat and mass transfer in porous media where multi-dimensional transfer effects and fuel mobility are fundamental.

1.3 Thesis Outline

This thesis is written in an “Integrated Article Format”. A brief description of each chapter is presented below.

1. Chapter 2: summarizes the scientific literature relevant to smouldering with the focus on the key theory used in the subsequent chapters.

2. Chapter 3 titled “Investigation of multi-dimensional transfer effects in applied smouldering systems: a 2D numerical modelling approach”, focuses on understanding the multi-dimensional transfer effects by developing and validating a multi-dimensional numerical model.

3. Chapter 4 titled “Investigation of applied smouldering in different conditions: the effects of oxygen mass flux”, details the experimental and numerical results for quantifying the effects of oxygen mass flux in applied smouldering systems.
4. Chapter 5 titled “Delineating the role of fuel mobility in applied smouldering systems”,
determines the effects of fuel mobility in applied smouldering systems and quantifies
the role of fuel saturation, air flow, and porous medium characteristics.

5. Chapter 6: summarizes the findings in this thesis as well as recommendations for future
work on applied smouldering systems.

6. Appendices: provide supplemental information, referenced throughout the thesis that
was not included in the manuscript chapters.

   a) Appendix A provides the Supplementary Material for Chapter 3 including
      additional numerical modelling and further details and assumptions.

   b) Appendix B provides the Supplementary Material for Chapter 4 including the
details on experimental results, chemistry, and energy analysis.

   c) Appendix C provides the Supplementary Material for Chapter 5 including
canola oil chemistry and energy analysis.

1.4 References


treatment of hydrocarbon-impacted soils: a review of technology innovation for sustainable


[15] T.A. Fournie, Exploring Valuable and Potentially Harmful By-Products Formed and/or Released from Smouldering Treatment of Sewage Sludge, The University of Western Ontario (Canada), 2022.


Chapter 2

2 Literature Review

2.1 Introduction

This literature review focuses on environmental contamination, contaminant remediation technologies, and smouldering combustion. This review places most emphasis on the smouldering principles, processes, and engineering applications associated with the research in this thesis, specifically looking at heat transfer through porous media, multi-dimensional transfer effects associated with radial heat losses, heterogeneity, oxygen mass flux, fuel mobility, and local and global energy balances.

2.2 Contamination and Remediation Technologies

A large class of industrial organic compounds are non-aqueous phase liquids (NAPLs), which are among the most hazardous contaminants impacting soil and groundwater [1]. NAPLs are generally categorized into (i) LNAPLs (e.g., hydrocarbon fuels such as heating oil with density < 1000 kg m\(^{-3}\)) and (ii) DNAPLs (e.g., chlorinated hydrocarbon such as trichloroethylene (TCE) and tetrachloroethylene (PCE) with density > 1000 kg m\(^{-3}\)). DNAPLs are highly challenging contaminants as they can penetrate the water table, distribute heterogeneously in the saturated zone, and remain there for many decades due to their low solubility and high resistance to degradation [2]. Figure 2.1 presents a conceptual model of a DNAPL source zone.

DNAPLs can exist in gaseous and liquid phases within the subsurface. DNAPLs can evaporate and volatilize within the vadose zone, while undissolved DNAPLs can exist as free (pool) and/or residual phases. DNAPLs can also exist as dissolved phase concentrations within groundwater, which can extend large distances and pose significant risks to human health and the environment [3].
A range of remediation technologies have been developed and implemented at DNAPL-contaminated sites. Depending on the phase of DNAPL existing within the subsurface, remediation could involve: (i) in-situ methods, such as chemical oxidation \[5\], biodegradation \[6\], and thermal treatment \[7\]; and (ii) extraction for subsequent ex-situ treatment, such as the pump-and-treat method where contaminated groundwater is pumped out of the ground and subsequently treated \[49\].

Thermal treatment technologies are in-situ remediation techniques that includes: (i) hot air injection, which increases contaminant mobility and extraction efficiency \[8\]; (ii) steam injection to increase both contamination mobility and biodegradation rates \[9\]; (iii) radio frequency heating/microwave heating that volatilizes contamination, increases mobility, and enhances microbial degradation rates \[10\]; (iv) in-situ vitrification which melts and fuses contaminants and soil into a glass-like solid using very high temperatures (1600-2000
°C) [11]; (v) pyrolysis that desorbs the contaminants and breaks their chemical bonds [12]; (vi) incineration to destroy contaminants in high temperatures [13]; (vii) thermal desorption to volatilize/desorb the contaminants [14]; and (viii) applied smouldering for desorption, pyrolysis and exothermic oxidation.

2.3 Smouldering Remediation

2.3.1 Smouldering Combustion

Smouldering is defined as a flameless form of combustion driven by oxygen attacking the surface of a condensed phase fuel [15], as shown by the charcoal barbeque and cigarette examples in Figure 2.2. The fuel must be porous, meaning it should be either a (i) porous organic solid or (ii) organic liquid or solid fuel embedded in an inert porous matrix where air can flow through the pore space.

Porous organic solids (as fuel) are characterized by low thermal conductivity [16, 17] and volumetric heat capacity [16-18], high porosity [16, 18, 19], and relatively homogeneous fuel concentration. The best examples are polyurethane foam [20, 21], peat [19, 22], and tobacco [23]. Smouldering of such fuels is the leading cause of death in residential and wildfires [24] and a source of concern in space and commercial flights [25, 26].
Examples of organic liquids or solids fuel applicable in various engineering applications are oil [29], faeces [30], wastewater sludge [31], granular activated carbon [32, 33], coal tar [34], and bitumen [35]. These fuels can be mixed in an inert porous medium (e.g., sand) to support smouldering treatment. These mixtures are characterized by low fuel concentrations (e.g., 1-10% by mass), low porosity [16, 18, 19], high volumetric heat capacity [16-18], and an inert porous medium [36, 37] in which energy can be stored and recycled more efficiently than from smouldering porous organic solids. These features allow smouldering to have self-sustained propagation, meaning the heat released during the exothermic process sustains combustion, as long as the local energy balance rate is positive [38].

2.3.2 Applied Smouldering for NAPL Remediation

The application of smouldering combustion for remediating contaminants in an inert porous medium is called Self-Sustaining Treatment for Active Remediation (STAR) [34,
During the STAR process, energy is injected into contaminated soil using convection, conduction, or radiation to heat a small volume of soil to the contaminant’s smouldering ignition temperature. By supplying oxygen via air injection, smouldering combustion will be ignited. If the mixture conditions promote “self-sustaining” smouldering, then the external heater energy can be removed. The pyrolysis and oxidation reactions convert the contaminant primarily into carbon dioxide (CO₂), water (H₂O), and heat, leaving only clean treated soil behind [45]. An example of contaminated soil before and after STAR remediation is shown in Figure 2.3.a.

Figure 2.3: Examples of condensed liquid fuel in an inert porous medium: (a) oil-contaminated soil before (left) and after (right) remediation (photo courtesy of Savron Solutions) and (b) oil shale (adapted from Martins et al. [29]).

The opportunities associated with this technology are:

1. It can safely treat a wide range of contamination including: (i) fecal matter [44], (ii) biosolids from wastewater treatment plants [30, 31, 46], (iii) organic liquid waste from industrial activities [34, 39-41, 43, 47-49], and (iv) recalcitrant compounds found widely in the environment, e.g., per- and polyfluoroalkyl substances (PFAS) [33, 50, 51].

2. STAR can be applied (i) in-situ, which has been shown by several successful pilot-scale field tests [41, 52]; or (ii) ex-situ in the reactors above ground that can stretch across scales, from the laboratory (e.g., 0.003 m³), to intermediate (e.g., 0.3 m³), to pilot-field (e.g., 3 m³ and larger [37, 53-55]). These ex-situ systems are currently most used to treat organic liquid wastes with limited disposal options (e.g., oil sludge) [56-58].
3. The self-sustaining nature of smouldering combustion offers a relatively low-cost and low-energy engineering technique. For example, compared to common methods for organic liquid waste treatment (e.g., incineration [7], pyrolysis [59], and gasification [60]) which require a continuous supply of additional fuel or heat), smouldering can operate without additional heat or fuel and therefore is a cost-effective and technically efficient method [7].

However, the challenges associated with this technology are:

1. Radial heat losses from smouldering reactors cause multi-dimensional effects (e.g., in temperature, air flow, and chemical reactions), which control system performance and operational limits (e.g., peripheral extinction can decrease the remediation efficiency and possibly lead to process failure).

2. Sufficient oxygen transport to the smouldering front is required; therefore, low soil permeability (e.g., in fine-grained soil) or high permeability heterogeneity (e.g., in poorly sorted media) may limit oxygen transport and lead to slower front propagation, lower peak temperatures, and global quenching in critical cases.

3. Minimum contamination (i.e., fuel) saturation is required and liquid fuel mobility during the process might introduce the contamination to areas that were previously clean.

4. Air pollution control is required to capture vaporized/volatilized contaminants and emissions from chemical reactions, e.g., incomplete combustion by-products like carbon monoxide (CO).

5. Soil destruction or undesirable transformations due to smouldering at high temperatures (600-1100 °C). Figure 2.4 illustrates smouldering propagation in the in-situ STAR process.
Recently, a smouldering-driven pyrolysis reactor was developed as a novel technology for pyrolyzing waste (e.g., plastics and propylene). This reactor is composed of two chambers: (i) smouldering chamber to drive energy needed for pyrolysis (e.g., a mixture of sand and char with 2.0 to 2.8% char concentration), which generates a heat wave characterized by a consistent peak temperature and propagation speed; and (ii) pyrolysis chamber for waste valorization using the energy released from smouldering [61, 62]. A highly thermal conductive porous medium enables a uniform radial temperature distribution. An illustration of the reactor is shown in Figure 2.5.

The bottom of the smouldering chamber is equipped with a cone heater that provides heat to ignite the char through quartz glass, also an insulation layer (e.g., ceramic fibre) outside of the smouldering chamber to reduce heat losses. After char ignition, smouldering will
propagate in a self-sustaining manner without the external energy input and drive the energy needed to pyrolyze the waste in the centre of the system.

Figure 2.5: Illustration of smouldering-driven pyrolysis reactor (adapted from Pan et al. [61]).

Applied smouldering has also been used in other applications, including (i) resource recovery [63], (ii) waste-to-energy [64, 65], (iii) pyrolysis and gasification (e.g., for CO and H₂ production) [66-69], (iv) enhanced oil recovery [29, 70], (v) underground coal gasification [71], and (vi) iron ore sintering [72, 73]. Overall, the industrial applications of smouldering combustion are evolving, despite challenges and operational problems; therefore, robust numerical modelling can enhance our understanding of smouldering combustion and raise the effectiveness of smouldering-based technologies.
2.4 Numerical Modelling of Smouldering

Numerical models are effective tools to better understand the complex phenomena associated with smouldering. These models are typically developed at the Representative Elementary Volume (REV) scale, over which average properties can be estimated. Although analytical solutions are useful for a general understanding of various phenomena, they are not possible in most smouldering contexts, e.g., in where many chemical reactions compete and overlap in space and time, and when local thermal equilibrium (LTE) is not valid. In these cases, numerical models are needed to understand smouldering dynamics.

Smouldering combustion is a complex phenomenon including heat transfer processes and chemical reactions. Heat transfer mechanisms relevant to forced air through an inert porous medium are central to smouldering applications. The heat released by exothermic reaction during smouldering propagation is partially stored in the porous medium, partially transferred ahead by heat transfer mechanisms at the pore scale (e.g., conduction between two grains of sand, convection between the sand and air, and radiation between two grains), and partially lost to the surroundings [74-77]. Hot combustion gases pre-heat the virgin fuel ahead of the smouldering front, creating the pyrolyzed material called char, which is subsequently oxidized by oxygen attack on its surface [38]. As smouldering occurs with highly exothermic reactions and with a large range of time and length scales, the Local Thermal Non-Equilibrium (LTNE) approach [78] is required in which solid temperature \( T_s \) differs from the gas temperature \( T_g \) [79, 80].

Figure 2.6a shows a schematic of the smouldering of organic contamination (e.g., bitumen) embedded in an inert porous medium (e.g., sand) to clarify the heat transfer mechanisms at the pore scale and main physical, energy, and temperature zones in smouldering systems. As it is extremely challenging to quantitatively describe or model all of the relevant heat transfer mechanisms at the pore scale, it is therefore practical to consider the transport of mass, momentum, and energy at the REV scale [17]. Figures 2.6b, 2.6c, and 2.6d determine the physical, energy, and temperature zones at the macro-scale including (i) treated ambient (treated cold clean sand), (ii) cooling (treated hot clean sand where the energy is stored), (iii) smouldering (smouldering front where energy is generated), (iv) preheating (pyrolysis
front where energy is deposited), and (v) treated ambient (e.g., a mixture contaminated with the organic fuel in sand).

Figure 2.6: Conceptual model of an upward-forward smouldering front of an organic contamination (e.g., bitumen) embedded in an inert porous medium (e.g., sand) that clarifies (a) heat transfer processes in pore scale between solid and gas phases, (b) physical, (c) energy, and (d) temperature in macro-scale, also temperature distribution along the reactor where the smouldering front is in the middle of the reactor (modified from Hobbs et al. [81] and Gerhard et al. [45]).

2.4.1 1D Numerical Models

One-dimensional (1D) numerical models are powerful tools to investigate the kinetics of key reactions [16, 20, 82] and the interaction between local and global energy balances in smouldering systems that govern self-sustained propagation [35, 38, 83-85]. In 1D models, a global heat loss coefficient is used as a sink term to simulate the net effect of heat losses [35, 38, 84], which is often calibrated to experimental observations [86].
### 2.4.2 2D Numerical Models

While 1D smouldering models have elucidated various fundamental smouldering characteristics described above [83], they are unable to (i) simulate the multi-dimensional transfer effects across the radius of the reactor, (ii) energy redistribution in the weak smouldering systems by changing the effective radius of the reactor due to peripheral extinction [85], (iii) multi-dimensional smouldering propagation due to the intrinsic permeability and fuel concentration heterogeneity.

Therefore, two-dimensional (2D) models are required to (i) more realistically capture multi-dimensional transfer effects in temperature, air mass flux, oxygen mass flux, and chemical reactions associated with radial heat losses, which can deteriorate smouldering robustness [22, 77, 87-91]; (ii) consider the effective radius of smouldering that could shrink due to peripheral extinction, especially if smouldering is propagating in a weak condition; (iii) quantify the smouldering front deformations due to heterogeneities in porous medium or fuel concentration, or changing the smouldering robustness across weak to robust conditions [37]; and (iv) capturing the radial heat wave produced by smouldering for pyrolyzing purposes [61, 62].

These multi-dimensional effects are generally poorly understood, particularly at larger scales. Without a clear understanding of multi-dimensional effects, it is difficult to design larger, commercial-scale smouldering systems [92]. Therefore, robust numerical models are needed.

Figure 2.7 shows the output from a 2D smouldering model that developed to better understand the dynamics in a char smouldering-driven reactor for plastic waste pyrolysis [62]. Figure 2.7a shows the char mass fraction (i.e., in the smouldering chamber) where all of the char was consumed at the front and only clean sand remains behind. Figure 2.7b confirms all of the oxygen was not consumed at the front (i.e., oxygen-rich condition), also Figures 2.7c, and 2.7d shows a thin smouldering front generated intense heat of $1.34 \times 10^7$ W m$^{-3}$, which resulted in a high peak temperature of 773 °C (Figure 2.7e).
Figure 2.7: 2D numerical modelling of smouldering combustion. (a) char mass fraction ($Y_{\text{char}}$), oxygen mass fraction ($Y_{O2}$), char reaction rate ($R_{\text{char}}$), smouldering heat source, and solid temperature ($T_p$) (adapted from Pan et al. [62]).

Previous 2D smouldering modelling studies are summarized in Table 2.1. Note that most of the studies in Table 2.1 explore the smouldering of porous organic solids rather than organic fuels in inert matrices. However, a phenomenological 2D smouldering model did successfully predict smouldering front evolutions in heterogeneous domains relevant for applied smouldering [36, 37, 93]; however, it did not simulate heat transfer and chemical reactions [36, 93, 94]. This validated phenomenological model has been used for sensitivity analyses on key design parameters including soil permeability and fuel concentration heterogeneity (i.e., measured as waste oil sludge (WOS) saturation). The model showed that smouldering systems could operate well with high levels of heterogeneity in WOS saturation (e.g., due to poor mixing), but were highly sensitive to heterogeneity in the soil permeability (e.g., from using poorly sorted soil).
Table 2.1: 2D Numerical Smouldering Models Available in the Literature

<table>
<thead>
<tr>
<th>Porous Medium</th>
<th>Fuel</th>
<th>Motivation</th>
<th>Discussion</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina Bead</td>
<td>Carbon</td>
<td>- Heat loss</td>
<td>- Effect of radial heat loss</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Front shape stability</td>
<td>- Smouldering front shape</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>Char</td>
<td>- Waste pyrolysis</td>
<td>- Effects of char concentration, air inlet velocity, and oxygen concentration</td>
<td>[61]</td>
</tr>
<tr>
<td>Sand</td>
<td>Char</td>
<td>- Plastic waste pyrolysis</td>
<td>- Effects of char concentration, Darcy air velocity, and pyrolysis chamber radius</td>
<td>[62]</td>
</tr>
<tr>
<td>Peat</td>
<td>Peat</td>
<td>- Heat loss</td>
<td>- Effect of radial heat loss, sample width, ambient temperature, and oxygen mass fraction</td>
<td>[95]</td>
</tr>
<tr>
<td>Peat</td>
<td>Peat</td>
<td>- Quenching distance</td>
<td>- Effect of oxygen concentration and wind velocity</td>
<td>[96]</td>
</tr>
<tr>
<td>Peat</td>
<td>Peat</td>
<td>- Chemistry analysis</td>
<td>- Introducing transition thresholds for smouldering types</td>
<td></td>
</tr>
<tr>
<td>Cellulosic material</td>
<td>Cellulosic material</td>
<td>- Heat loss</td>
<td>- Investigation of the mechanisms controlling smouldering</td>
<td>[87]</td>
</tr>
<tr>
<td>Polyurethane foam</td>
<td>Polyurethane foam</td>
<td>- Heat loss</td>
<td>- Investigation of the complexity of the reaction mechanism</td>
<td>[89]</td>
</tr>
<tr>
<td>Charcoal</td>
<td>Charcoal</td>
<td>- Heat loss</td>
<td>- Investigation of oxygen concentration</td>
<td>[90]</td>
</tr>
<tr>
<td>Foam insulation</td>
<td>Foam insulation</td>
<td>- Heat loss</td>
<td>- Effect of radial heat loss</td>
<td>[91]</td>
</tr>
<tr>
<td>Foam insulation</td>
<td>Foam insulation</td>
<td>- Heat loss</td>
<td>- Effect of radial heat loss</td>
<td>[97]</td>
</tr>
<tr>
<td>Carbonaceous rod</td>
<td>Carbonaceous rod</td>
<td>- Heat loss</td>
<td>- Effect of radial heat loss and oxygen distribution</td>
<td>[98]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Diffusion of oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cigarette</td>
<td>Cigarette</td>
<td>- Heat loss</td>
<td>- Effect of radial heat loss</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Diffusion of oxygen</td>
<td>- Radial oxygen mass transfer</td>
<td></td>
</tr>
</tbody>
</table>
Most of the 2D numerical models in Table 2.1 were developed and validated to show multi-dimensional transfer effects of temperature [22, 23, 95, 98], air mass flux [77, 99], oxygen mass fraction [90, 97], heat release rate [95], smouldering front shape, smouldering velocity, and propagation [22, 77, 96, 98], and peripheral extinction [22, 87, 89, 95]. These effects were largely driven by heat losses, which decrease temperatures [23, 95] and therefore the rate of chemical reactions and oxygen consumption near the wall relative to the centerline [97].

2.5 Effects of Radial Heat Losses

The key parameters that control smouldering are the chemistry (e.g., pyrolysis and oxidation), and heat and mass transfer processes in the porous medium. Self-sustained smouldering depends on a positive energy balance, in which the rate of energy gained from oxidation exceeds the energy lost to heat sinks (e.g., water), endothermic reactions (e.g., pyrolysis), and radial losses [31, 44, 100]. When this balance becomes negative, the reaction can decline toward extinction [38, 101].

Of these loss terms, radial heat loss is one of the most significant [19, 22, 75, 102]. It negatively affects the energy balance and causes a non-uniform temperature distribution along the radius of the smouldering reactor (i.e., introduces multi-dimensional transfer effects). Heat losses, in particular, affect the smouldering energy balance in bench-scale reactors with high surface area to volume ratios, where 28-52% of total energy is often transferred out of the system [35, 77]. Heat losses at the system walls have a strong impact locally, despite the large diameter of the system (e.g., 0.50 m) [77]. Moreover, the spatial distribution of temperature can cause thermal heterogeneity due to the temperature-
dependent density and viscosity of air, which in turn may have a significant impact on air flow distributions and smouldering characteristics [103].

Heat losses can significantly affect the smouldering front shape curvature, its velocity [29, 77], inclination, and stability near the system wall, as it decreases the smouldering temperature and, consequently, the chemical reaction rates. The fraction of carbon oxidized and the fraction of oxygen consumed by the front depend on the front temperature, which is affected by heat loss. Also, peripheral extinction (i.e., unconsumed fuel near the wall) can occur due to high heat losses [22]. Altogether, heat losses lead to many complications.

Figure 2.8 shows a comparison of smouldering front shapes in separate numerical and experimental investigations. Figure 2.8a shows that by changing the fuel saturation from 3.6 to 2.3%, the smouldering front shape was predicted to change from concave to convex shape, relative to the air flow direction. When radial heat losses are negligible, the front is mostly flat and propagates faster [77, 89, 91]. Figure 2.8b provides experimental evidence of more rapid progress of the front at the walls (concave shape). The authors hypothesized that the results in Figure 2.8b were due to local increased density and decreased viscosity of air near the walls because of the lower local temperatures from radial heat losses [29].
2.6 Effects of Heterogeneity

Smouldering is a process that changes the porous medium properties in time as well as space. Heterogeneity is defined as the non-uniform distribution of properties in space. Two main types of heterogeneity include (i) physical heterogeneity associated with spatial differences in porous medium permeability, fuel concentration, porosity, bulk density, or water content; and (ii) thermal heterogeneity associated with spatial differences in porous medium thermal conductivity, heat capacity (porous medium energy sink), bulk density (heat storage per unit volume), and water content (intergranular heat sink).

Physical and thermal heterogeneity can change over time; for example, the fuel accumulation (in the preheating zone) and elimination (in the cooling zone) will increase and decrease the effective air permeability, respectively, mobilization and volatilization of contamination during smouldering remediation will redistribute the fuel concentration, and heat capacity is a function of temperature. For each of these parameters, there are limits outside of which self-sustained smouldering propagation is not possible. For example, smouldering propagation is difficult in clay due to its low air permeability [104].
2.6.1 Physical Heterogeneity

Physical heterogeneity can be associated with spatial differences in porous medium intrinsic permeability, fuel concentration, porosity, bulk density, and water content. All of these are expected to impact the heterogeneity of effective air permeability, which is a critical parameter since it has a dominant effect on air flow patterns, which in turn dictate smouldering reaction robustness and propagation. Nevertheless, very few smouldering studies have explored the influences of physical heterogeneity.

Permeability heterogeneity is typically associated with the distribution of less permeable material in a more permeable matrix (or vice versa). A modelling study of smouldering soil piles revealed a large contrast in effective air permeability between less and more (i) porous medium intrinsic permeability (Figure 2.9a, 2.9b, and 2.9c) and (ii) contaminated material (regions with different fuel saturations) (Figure 2.9d, 2.9e, and 2.9f) that may cause preferential air flow and smouldering channelling in the high permeable and less contaminated regions [37]. Smouldering channelling is defined as faster smouldering propagation in one zone relative to others, which may smoulder later (or not at all), and may cause extinction in several ways. For example, extinction can occur when the fraction of air that passes through a high permeability zone increases and the smouldering front in the low permeability zone is starved of oxygen [105]. Generally, it is well known that smouldering front velocity is proportional to Darcy air flux [38], smouldering often quenches in locations where the Darcy air flux is less than 0.5 cm s\(^{-1}\) [36, 48, 93, 94].

Figures 2.9b and 2.9c illustrate fast smouldering in the most permeable material, slow smouldering in the porous medium of intermediate permeability, and no smouldering in the porous medium with the finest particles. This means that the formation of preferential smouldering channels can leave sections of the fuel bed untreated [36] and therefore cause poor performance of an applied smouldering treatment system [41].

One laboratory-based study was conducted to explore the practical limits of smouldering treatment with layers of varying permeability and orientation relative to the direction of smouldering (i.e., layers in series, parallel, and combined). The results suggested that, under fixed air flux delivered to a column, smouldering can successfully propagate through
the layers in series despite having a permeability contrast of more than 1000:1. However, parallel layers with a permeability ratio above 3:1 can challenge smouldering and even cause extinction by distorting or channelling the smouldering front [106].

Also, heat losses via conductive heat transfer between two parallel layers with different permeabilities, termed “thermal coupling”, can retard the smouldering propagation velocity in the high permeability layer and slightly increase the propagation velocity in the low permeability layer [107]. Conductive heat transfer between layers can even cause sufficient energy losses from the reactions to cause extinction [107]. However, there is only one study with column experiments [104] and one analytical modelling study [107] that hypothesize that smouldering channelling and thermal coupling can cause extinction.

Overall, limited studies suggest that smouldering channelling may occur and deteriorate treatment performance under conditions of (i) high heterogeneity of fuel saturation or (ii) moderate to high heterogeneity of porous medium permeability. However, it is noted that the modelling that produced Figure 2.9 neglected numerous system properties such as water content, temperature-dependent fluid properties, and heat transfer between layers as the model did not solve the energy equations [36]. Therefore the results in Figure 2.9 are phenomenological and need to be further explored.
Figure 2.9: (a-f) Predicted smouldering front positions at breakthrough (200 m) and end of treatment (2300 m) for cases with high variance in permeability (a-c, simulation 3m) and saturation (d-f, Simulation 3r) (adapted from Solinger et al. [94]). (g) model domain set up, (h) distribution of air and the position of the smouldering front at 10.4 min, (i) contour plot depicting the position of the smouldering front at 2.1 min intervals from $t = 0$ to 1500 s (25.0 min) (adapted from MacPhee et al. [36]).
2.6.2 Thermal Heterogeneity

Thermal heterogeneity can be associated with spatial differences in key porous media properties, e.g., thermal conductivity, heat capacity (porous media energy sink), bulk density (heat storage per unit volume), and water content (intergranular heat sink), which all cause spatial and temporal variations in the temperature.

Considering previous research, a few examples explored the role of mineral (e.g., soil) and moisture content heterogeneity in peat (i.e., a porous organic solid). Peat is partially decayed vegetation matter that accumulated and decomposed in wetlands. The mineral and moisture content reduces the fuel load (i.e., organic content) per total mass and also results in a lower net heat release value because of the evaporation of water and the heat capacity of the mineral [108]. Heat capacities and thermal conductivities of the mineral content affect temperature distribution, as they act as a heat sink and enhance heat transfer via its higher thermal conductivity [19].

Moisture content is an important energy sink that can seriously impact smouldering ignition and propagation [108-111]. As the moisture content increases, smouldering propagation becomes less sensitive to other parameters (e.g., depth of peat layer and air flow rate), because it is a dominant factor in the energy balance [109]. The distribution of water changes during smouldering occurs due to water boiling immediately ahead of the front and condensation in colder regions distant from the front [111]. If smouldering is robust, then small amounts of water can be easily evaporated by hot gases ahead of the smouldering zone; if smouldering is not robust, then peak temperature decreases as the moisture content increases, eventually leading to extinction at critical conditions. If the amount of water exceeds a limiting value during upward smouldering, there is the possibility that water ahead of the reaction may flow downward into the reaction and quench smouldering [44]. There are important feedback mechanisms at work in smouldering systems, where air flow patterns affect temperature distribution, and temperature distribution affects reaction chemistry and rates, and chemistry impacts smouldering front propagation, which in turn affects air flow patterns. Moreover, the properties of both the air and the porous media are themselves a function of temperature, as shown in Table 2.2.
Table 2.2 reveals key thermophysical effects relevant to applied smouldering. For example, as temperatures increase from ambient to 1000 °C, Table 2.2 reveals that the heat capacity of air increases by 36% and sand increases by 229%, while the viscosity of air increases by 118%. Thus, heterogeneity in system thermal properties can therefore both cause and result from spatial differences in temperature [77].

Table 2.2: Thermal Properties of Sand and Air at the Temperatures relevant to Applied Smouldering.

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
<th>Temperature Range (K)</th>
<th>Thermal Property Range</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>Thermal Conductivity</td>
<td></td>
<td>0.278-0.730 (W/ m K)</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td>Heat Capacity</td>
<td></td>
<td>768.6-2530 (J/ kg K)</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
<td>293-1000</td>
<td>1.7e-5 – 3.7e-5 (Pa. s)</td>
<td>[113]</td>
</tr>
<tr>
<td>Air</td>
<td>Heat capacity</td>
<td></td>
<td>1004-1136.5 (J/ kg K)</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td>Thermal Conductivity</td>
<td></td>
<td>0.026-0.0743 (W/ m K)</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td></td>
<td>1.2-0.35 (kg/ m³)</td>
<td>[113]</td>
</tr>
</tbody>
</table>

There are numerous implications of temperature-sensitivity properties. For example, air that travels through hot zones increases in viscosity and decreases in density, which induces a low air-conductivity zone. This low conductivity causes air to preferentially flow in higher conductivity and cooler regions, which can impact the smouldering pattern [103, 114]. This effect is shown by the simulated air velocity distribution in Figure 2.10, which shows a central ignition point causing a non-uniform smouldering front growing radially, corresponding to temperature variations that, in turn, affect air flow distribution. However, the specific link between the air flow and temperature distributions shown in the simulation [99] was not explored in detail.
Figure 2.10: Field of gas velocity at (a) t=2 and (b) t=6 after the time of ignition when the ignition zone is located in the central part of porous media, (c, d) contours bounding that completely burnt combustible component of the solid medium at different times after the ignition: t = 1 (curve 1), t = 3 (2), t = 5 (3), t = 7 (4), t = 9 (5), and t = 11 (6), when the ignition zone is located in the central part of object bottom (adapted from Lutsenko [99]).

Heterogeneity in each of the mentioned parameters can challenge real-world applications [41]. For example, subsurface heterogeneity of physical soil properties and contaminant distribution can affect the performance of all in-situ remediation systems (e.g., STAR) directly and indirectly via their effects on air flow rates and patterns [48]. Therefore, a failure to understand or appreciate the effects of heterogeneity on smouldering can result in poor performance or failure of smouldering based engineering processes [37, 104].
2.7 Effects of Oxygen Mass Flux

In engineering applications, oxygen supply (which is often moderated via air delivery) controls many smouldering features including (i) processing rate [61], (ii) ignition time and temperature [17], (iii) peak temperatures, (iv) smouldering front velocity and thickness [61], (v) residual fraction of organic compounds, and (vi) the fate of smouldering in critical cases [38, 95, 115].

Smouldering systems are generally operated in robust oxygen-limited conditions, where oxygen diffuses from the bulk phase (i.e., in the pore space) to the surface of condensed fuel, adsorbs onto the surface of the fuel, reacts, and then the emissions of these reactions desorb and diffuse into to the bulk phase. See a simplified global reaction for granular activated carbon (GAC), which is nearly entirely carbon [116]:

\[
GAC + \left(\frac{Fr_{co}}{2} + (1 - Fr_{co})\right)O_2 \xrightarrow{R_{GAC}} Fr_{co} CO + (1 - Fr_{co}) CO_2
\]  

(2.1)

where \( Fr_{co} \) is the mole fraction of CO. \( Fr_{co} \) is an important parameter as it strongly affects \( \Delta H_{GAC} \), e.g., as \( Fr_{co} \) decreases from 1 to 0, \( \Delta H_{GAC} \) increases from 110.5 to 393.5 kJ mol\(^{-1}\) [117]. While pure carbon with \( Fr_{co}=0.27 \) results in \( \Delta H_{GAC} = 26.4 \) MJ kg\(^{-1}\), this value was corrected for the 2.2% unreactive and 3.2% water content measured in the GAC (which lowered \( \Delta H_{GAC} \) by 1.5 MJ kg\(^{-1}\)); therefore, \( \Delta H_{GAC} = 24.9 \) MJ kg\(^{-1}\) is the corrected value to be used in the numerical modeling, agreeing with [117]. Therefore, oxygen transport equations at the bulk (\( bk \)) and surface of fuel (\( sf \)) might be separated and described as [91]:

\[
\frac{\partial (\phi_{bk} \rho_g Y_{O_2,bk})}{\partial t} + \frac{\partial (\rho_g u_r Y_{O_2,bk})}{\partial r} + \frac{\partial (\rho_g u_z Y_{O_2,bk})}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \phi_{bk} \rho_g D_{g,bk} \frac{\partial Y_{O_2,bk}}{\partial r} \right) \\
+ \frac{\partial}{\partial z} \left( \phi_{bk} \rho_g D_{g,bk} \frac{\partial Y_{O_2,bk}}{\partial z} \right) + h_m a_{sg} (Y_{O_2,sf} - Y_{O_2,bk})
\]  

(2.2)
\[ \frac{\partial (\phi_{sf} \rho_g Y_{O_2,sf})}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \phi_{sf} \rho_g D_{g,sf} \frac{\partial Y_{O_2,sf}}{\partial r} \right) \]
\[
+ \frac{\partial}{\partial z} \left( \phi_{sf} \rho_g D_{g,sf} \frac{\partial Y_{O_2,sf}}{\partial z} \right) + h_m a_{sg} (Y_{O_2,bk} - Y_{O_2,sf}) - \dot{Q}_{O_2} \]

(2.3)

where \( \phi = \phi_{bk} + \phi_{sf}, a_{sg} = 6(1 - \phi)/d_p \), and \( \dot{Q}_{O_2} \) represents the porosity, specific surface area, and volumetric oxygen sink term. \( h_m \) is the volumetric mass transfer coefficient determined by the analogy to heat transfer according to Incroprera [113]:

\[ h_m = \frac{h_{sg}}{\rho_g C_p g Le^{(1-n)}} \]

(2.4)

where \( h_{sg} \) is the interfacial heat transfer coefficient between solid and gas, \( Le = \alpha/D_g \) is the Lewis number, \( \alpha \) is the thermal diffusivity, and \( D_g \) is the diffusion coefficient. Currently, there is no robust description for \( h_m \), and further investigation into this parameter is needed [15]. The oxygen supply and consumption rates can be adjusted in applied smouldering systems for process optimization [38, 118], where it plays a key role in defining (i) ignition time and temperature, (ii) smouldering robustness, (iii) oxygen- or fuel-rich conditions, and (iv) quenching conditions due to dynamics that need to be resolved in space and time [15, 38, 61, 95].

Some smouldering dynamics are intuitive, and others are not. Low oxygen concentration will result in weak fuel-rich smouldering (i.e., where all oxygen is consumed at the front and global net energy balance is still positive but close to 0) with cooler peak temperatures, slower smouldering velocities, peripheral extinction or global quenching (i.e., negative global energy balance) as a form of system failure [17, 18, 119-121]. Conversely, in a fire safety context, smouldering quenching is desired while robust smouldering should be avoided [15]. In this context, oxygen concentration is a critical parameter that controls
smouldering propagation and transition to flaming where the oxygen concentration threshold for fire activity on the earth is defined as 11-16 % [96, 122]. In both fire safety and engineering application, oxygen reductions can also lead to unexpected effects due to the interplay between chemical and physical processes (e.g., super-adiabatic effects).

Figure 2.11a shows the effect of oxygen concentration where the smouldering ignition time (i.e., due to a higher oxidation rate and local energy generation rate) and temperature, decreased by increasing the oxygen concentration where higher oxygen concentration was consumed. Figure 2.11b shows the radial mean peak temperature ($T_s$) was insensitive to oxygen concentration as the process was in oxygen-rich condition; however, smouldering peak temperature ($T_{s,p}$) decreased slightly due to decreasing the smouldering front thickness (Figure 2.11c). Also, by increasing the smouldering front velocity ($v_f$), smouldering duration decreased (Figure 2.11d) [61].
Figure 2.11: Effects of oxygen concentration on (a) ignition time and temperature, (b) longitudinal radial-mean $\overline{T_s}$ profile, (c) average peak temperature ($T_{s,p}$), and smouldering front velocity ($v_{f,s}$), (d) smouldering duration (modified from Pan et al. [61]).

Across the smouldering literature, inlet air flux is routinely investigated as a key sensitivity parameter, as it controls both oxygen supply, convective heat transfer rates in smouldering systems [21, 34, 44, 46, 118], and cooling front velocity ($v_c$), defined as:

$$v_c = \frac{\rho g C_p u_g}{(\rho C_p)_{eff}}$$  \hspace{1cm} (2.5)

In applied smouldering systems, low inlet air flux systems (~0.5 to 1.4 cm s$^{-1}$) foster decreased oxygen supply and convective heat transfer, which therefore results in low peak temperatures and slow smouldering velocities [123, 124]. High inlet air flux systems (~2.5 to 8.3 cm s$^{-1}$) exhibit high temperatures and fast smouldering velocities (up to 0.5 cm min$^{-1}$).
However, at very high inlet air flux (i.e., greater than 30 cm s$^{-1}$), convective cooling can decrease peak temperatures [125, 126].

A previous study [127] provides experimental, numerical, and asymptotic analysis to determine adiabatic temperature, and smouldering front velocities for transition from fuel-rich to oxygen-rich in opposed smouldering of wood particles by increasing the inlet air flux beyond the stoichiometric limit. In the fuel-rich condition, oxygen was fully consumed in the reaction zone, leaving the char unconsumed after the smouldering front passed. However, oxygen-rich was characterized by total fuel consumption and excess oxygen flow downstream of the smouldering front (Figure 2.12).
Figure 2.12: The effects of increasing inlet air flux on (a) adiabatic temperature, and (b) smouldering front velocity, by transition from fuel-rich to oxygen-rich. (c, d) the comparison between experimental, numerical, and asymptotic results (modified from Fatehi et al. [127]).
Aldushin et al. [128] showed how the structure of the forward smouldering smoulder wave is fundamentally dictated by the difference between smouldering front velocity \( (v_f) \) and cooling front velocity \( (v_c) \), which may be described as reaction leading (i.e., \( v_f > v_c \) [15, 37, 41, 45, 64], reaction trailing (\( v_f < v_c \)), or super-adiabatic (\( v_f = v_c \)) [128]. Super-adiabatic singularity is a local temperature higher than the adiabatic flame temperature which refers to combustion process that takes place adiabatically (i.e., no heat losses) with no external work in which the maximum temperature of products will achieve [129]. Figure 2.13 shows a conceptual model of these three descriptions, where diluted oxygen with an inert gas, e.g., nitrogen (N\(_2\)), can slow down \( v_f \) to equal \( v_c \), as \( v_c \) is largely insensitive to the oxygen concentration [120, 130]. This condition leads to a super-adiabatic singularity where all energy released from robust smouldering accumulates in a thin reaction region and increases the peak temperature towards infinity [128, 131].
Figure 2.13: (a) reaction leading (i.e., \( v_f > v_c \)), (b) reaction trailing (i.e., \( v_f < v_c \)), (c) super-adiabatic (i.e., \( v_f = v_c \)) for forward smouldering front. The ambient temperature \( (T_0) \), peak temperature \( (T_p) \), smouldering front velocity \( (v_f) \), Darcy air flux \( (u_g) \), and cooling front velocity \( (v_c) \) are noted (modified from Aldushin et al. [128] and Rashwan et al. [132]).
A simplified description of $T_p$ from smouldering propagation can be used to highlight super-adiabatic ($v_f = v_c$) condition [29, 128]:

$$T_p = T_{amb} + \frac{m_{fuel}}{m_s} \frac{\Delta H_{fuel}}{C_p s \left(1 - \frac{v_c}{v_f}\right)} = T_{amb} + \frac{T_{adiabatic}}{C_p s \left(1 - \frac{v_c}{v_f}\right)}$$  \hspace{1cm} (2.6)

Where $m_{fuel}/m_s$ is the mass fraction of fuel to sand, $\Delta H_{fuel}$ is the heat released per mass of fuel, and $T_{adiabatic}$ is the adiabatic combustion temperature assuming all heat released from the fuel is absorbed in the remaining neighbouring solid (e.g., ash or surrounding porous media), $T_{amb}$ is the ambient temperature. $T_p$ is peak temperature, which can be estimated by asymptotic analyses [133-137].

2.8 Effects of Fuel Mobility

Many studies investigated NAPL mobilization in the subsurface as a source of underground water and soil contamination. Under ambient surface conditions, NAPL mobilization may occur over a period of months to years before reaching a stable distribution, depending on fluid and subsurface properties [2, 138, 139].

For NAPL remediation from soil, various thermal technologies (e.g., steam injection [140, 141], hot air injection [142], and applied smouldering [45]) may be applied, where heat is used to change NAPLs properties (e.g., drive viscosity reduction) and enhance hydraulic displacement and therefore facilitate mobilization. However uncontrolled remobilization may be a significant concern, where contamination can be introduced into areas that were previously uncontaminated [9].

With steam injection technologies, the NAPLs will be volatilized within the high-temperature region but condense and accumulate ahead of the steam condensation front. When sufficient NAPLs accumulate in the condensation region, they may form a continuous phase, where gravitational force will overcome the viscous force and permit
downward mobilization of NAPLs outside of the target treatment areas [143]. Various
techniques are being investigated to minimize unintended mobilization, such as air
injection with steam [143], but the risk is still present. Increasing the temperature during
this process enhances NAPL recovery, but also accelerates downward NAPL mobilization
due to reduced viscosity. Altogether, more investigation on the effects of temperature
effects on NAPL thermal properties and mobilization in field scenarios would be beneficial
to improve the outlook of these thermal remediation techniques [7, 144].

In smouldering-based remediation (e.g., in-situ and ex-situ remediation of contaminated
soil [39-41, 45], and organic liquid waste treatment [57, 58]), the fuel (i.e., NAPL) is in the
liquid phase; therefore, mobilization during remediation is inevitable [145]. Previous
experimental studies on applied smouldering for organic liquid waste treatment (e.g., oil
sludge) delineated key conditions that lead to undesirable fuel mobility, including (i) low
Darcy air flux, (ii) low viscosity of preheated organic liquid ahead of the front, and (iii)
high height of preheating zone with a sufficient volume of low viscosity fuel. Kinsman et
al. [145] conducted a key laboratory study showing the impacts of mobility on upward
applied smouldering. This study showed that the length of the reaction zone adjusts to
accommodate the influx of organic liquid; however, in critical a condition (i.e., when the
preheating zone height > 10.5 cm and Darcy air flux ≤ 2.5 cm s⁻¹), smouldering exhibited
atypical behaviour with chaotic local extinction and high temperature reignition (Figure
2.14).
Figure 2.14: Temperature history for 90 cm column with forced air flux of 2.5 cm s\(^{-1}\). Thermocouples increase in temperature from ambient in order from left to right, with TC1 increasing first and TC26 increasing last. Atypical behaviour with local extinction and reigniting is captured (adapted from [145]).

In a similar context but separate application, in-situ combustion (ISC) also uses fuel mobilization. ISC is defined as an enhanced oil recovery technique applied to non-conventional reservoirs of heavy oil and bitumen with high viscosities (e.g., 1-1000 Pa s) and therefore low mobility [146-148]. The main objective of ISC is to maximize oil recovery while minimizing oil destruction. During this process, hot air (or a combination of air and steam) is injected at the ignition point. Heavy oil is pyrolyzed to char, and this char is oxidized. The released energy from char oxidation is then transferred ahead and used to pyrolyze and mobilize neighbouring heavy oil. The heat generated from the char
oxidation reaction decreases the oil viscosity, and the injected air and steam is used to displace the hot and low-viscosity oil ahead of the combustion front toward the recovery well [146, 148-150].

Significant operational problems may occur due to fuel accumulation in the preheating zone by progressing the smouldering front (e.g., pore blocking [151]) in which oil saturation may peak at 1.0 (i.e., fully block a pore). This blocking decreases the air permeability and restricts air flow to a critical level where oxidation reactions cannot be self-sustained [57, 151-154], thereby causing significant fluctuation in the reservoir pressure, decreasing the mobility of the oil, and decreasing the oil recovery efficiency [154]. Figure 2.15a defines different zones during the in-situ combustion process for enhanced oil recovery. The six main zones include the (i) burned zone (i.e., cooling zone), (ii) combustion zone (i.e., smouldering front), (iii) cracking/vaporization zone (i.e., preheating zone), (iv) steam zone, (v) altered saturation zone, and (vi) native reservoir zone. Figure 2.15 illustrate how smouldering propagation pushes low viscosity oil at elevated temperatures ahead of the steam zone toward the extracting well, Figures 2.15.b, and 2.15c show the temperature and saturation distributions, where the maximum temperature is at the combustion zone and maximum oil saturation is ahead of the steam zone [152].
Figure 2.15: (a) schematic diagram of different zones during the in-situ combustion process for enhanced oil recovery, illustrating how the smouldering propagation pushes low viscosity oil (with elevated temperatures) to the extracting well, (b, c) schematic diagram illustrating temperature and saturations associated with the in-situ combustion process, respectively (adapted from Ursenbach et al. [152]).
In smouldering-based technologies, the preheating region has the main potential for organic liquid mobilization, where absorbed thermal energy leaves the reaction zone, increases temperatures between 50-200 °C, and decreases the liquid fuel viscosity by a factor of 10-1,000,000 [145]. Above the preheating zone where the temperature is at ambient temperature, the high viscosity of liquid fuel associated with typical liquid fuels in applied smouldering systems (e.g., long-chain hydrocarbons) inhibits mobilization, even in the presence of significant pressure gradients [2]. Differences in smouldering system and fuel conditions will result in differences in heat transfer conditions [128, 155] and chemical reactions [156] that govern smouldering characteristics.

2.9 Energy Balances

Applied smouldering systems are typically operated as a “self-sustaining” process, meaning that the reaction will propagate after a local and brief ignition event without further external energy. This propagation implies that a local, positive energy balance (i.e., the energy rate released from smouldering exceeds all losses locally at the reaction front) is facilitated by chemistry and influenced by neighbouring physical processes [15, 83]. Local and global processes depend on the region where Eq. 2.7 is integrated, and the differences are highlighted in Figure 2.17.

\[ \dot{E}_{\text{net}}(t) = \dot{E}_{\text{in}}(t) + \dot{E}_{\text{oxid}}(t) - \dot{E}_{\text{out}}(t) - \dot{E}_{\text{loss}}(t) - \dot{E}_{\text{pyr}}(t) \]  

(2.7)

where \( \dot{E}_{\text{net}} \), \( \dot{E}_{\text{in}} \), \( \dot{E}_{\text{oxid}} \), \( \dot{E}_{\text{out}} \), \( \dot{E}_{\text{loss}} \), and \( \dot{E}_{\text{pyr}} \) are net, inlet, oxidation, outlet, radial loss, and pyrolysis energy rates. Zanoni et al. [35, 38] investigated the energy balance terms highlighted in Figure 2.16 to quantify whether smouldering was robust, weak, or towards quenching. Figure 2.16a shows a conceptual model of a smouldering front, Figure 2.16b illustrates the temperature distribution with the maximum temperature at the smouldering front. This figure shows that energy balances can be applied locally across the reaction zone (Figure 2.16c) and globally across the system boundaries (Figure 2.16d) [35, 38].
Figure 2.16: Illustration of a one-dimensional 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 (smoulder front) and (d) global (bed) energy balance. Energy rate components ($\dot{E}$) accounts for (red) energy rate added into and (black) removed from the system (adapted from Zanoni et al. [38]).

2.9.1 Local Energy Balance

The local energy balance focuses on the chemically active regions and determines the fate of smouldering (Figure 2.16c). Research progress on local energy balance analyses continues to provide insight into processes governing smouldering. Importantly, self-sustained smouldering results from positive local energy balance, but other key smouldering metrics can also be solved by analyzing the smouldering front.

Smouldering front velocity ($\nu_f$) can be estimated from an energy balance over the reacting region [157]. For forward smouldering propagation, Bar-Ilan et al. [158-160] described
forward smouldering, including perimeter heat losses and heater effects (from Torero et al. [161]), that compared well to microgravity experiments:

$$v_f = \frac{\Delta Y_{O_2} \rho_g u_g \Delta H_{oxi} \Delta q_{loss} \left( \frac{A_L}{A_c} \right) + \Delta Y_{O_2} \rho_g \Delta H_{oxy}}{(\rho C_p)_{eff} (T_p - T_{amb}) - (1 - \phi) \rho_s \Delta H_{pyr} + \Delta Y_{O_2} \rho_g \Delta H_{oxi}} \quad (2.8)$$

where $\Delta Y_{O_2}$, $\Delta H_{oxi}$, $\Delta H_{pyr}$, $\Delta q_{loss}$, $q_{ig}$, $A_L$, $A_c$, $T_p$, $T_{amb}$, $\phi$, $u_g$, $\rho_g$, and $\rho_s$ note the oxygen mass fraction consumption (which is assumed entirely consumed in fuel-rich condition), heat of oxidation released per mass of oxygen consumed (absorbed in the nearby solid), heat of pyrolysis consumed per mass of the fuel, radial heat loss, ignition heat flux, lateral and cross-sectional areas, peak and ambient temperature, porosity, Darcy air flux, and density of gas and sand, respectively. The effective volumetric heat capacity for sand and fuel is defined as:

$$ (\rho C_p)_{eff} = (1 - \phi)(\rho_s C_{p_s}) + (\phi_f)(\rho_f C_{p_f}) \quad (2.9)$$

where $C_{p_s}$, $C_{p_f}$, $\rho_f$, $\phi_f$ are the heat capacity of sand and fuel, and density and porosity of fuel, respectively. Torero et al. [76, 126, 159, 161, 162] developed an analytical expression for the front velocity based on an energy balance at the fuel-rich condition and local thermal equilibrium (LTE). These studies investigated many additional phenomena acting on smouldering propagation including (i) the effects of buoyancy, (ii) two-step reactions including pyrolysis ahead of oxidation, and (iii) the influence of ignition. In another study, Wang et al. [163, 164] embedded the effect of local mass transfer limiting the heat release rate and ambient heat losses.

The Damköhler number ($Da$) is defined as the ratio of mass transport ($\tau_f$) to the reaction time scales ($\tau_R$) used in many combustion science analyses to identify extinction conditions at a critical value ($Da_{crit}$). This approach can be applied to smouldering [165] using the same definition:

$$Da = \frac{\tau_f}{\tau_R} \quad (2.10)$$
In many smouldering problems, it is necessary to resolve the governing equations, throughout the system (space and time) to provide meaningful insight into the processes affecting the local energy balance that governs smouldering propagation.

### 2.9.2 Global Energy Balance

Torero et al. [15] delineated the difference between “self-sustained smouldering”, which is governed by a local energy balance, and “self-sustained smouldering propagation”, which is characterized by global energy balance (Figure 2.16d). Therefore, it is necessary to resolve the system’s conditions at the boundaries, i.e., far away from the reaction zone, to describe the local condition that drives extinction or other key results in the reaction zone. Zanoni et al. [38] resolved the governing equations through space and time to obtain insight by conducting a global energy balance on the smouldering systems and measuring the smouldering system’s robustness (i.e., resilience to extinction).

Considering the global $\dot{E}_{net}$ and $D_{a_{cr}}$, four different scenarios are possible during “smouldering propagation”, where the level of robustness is determined by the energy accumulated in the system that acts as a buffer against quenching and stabilizes the reaction [38]. In scenario (i), $\dot{E}_{net} >> 0$ & $Da > D_{a_{cr}}$ represents robust self-sustaining smouldering where energy accumulation increases the system’s robustness. In scenarios (ii) and (iii), $\dot{E}_{net} \sim 0$ & $Da > D_{a_{cr}}$ represents either (ii) robust smouldering where there is a large energy buffer and a cooling zone has fully developed so the rate of total heat losses balance the rate of energy released via oxidation (i.e., this will occur theoretically in very tall reactors or possibly continuous systems [166]); or (iii) weak self-sustaining smouldering without or with very small rate of energy accumulation, where the energy buffer is relatively small and it could not completely overcome heat losses, therefore the system is highly sensitive to lateral heat losses. In scenario (iii), peripheral extinction occurs and some layers of the fuel around the reactor wall will remain unburned (i.e., crust formation) that insulates the centerline allowing for smouldering to persist but facilitate the air channeling near the wall [21]. In scenario (iv), $\dot{E}_{net} < 0$ & $Da < D_{a_{cr}}$ represents global quenching (i.e., non-self-sustaining smouldering) [38, 102, 165, 167].
These trends are common to many applied smouldering systems, where $\dot{E}_{\text{net}}$ is determined from the interplay between $\dot{E}_{\text{oxi}}$ (roughly constant throughout the time, which aligns with many other applied smouldering studies [30, 35, 38, 42]) and $\dot{E}_{\text{loss}}$, as the $\dot{E}_{\text{in}}$ and $\dot{E}_{\text{out}}$ are boundary effects therefore are negligible when smouldering propagation is sufficiently far from the system boundaries. Moreover, $\dot{E}_{\text{pyr}}$ was shown to be negligible in many applied smouldering systems [38]. Therefore, $\dot{E}_{\text{net}}$ is governed by $\dot{E}_{\text{oxi}}$ and $\dot{E}_{\text{loss}}$, and the balance between these terms defines if smouldering is propagating self-sustaining or transitioning toward the extinction. Moreover, $\dot{E}_{\text{net}} \geq 0$ indicates that the smouldering system is accumulating released reaction energy, which effectively strengthens a buffer against extinction. In a sufficiently robust smouldering system, this buffer moderates modest endothermic effects (from phase change processes or perimeter heat losses), so they may not have noticeable effects on the reaction zone characteristics [29, 38, 77, 131].

By increasing endothermic effects to the same magnitude of $\dot{E}_{\text{oxi}}$ (e.g., higher $\dot{E}_{\text{loss}}$ or $\dot{E}_{\text{pyr}}$), or declining $\dot{E}_{\text{oxi}}$ (e.g., by decreasing fuel concentration or air fluxes), then the buffer against extinction may be reduced and lead to weak smouldering [31, 35, 38, 44, 102, 131, 165, 168, 169]. Under weak smouldering conditions, smouldering propagation is sensitive to the endothermic effects that may drop temperatures and propagation velocities [102, 170]. However, weak smouldering may still propagate indefinitely.

### 2.10 Summary and Gaps

Applied smouldering systems are evolving as they can be performed for various environmentally beneficial applications including the remediation of a wide range of contaminants such as (i) fecal matter [44], (ii) biosolids from wastewater treatment plants [30, 31, 46], (iii) organic liquid waste from industrial activities [34, 39-41, 43, 47-49], and (iv) challenging compounds found throughout the environment (e.g., PFAS) [33, 50, 51]. These systems can also provide energy needed for waste pyrolysis [61, 62, 69, 171] and support resource recovery from the gaseous emissions or solid ash residue [46, 172, 173].
The benefits of applied smouldering systems include (i) high energy efficiency [117], (ii) reaction stabilization using an inert porous medium [174, 175], (iii) slow reaction time scales (which therefore offers higher resilience than other thermal techniques based on flaming combustion [15]), and (iv) production beneficial by-products [15, 63]. However, there are challenges and unaddressed aspects of these systems, including (i) multi-dimensional transfer effects (i.e., non-uniformities in temperature, air mass flux, and chemistry) associated with radial heat losses [77], (ii) multi-dimensional smouldering propagation due to physical or thermal heterogeneity in applied smouldering systems [106], (iii) oxygen delivery sensitivities, (iv) undesirable dynamics due to liquid fuel mobility [145], and (v) smouldering instabilities near extinction [165, 168, 176, 177].

From an extensive review of the relevant literature, several unanswered research questions and knowledge gaps exist as follows:

- Limited studies on multi-dimensional transfer effects associated with perimeter heat losses on smouldering propagation and self-sustaining limits.
- Only a few studies considered the effect of heterogeneity on smouldering combustion; however, there is currently a growth in smouldering applications, and most of these applications involve some heterogeneity of the fuel or bed.
- Few studies have untangled the dynamics between local and global quenching and reignition in smouldering systems.
- Minimal work has been completed on sensitivities to oxygen variations in applied smouldering systems. The effects of oxygen variations may lead to non-intuitive system behaviour, which may constitute a system risk or perhaps be harnessed for improved operation.
- The effects and dynamics of liquid fuel mobility in applied smouldering systems have not been investigated in detail. This is a key gap, as many smouldering applications treat hazardous organic liquids (e.g., crude oil sludge).

Applied smouldering presents many fundamental and commercial benefits across different contexts. However, there are also challenges. This study provides valuable and novel insight via multi-dimensional numerical modelling that enables researchers and scientists
to overcome some existing challenges to better control the process, increase the system efficiency, and ultimately provide cost-effective smouldering-based technologies [178].

Overall, this thesis aims to provide novel insights into three key system parameters including: (i) multi-dimensional transfer effects associated with radial heat losses, (ii) oxygen mass flux, and (iii) fuel mobility. This insight is intended to help advance smouldering-based technologies for a wide range of environmentally positive applications.

### 2.11 References


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Chapter 3

3 Investigation of Multi-Dimensional Transfer Effects in Applied Smouldering Systems: A 2D Numerical Modelling Approach

3.1 Introduction

Smouldering reactors are performed for a variety of applications, including: (i) energy and resource recovery [1, 2], (ii) waste-to-energy [3], (iii) pyrolysis and gasification (e.g., for CO and H₂ production) [4-7], and (iv) applied smouldering of organic liquids/solids (e.g., faeces [8], wastewater sludge [9], granular activated carbon [10, 11], coal tar [12], bitumen [13]) in different scales from the laboratory (e.g., column, 0.003 m³) to intermediate (e.g., Drum, 0.3 m³) and pilot field-scale (e.g., bin or Hotpad, 3 m³) [14-17].

Applied smouldering systems are typically operated as a “self-sustaining” process, meaning that the reaction will propagate, after a local and short ignition event, without further external energy. Self-sustained smouldering results from a local, positive energy balance (i.e., energy released from smouldering exceeds all losses locally at the reaction front). Self-sustaining makes applied smouldering an energy efficient, cost effective, and green technology [18]. When the energy balance becomes negative (e.g., due to high heat losses [13]), the reaction can weaken towards extinction [19]. Radial heat losses from the hot inert porous bed trailing smouldering are responsible for transferring 28-52% of total energy generated out of the system in lab scale experiments [13, 20]. Moreover, heat losses cause a multi-dimensional transfer effect of temperature and air flow along the radius of the reactor [20-23]. These factors can decrease the smouldering robustness (i.e., resistance of self-sustaining reaction to extinction) from the center to the wall (i.e., multi-dimensional transfer effect of reactions [24]). These multi-dimensional transfer effects can deteriorate the system performance and lead to unexpected failures; however, the interplay between these effects is not well understood [25].

The effects of radial heat losses in smouldering reactors were analyzed via analytical modelling [26]. A System Energy Efficiency (SEE) analysis was developed using a global energy balance to investigate the system sensitivity to reactor radius (R) and quality of the
surrounding insulation (represented by a heat loss coefficient, $H$) [26]. That study quantified the diminishing influence of radial heat losses with increasing reactor radius (e.g., 35% of the energy was lost radially in a batch reactor with $R = 8$ cm compared to 14% with $R = 30$ cm [26]). These results align with experimental studies that show increasing scale led to reduced heat losses and extended thresholds for self-sustained smouldering [27, 28] and smouldering robustness.

Smouldering includes heat and mass transfer processes in porous media coupled with chemical reactions. Figure 3.1 shows self-sustaining smouldering reactions, which propagate through the bed in the direction of air flow, and are composed of multiple distinct zones including (i) preheating, (ii) reaction, and (iii) cooling. Each exhibits dominant physical and chemical processes [29, 30]. The key processes happening in each zone are summarized in [30] and also in the methodology section. By propagating the self-sustained smouldering in the system, these three interdependent zones extend in thickness and intensity throughout space and time.
Figure 3.1: (a) Multiple distinct zones of an applied smouldering reactor. (b) Conceptual model showing a distorted smouldering front (red) that propagates through the contaminated region (gray) and leaves clean and hot sand (orange) behind while radial heat loss causes peripheral extinction. (c) Air mass flux and temperature distribution at a specific time. (d) Local and (e) global energy balance analysis.

One-dimensional (1D) smouldering models were used to investigate the effect of chemical mechanisms [31-33] and extinction criteria [13, 19, 34]. In such models, a global heat loss coefficient is employed as a sink term [13, 19, 30], and it is usually adjusted to match the slope of the experimental centreline temperature behaviour [21]. The fraction of carbon oxidized and the fraction of oxygen consumed depend on the front temperature, which is
affected by heat losses [23]. While these 1D models elucidate useful features, they cannot capture key multi-dimensional effects, e.g., smouldering front distortions [20, 23], and the multi-dimensional transfer effect of air flux [20, 35]. These important features have been suggested by analytical calculations [35] and experiments [22, 23, 25] to drive peripheral extinction (i.e., unconsumed fuel near the wall) due to radial heat losses [22, 24].

Previously developed and validated 2D numerical models show the effects of radial heat losses on the multi-dimensional transfer effect of temperature [24, 36-38], air flux [20, 35], oxygen mass fraction [39, 40], heat release rate [38], and chemistry distribution that affect the smouldering front shape, velocity, and propagation [20, 24, 36, 41]. Previous 2D studies showed peripheral extinction [24, 38, 42, 43] with the centerline self-sustaining smouldering weakening to global quenching (i.e., complete extinction) by increasing radial heat losses (e.g., H > 20 W/m² K). Heat losses also lowered temperatures [37, 38] and oxygen consumption near the wall in comparison to the centerline [40]. Increasing the radial heat loss decreased the smouldering front velocity because of decreasing temperature and reaction rate (i.e., char mass fraction distribution) [38, 43, 44] and, by increasing the radial heat transfer coefficient from 20 to 100 W/m² K, the maximum temperature and smouldering front velocity decreased to roughly one third [36]. Pozzobon et al. [20] performed a numerical and experimental investigation of the radial heat loss effect in temperature distribution, smouldering front shape, and oxygen consumption. They showed that, by decreasing the fuel mass concentration from 3.6 to 2.3%, the smouldering front shape was inverted from concave to convex. This shift in the smouldering front shape was hypothesized to result from a competition between the multi-dimensional transfer effect of reactions and air flux; but this hypothesis has not yet been rigorously tested.

Previously, an experimental study was performed to examine the effects of intrinsic permeability and heterogeneity on smouldering combustion [45], also a phenomenological 2D numerical model capable of simulating smouldering in heterogeneous domains was developed to simulate applied smouldering [17, 46, 47]. This model was validated to perform sensitivity analyses on key design parameters of commercial-scale systems, including permeability heterogeneity and fuel concentration (here, waste oil sludge (WOS) saturation). Valuable practical insight was achieved through this modelling. For example,
it was shown that smouldering systems could operate well with high levels of heterogeneity in WOS saturation (e.g., due to poor-mixing), but were highly sensitive to heterogeneity in the soil permeability (e.g., from using a widely graded soil). However, that model was not capable of simulating coupled effects with heat losses (e.g., multi-dimensional transfer effect of reactions and air flux).

Considering the previous research, it is not entirely clear how coupled multi-dimensional transfer effects (e.g., in temperature, air flux, and reactions) will affect applied smouldering under a range of conditions relevant to applications. Therefore, this study aims to address this knowledge gap by combining the most rigorous components of established smouldering models into a new, multi-dimensional numerical model. Towards this goal, this study aimed to: (i) develop a 2D numerical model to simulate 2D heat transfer in an inert porous medium; (ii) conduct heating experiments, i.e., no fuel within the porous medium, to validate the heat transfer model; (iii) develop a simple chemical mechanism for granular activated carbon (GAC) smouldering; (iv) develop a 2D smouldering model applying the developed chemical mechanism; (v) conduct 2D GAC smouldering experiments to validate the smouldering model; (vi) use the validated model to resolve the global energy balance dynamics, (vii) perform qualitative and quantitative analysis of multi-dimensional transfer effects over global smouldering quenching and intrinsic permeability heterogeneity scenarios. Altogether, this work provides novel insights into the global energy balance and multi-dimensional transfer effects in applied smouldering systems, which are also beneficial for other thermal porous media technologies.

3.2 Methodology

3.2.1 Experiments

This work conducted 3 experiments (with 3 repeats each, nine total) to provide a robust, unique data set for 2D heat transfer as well as 2D smouldering. Figure 3.2 (a) shows a schematic of the experimental setup. The smouldering experiments (Table 3.1) were carried out in a stainless-steel column (316 Stainless Steel) with a 1 cm layer of clean sand and a 75 cm layer of sand/GAC, topped by a 9 cm layer of clean sand. The clean sand cap was added in the experiments to moderate the temperature of the existing emission for
safety purposes when the smouldering front reaches the top of the column. However, this layer was not considered in the computational domain as it does not affect any trends discussed in this manuscript. The heat transfer experiments used the same setup, but only used clean sand (i.e., no GAC). GAC is a valuable by-product of coal pyrolysis composed of fixed carbon (91.4%) with very low volatile content (3.2%).

GAC is widely used as an adsorbent of harmful contaminants and recent studies have demonstrated that smouldering can robustly treat spent GAC with recalcitrant compounds, like per- and polyfluoroalkyl substances [11]. Moreover, GAC degradation is much simpler than other fuels routinely studied in applied smouldering systems and can be modelled with a 1-step oxidation reaction by neglecting pyrolysis reactions [10, 22, 27, 48, 49]. The column was wrapped in a 4 cm insulation layer (Superwool plus, Morgan Thermal Ceramics) and enclosed by an aluminum jacket to hold the insulation in place.

<table>
<thead>
<tr>
<th>Exp. # (-)</th>
<th>GAC Concentration ($C_{GAC}$)</th>
<th>Repeats (-)</th>
<th>Heater Stabilization Time ($t_{stab}$) [s]</th>
<th>Air on Time ($t_g$) [s]</th>
<th>Heater off Time ($t_h$) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>3</td>
<td>470</td>
<td>1023</td>
<td>2400</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>3</td>
<td>660</td>
<td>1020</td>
<td>4320</td>
</tr>
<tr>
<td>3</td>
<td>0.03</td>
<td>3</td>
<td>632</td>
<td>3655</td>
<td>4380</td>
</tr>
</tbody>
</table>

The thermocouples (Type K, Inconel, Omega) were placed at (i) the centerline spaced 3 cm apart and (ii) radially from 13 to 61 cm, spaced 12 cm apart (see the position of the thermocouples, Figure 3.2) and measured the temperature of the sand. Temperatures were recorded every two seconds by a data logger (Multifunction Switch/Measure Unit 34980A,
Agilent Technologies). The sand (K&E Sand and Gravel, WP #2) was sieved to achieve a grain size between 0.118 and 0.200 cm. GAC (McMaster-Carr, CAS Number: 7440-44-0 particle size between 0.425 and 0.85 mm) was combined with sand at 0.02 and 0.03 kg/kg sand using an electric mixer (Kitchen Aid), and then carefully packed in the column to ensure good homogeneity. The intrinsic permeability of the bed was measured in the column \( k_p \) \([45, 50, 51]\) and did not change after smouldering; unsurprising since the fuel load was so minor (i.e., 2% to 3% of the fuel bed by mass; see Appendix A, Section A1). An external radiative cone heater (500 W, 240 V, Fire Testing Technology Ltd.) was placed below the column. The heater temperature was set to 1000 °C, providing the heat flux required for smouldering ignition. The heat flux \( \dot{q} \) from the heater towards the column inlet boundary was calculated using inverse modelling and placed at the bottom of the column (Figure 3.2). See additional information on this calculation in Appendix A, Section A2.
Figure 3.2: Schematic view of (a) experimental setup and (b) computational domain. For smouldering experiments, the contaminated region (sand mixed with GAC) is represented by the gray layer. For heat transfer experiments, the contaminated region is fully replaced by clean sand (orange layer).

Table 3.1 shows the experimental conditions, which all followed a standard procedure [10]. The heater was turned on and stabilized at 1000 °C at $t_{\text{stab}}$, i.e., the time when the thermocouple at specific height above the heater (i.e., 1 cm and 4 cm in the heat transfer-only and smouldering experiments, respectively) reached 300 °C. The air supply was turned on at $t_g$, thereby causing ignition in the smouldering experiments, and the Darcy flux ($u_{g,\text{in}}$) was controlled via a mass flow controller (FMA5400 Series, 0-80 L min$^{-1}$, Omega Ltd). The heater was turned off at $t_h$ (i.e., when the thermocouple 4 cm and 7 cm above the heater peaked in the heat transfer-only and smouldering experiments,
respectively), while the air was kept on until the end of the experiment (see Figure A.2, Appendix A, Section A2).

3.2.2 Modelling

An axisymmetric, 2D numerical model was developed in COMSOL Multiphysics (Version 5.5) using 0.05 cm mesh size to capture the smouldering front thickness very well. The computational domain presented in Figure 3.2 (b), used cylindrical coordinates and simulated: (i) a porous medium composed of clean sand mixed with granular activated carbon (GAC) and (ii) a surrounding, solid metal sheet representing the column stainless steel wall. The governing equations (Eqs. (3.1-17)) were solved at every node in space and time using and finite element discretization method to simulate 2D smouldering and heat transfer. The numerical model considered two phases: (i) solid (i.e., GAC, sand) and (ii) gas in the Representative Elementary Volume (REV) scale, over which average properties (e.g., porosity and permeability) can be performed (Appendix A, Section A.1). Pyrolysis reactions were assumed to be negligible [27, 48, 49], as the GAC used was nearly entirely carbon (> 90%) and exhibited low volatiles content [10, 27]. Moreover, thermogravimetric experiments performed on GAC under an inert atmosphere (i.e., using nitrogen) resulted in a negligible mass loss (Appendix A, Section A.3). Therefore, the GAC smouldering kinetics followed a global, 1-step oxidation mechanism [10]:

\[
GAC + \nu_{O_2} O_2 \xrightarrow{R_{GAC}} \nu_{CO} CO + \nu_{CO_2} CO_2
\]  

(3.1)

where the oxidation reaction rate \( R_{GAC} \) was described as a first-order Arrhenius reaction [52]:

\[
R_{GAC} = A_{GAC} \exp \left( -\frac{E_{GAC}}{R_g T_s} \right) (Y_{GAC}) (Y_{O_2})
\]

(3.2)

where \( A_{GAC} \) is the pre-exponential factor, \( E_{GAC} \) is the activation energy, \( T_s \) is the solid temperature, and \( \nu_{O_2} \) is the oxygen stoichiometric coefficient. The mass fraction of GAC and oxygen are defined as \( Y_{GAC} = m_{GAC}/m_{GAC,0} \) and \( Y_{O_2} = m_{O_2}/m_{air} \), the subscript “0” refers to initial, and \( m_{GAC} \) and \( m_{O_2} \) are the mass of GAC and oxygen, respectively. The
kinetic parameters ($A$ and $E$) were estimated via a Genetic Algorithm (GA) optimization method coupled with thermogravimetric experiments performed under an oxidative atmosphere (i.e., using air; see Appendix A, Section A.3). Although the use of the Arrhenius equation and reaction rates for heterogeneous reactions has been questioned [53-56], this simplistic approach is extensively used in the literature of thermal degradation of solids and liquids [10, 29, 33, 57]. While it is beyond the scope of this paper, it is worth noting that the rate of a heterogeneous reaction should explicitly consider the decrease in reactant-product surface area as the reaction consumes the solid surface [53-56]. This dependency is approximated in Eq. (3.2) by including $Y_{GAC}$. The conservation of mass for the solid phase is [10]:

$$\frac{\partial (Y_{GAC})}{\partial t} = -R_{GAC}$$

(3.3)

and the gas phase is [20, 40]:

$$\frac{\partial (\rho_g \phi_g)}{\partial t} + \frac{1}{r} \frac{\partial (r \rho_g u_r)}{\partial r} + \frac{\partial (\rho_g u_z)}{\partial z} = Q_g$$

(3.4)

where $Q_g$ represents the volumetric mass generation rate for the gas phase:

$$Q_g = (\phi_{GAC} \rho_{GAC}) (R_{GAC})$$

(3.5)

Darcy’s Law was used to determine the gas velocity in radial and longitudinal directions, Eq. (3.6, 7) [58]:

$$u_r = -\frac{k_p}{\mu} \frac{\partial p}{\partial r}$$

(3.6)

$$u_z = -\frac{k_p}{\mu} \left( \frac{\partial p}{\partial z} + \rho_g g \right)$$

(3.7)

where $k_p, \mu, \rho_g, p,$ and $g$ represent intrinsic permeability, viscosity, gas density, pressure, and gravity respectively. The gas density was calculated via the ideal gas law [59] which is a simple equation that demonstrates the relation of pressure, temperature, and density of
the gas. While ideal gas is a theoretical conception, systems with either low pressure or high temperature enable real gases to be estimated as ideal gas [60].

\[ \rho_g = \frac{p}{RT_g} \]  

(3.8)

where \( R \) is the gas constant. The bulk transport of oxygen in the gas phase was described by Eq. (3.9) [10]:

\[
\frac{\partial (\rho_g \rho_g Y_{O_2})}{\partial t} + \frac{\partial (\rho_g u_r Y_{O_2})}{\partial r} + \frac{\partial (\rho_g u_z Y_{O_2})}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \phi_g \rho_g D_g \frac{\partial Y_{O_2}}{\partial r} \right) + \frac{\partial}{\partial z} \left( \phi_g \rho_g D_g \frac{\partial Y_{O_2}}{\partial z} \right) + Q_{O_2}
\]

(3.9)

where \( D_g \) is the diffusion coefficient, \( Y_{O_2} \) is the mass fraction of oxygen in the air, and \( Q_{O_2} \) represents the mass per unit volume per unit time for oxygen consumption and was defined by Eq. (3.10):

\[ Q_{O_2} = - (\phi_{GAC} \rho_{GAC}) \nu_{O_2} R_{GAC} \]  

(3.10)

where \( \phi_{GAC} \) and \( \rho_{GAC} \) is the GAC porosity and density, respectively. The conservation of energy considers local thermal non-equilibrium (LTNE), i.e., the temperature of the solid \( (T_s) \) differs from the temperature of the gas \( (T_g) \) [10, 26, 30]:

\[
(\rho C_p)_{eff} \frac{\partial T_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r k_{eff} \frac{\partial T_s}{\partial r} \right) + \frac{\partial}{\partial z} \left( k_{eff} \frac{\partial T_s}{\partial z} \right) 
+ h_{sg} \left( \frac{A_{s,sp}}{V_{sp}} \right) (T_g - T_s) + Q_{gen}
\]

(3.11)

\[
\phi_g \rho_g C_{pg} \frac{\partial T_g}{\partial t} + \rho_g C_{pg} (u_r \frac{\partial T_g}{\partial r} + u_z \frac{\partial T_g}{\partial z}) 
= \frac{1}{r} \frac{\partial}{\partial r} \left( r \phi_g k_g \frac{\partial T_g}{\partial r} \right) + \frac{\partial}{\partial z} \left( \phi_g k_g \frac{\partial T_g}{\partial z} \right) + h_{sg} \left( \frac{A_{s,sp}}{V_{sp}} \right) (T_s - T_g)
\]

(3.12)
where $A_{s,sp}$ and $V_{sp}$ are the surface area and volume of the sand, respectively, and $Q_{gen}$ represents the volumetric energy production rate from GAC oxidation ($\Delta H_{GAC}$):

$$Q_{gen} = \phi_{GAC}\rho_{GAC}(\Delta H_{GAC}R_{GAC})$$  (3.13)

The interfacial heat transfer coefficient ($h_{sg}$) between the solid and gas phases is based on an empirical Nusselt ($Nu$) versus Reynolds ($Re$) and Prandtl ($Pr$) correlation [50]:

$$Nu = \frac{h_{sg}d_p}{k_g} = 0.001 \left(Re^{1.97}Pr^{1/3}\right)$$  (3.14)

Eq. (3.12) assumes effective thermal properties for solid phase [10]:

$$(\rho C_p)_{eff} = (\phi_s)(\rho_s C_{Ps}) + (\phi_{GAC})(\rho_{GAC} C_{PGAC})$$  (3.15)

$$k_{eff} = (\phi_s)(k_s + k_{rad}) + (\phi_{GAC})(k_{GAC})$$  (3.16)

$$\phi_g = \phi - \phi_{GAC}$$  (3.17)

$$\varphi_s = 1 - \varphi$$  (3.18)

where $\rho_s$, $\rho_{GAC}$, $\rho_g$; $\phi_s$, $\phi_{GAC}$, $\phi_g$; $C_{Ps}$, $C_{PGAC}$, $C_{Pg}$; and $k_s$, $k_{GAC}$, $k_g$ are the densities, porosities, heat capacities, and thermal conductivities of the sand, GAC, and gas, respectively. Radiative heat transfer was embedded in the effective solid conductivity following the Rosseland approximation ($k_{rad} = 16\sigma d_p T_s^3 / 3$) [50], where $\sigma$ is the Stefan-Boltzmann constant [61]. Conductive heat transfer within the metal sheet was also modeled [20]:

$$\left(\rho_i C_{pi}\right) \frac{\partial T_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r(k_i) \frac{\partial T_s}{\partial r}\right) + \frac{\partial}{\partial z} \left(k_i \frac{\partial T_s}{\partial z}\right)$$  (3.19)

where $\rho_i$, $C_{pi}$, $k_i$ are density, heat capacity and thermal conductivity of the metal sheet. The model parameters not described above are presented in Table 3.2 and the initial and boundary conditions are provided in Table 3.3. The heater was simulated by a constant heat
flux (Appendix A, Section A2) delivered at the inlet boundary. The Darcy air flux was initiated at x=0 m by a constant $u_{g,in}$ (measured).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log(A_{GAC})$</td>
<td>3.79</td>
<td>log(s$^{-1}$)</td>
<td>This work</td>
</tr>
<tr>
<td>$C_{PGAC}$</td>
<td>1100</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>[62]</td>
</tr>
<tr>
<td>$C_{p_i}$</td>
<td>440.8</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>[63]</td>
</tr>
<tr>
<td>$C_{GAC}$</td>
<td>0.03</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>$D_g$</td>
<td>$4.35 \times 10^{-5}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[64]</td>
</tr>
<tr>
<td>$\Delta H_{GAC}$</td>
<td>-24.9</td>
<td>MJ kg$^{-1}$</td>
<td>[27]</td>
</tr>
<tr>
<td>$E_{GAC}$</td>
<td>72.9</td>
<td>kJ mol$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>$H$</td>
<td>7</td>
<td>W m$^2$ K$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>$h$</td>
<td>0.003</td>
<td>m</td>
<td>This work</td>
</tr>
<tr>
<td>$k_{GAC}$</td>
<td>0.25</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[62]</td>
</tr>
<tr>
<td>$k_i$</td>
<td>14.7</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[65]</td>
</tr>
<tr>
<td>$k_p$</td>
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<td>m$^2$</td>
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</tr>
<tr>
<td>$m_s$</td>
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<td>This work</td>
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<tr>
<td>$m_{GAC}$</td>
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<td>kg</td>
<td>This work</td>
</tr>
<tr>
<td>$M_g$</td>
<td>28.97</td>
<td>g mole$^{-1}$</td>
<td>[66]</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.442</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>Parameter ( \phi_{\text{GAC}} )</td>
<td>Value</td>
<td>Unit</td>
<td>Source</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------</td>
<td>------</td>
<td>--------</td>
</tr>
<tr>
<td>( \rho_{\text{GAC}} )</td>
<td>0.05</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>( \rho_{b_{\text{GAC}}} )</td>
<td>1311</td>
<td>kg m(^{-3})</td>
<td>This work</td>
</tr>
<tr>
<td>( \rho_{i} )</td>
<td>44.4</td>
<td>kg m(^{-3})</td>
<td>This work</td>
</tr>
<tr>
<td>( \dot{q} )</td>
<td>8000</td>
<td>kg m(^{-3})</td>
<td>[67]</td>
</tr>
<tr>
<td>( R )</td>
<td>35000</td>
<td>W m(^{-2})</td>
<td>This work</td>
</tr>
<tr>
<td>( R_{g} )</td>
<td>5.4</td>
<td>cm</td>
<td>This work</td>
</tr>
<tr>
<td>( u_{g,in} )</td>
<td>8.314</td>
<td>J mol(^{-1}) K(^{-1})</td>
<td>[50]</td>
</tr>
<tr>
<td>( v_{O_2} )</td>
<td>0.05</td>
<td>m s(^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td>( v_{CO} )</td>
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<td>kg. O(_{2}) kg. fuel(^{-1})</td>
<td>[27]</td>
</tr>
<tr>
<td>( v_{CO_2} )</td>
<td>0.63</td>
<td>kg. CO kg. fuel(^{-1})</td>
<td>[27]</td>
</tr>
<tr>
<td>( v_{CO_2} )</td>
<td>2.67</td>
<td>kg. CO(_{2}) kg. fuel(^{-1})</td>
<td>[27]</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>5.67\times10^{-8}</td>
<td>W m(^{-2}) K(^{-4})</td>
<td>[50]</td>
</tr>
</tbody>
</table>
Table 3.3: Initial and Boundary Conditions in Numerical Simulation

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Initial Condition</th>
<th>Boundary Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t = 0)</td>
<td>( Y_{GAC} = 1 )</td>
<td>( z = 0 &amp; 0 &lt; r &lt; 0.054 )</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
- (k_s + k_{rad}) \frac{\partial T_s}{\partial z} &= \dot{q} \to 0 \leq t \leq t_h \\
- (k_s + k_{rad}) \frac{\partial T_s}{\partial z} &= 0 \to t_h \leq t \leq t_f \\
\end{align*}
\]

\[
\begin{align*}
T_g &= T_0 \\
\rho_g u_g &= \rho_g u_g(t) \quad \{ u_g = 0 \to 0 \leq t \leq t_g \\
\rho_g u_g &= u_0 \to t_g \leq t \leq t_f \\
Y_{O_2} &= Y_{O_2,0} \\
\end{align*}
\]

\[
\begin{align*}
P &= 101375 \text{ Pa} \\
\end{align*}
\]

\[
\begin{align*}
- (k_i) \frac{\partial T_s}{\partial z} &= \dot{q} \to 0 \leq t \leq t_h \\
- (k_i) \frac{\partial T_s}{\partial z} &= 0 \to t_h \leq t \leq t_f \\
\end{align*}
\]

\[
\begin{align*}
T_s &= T_g = 295K \\
r &= 0 \& 0 < z < 0.76 \to \\
- (k_s + k_{rad}) \frac{\partial T_s}{\partial r} &= 0 \\
- (k_g) \frac{\partial T_g}{\partial r} &= 0 \\
- (D_g) \frac{\partial (\rho_g Y_{O_2})}{\partial r} &= 0 \\
u_r &= 0 \\
\end{align*}
\]

\[
\begin{align*}
\rho_g u_g &= \rho_g u_g(t) \quad \{ u_g = 0 \to 0 \leq t \leq t_g \\
\rho_g u_g &= u_0 \to t_g \leq t \leq t_f \\
Y_{O_2} &= Y_{O_2,0} \\
\end{align*}
\]
\[ T_s = 295 \, K \quad z = 0.76 \, \& \, 0.054 < r < 0.057 \rightarrow \left\{ -(k_i) \frac{\partial T_s}{\partial z} = 0 \right\} \]

\[ T_s = 295 \, K \quad r = 0.057 \, \& \, 0 < z < 0.76 \rightarrow \left\{ -(k_i) \frac{\partial T_s}{\partial r} = H(T_s - T_\infty) \right\} \]

The effective radial heat loss coefficient \((H)\) determines the rate of radial heat loss between the column wall and ambient air (see Figure 3.2b), which includes the effect of insulation; therefore, \(H\) is a complicated parameter that requires a separate sensitivity analysis. \(H\) is expected to change under different smouldering conditions with different temperature profiles because it is affected by the thermal properties of the insulation (e.g., \(C_p\) and \(k\)) and the convection conditions just outside of the column, which are both temperature-dependent. \(H\) was determined by a sensitivity analysis (Appendix A, Section A2) based on an established methodology \([26]\). To directly compare the results from smouldering experiments and simulations, parameters including temperature, air mass flux, GAC bulk density, and oxygen mass fraction were normalized in Table 3.4. The time also was normalized to a Dimensionless Time \((DT)\) \([13]\) to account for differences in the smouldering front velocities and ignition times \([51]\).
Table 3.4: Dimensionless Parameters Used in Smouldering Experiments and Simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>$DT = \frac{(t - t_g)ν_f}{L}$</td>
</tr>
<tr>
<td>Solid Temperature</td>
<td>$DT_s = \frac{T_s}{T_{sp}}$</td>
</tr>
<tr>
<td>Air Mass Flux</td>
<td>$Dρu_g = \frac{ρ u_g}{(ρ u_g)_{in}}$</td>
</tr>
<tr>
<td>GAC Bulk Density</td>
<td>$Dρ_{bgAC} = \frac{ρ_{bgAC}}{(ρ_{bgAC})_0}$</td>
</tr>
<tr>
<td>Oxygen Mass Fraction</td>
<td>$DY_{O_2} = \frac{Y_{O_2}}{(Y_{O_2})_{in}}$</td>
</tr>
</tbody>
</table>

where $ν_f$ is the average smouldering front velocity (calculated using the procedure from [68]) and $L$ is the length of the packed bed. $DT < 0$ represents the preheating period before air injection (i.e., when conduction and radiation dominated); $DT = 0$ signals the beginning of air injection and smouldering ignition (i.e., when the temperature near the heater rapidly increases due to the energy released by oxidation); and $0 < DT ≤ 1$ represents the smouldering propagation time, where $DT = 1$ is the time when smouldering reached the top of the column and the reaction finished. Other parameters are also explained in Table 3.2. Table 3.5 shows the equations for a new global energy balance in 2D based on the approach developed by [13, 19]. The energy rates at the inlet (heat influx, $E_{in}$) and the outlet (convective outflux, $E_{out}$) were calculated by integrating the energy fluxes over the column radius. The radial heat loss rate ($E_{loss}$) was integrated over the column outer surface area and the oxidation rate ($E_{ox}$) was integrated over the column volume. The net energy rate ($E_{net}$) corresponds to the sum of these four components (Eq. 3.29). The integral over time of the energy rates results in the net energy ($E_i$) associated with each component $j$. 
Table 3.5: The Rate and Accumulation of Energy

<table>
<thead>
<tr>
<th>Energy</th>
<th>Eq.</th>
</tr>
</thead>
</table>
| Rate of cone heater           | \[
|                               | \hat{E}_{in} = \int_{0}^{(R+h)} \dot{q} 2 \pi r \, dr \tag{3.25} \]                                                                 |
| Rate of GAC oxidation         | \[
|                               | \hat{E}_{oxi} = \int_{0}^{R,L} -\Delta H_{GAC}(\phi_{GAC}\rho_{GAC})R_{GAC} 2 \pi r \, dr \, dz \tag{3.26} \]                     |
| Rate of radial heat loss      | \[
|                               | \hat{E}_{loss} = \int_{0}^{L} H (T_{s(r=R+h)} - T_{\infty}) 2 \pi (R+h) \, dz \tag{3.27} \]                                  |
| Rate of convective hot air    | \[
|                               | \hat{E}_{out} = \int_{0}^{R} (\rho_{g} u_{g}) C_{pg} (T_{g(z=0.76)} - T_{\infty}) 2\pi r \, dr \tag{3.28} \]               |
| Rate of net                   | \[
|                               | \hat{E}_{net} = \hat{E}_{in} + \hat{E}_{oxi} - \hat{E}_{out} - \hat{E}_{loss} \tag{3.29} \]                                 |
| Accumulation                  | \[
|                               | E_{j}(t) = \int_{0}^{t} \dot{E}_{j} \, dt \tag{3.30} \]                                                                 |
| Accumulation of net           | \[
|                               | E_{net}(t) = E_{in}(t) + E_{oxi}(t) - E_{out}(t) - E_{loss}(t) \tag{3.31} \]                                                  |

A multi-dimensional global energy balance [13] was performed to determine System Energy Efficiency (SEE) which normalizes the effects of heat losses against the energy generated, following the approach of [26]:

\[
\text{System Energy Efficiency} = \frac{E_{net}(t)}{E_{net,adiabatic}(t)} \sim \frac{E_{oxi}(t) - E_{loss}(t)}{E_{oxi}(t)} \tag{3.32}
\]

where \(E_{net,adiabatic}(t)\) was estimated by assuming a perfectly insulated column \((H = 0 \, W \, m^{-2}K^{-1})\). Moreover, Eq. (3.32) assumes that the net accumulated energy (Eq. 3.31) is dominated by \(E_{oxi}(t)\) and \(E_{loss}(t)\), since \(E_{in}(t)\) is an initial effect and is negligible compared to the energy added through smouldering. Then, a SEE sensitivity analysis was conducted by changing the radius of the column \((R)\) and heat loss coefficient \((H)\). Model
simulations were compared with published studies showing: (i) analytical [26], (ii) numerical [19, 20], and (iii) experimental [23, 27] results.

3.3 Results and Discussion

3.3.1 2D Heat Transfer Model

Figure 3.3 compares the heat transfer-only experiments and simulations. This figure shows excellent agreement between the experimental and simulated temperature evolutions of sand with errors of 6% and 5.7% at the centerline and wall, respectively. Temperature of air might be lower or higher than sand temperature depending on the time and position of the smouldering front. When the heater was turned on, the temperatures increased by conduction and radiation. Then, the air supply was turned on and convection drives heat transfer. As the heat wave progresses upwards, it is dissipated axially (due to axial convection) and radially (due to heat losses). The radial boundary condition applied to the simulations in Figure 3.3 used \( H = 3 \text{ W m}^{-2}\text{K}^{-1} \). The slight difference between numerical simulation and experimental results is associated with non-uniform heat flux delivered from the cone heater to the bottom boundary where it is more concentrated at the centerline in comparison to the wall.
Figure 3.3: Temperature evolution for the heat transfer experiments and simulation along various radial positions: a) centerline, b) r = 1.5 cm, c) r = 2.8 cm, and d) wall. The solid lines represent numerical results and the shaded region shows 95% confidence interval of experimental results.

### 3.3.2 2D Smouldering Model

Figure 3.4 includes the complexity of GAC smouldering revealed by the numerical model. Like Figure 3.3, Figure 3.4 also shows excellent agreement between GAC smouldering (0.03 kg GAC/kg sand) experiments and numerical results at the centerline (error = 5%, Figure 3.4a), wall (error = 8%, Figure 3.4b), r = 1.5 cm (error = 5%, Figure 3.4c), and r = 2.8 cm (error = 7%, Figure 3.4d). The peak temperatures ($T_p$) were quite constant along the column, where the average centerline $T_p$ was 732 ± 6 °C (experimental) and 718 °C (numerical) and the average wall $T_p$ was 609 ± 23 °C (experimental) and 480 °C (numerical). The good match between experimental and numerical results at the centerline
confirms that the thermo-physical properties of sand are well defined, also GAC was used as a simple fuel, however, the temperature differences at the wall are likely associated with wall effects that were not completely captured by the numerical model. That is, the wall boundary condition only approximated the thermal resistance offered by the insulation and did not model all thermophysical properties in the wall materials (i.e., surrounding insulation), for computational efficiency. A sensitivity analysis of the heat loss coefficient \((H)\) resulted in \(H = 7 \text{ W/m}^2\text{K}\), which is within the range expected due to free convection \([69]\). Further discussion is included in Appendix A, Section A2. Although slight differences between model results and experiments at the wall, the model was able to accurately reproduce the key trends governing the multi-dimensional interplay between heat transfer mechanisms and chemical reactions during smouldering.

Figure 3.4: Temperature evolution at multiple radial positions: a) centerline, b) \(r = 1.5\) cm, c) \(r = 2.8\) cm, and d) wall. The solid lines represent numerical results and the shaded region shows three repeats of experimental results.
While Figure 3.4 focused on the good matching in the transient smouldering behaviour, Figure 3.5 illustrates that the key spatial trends were also well-simulated. Figure 3.5a shows excellent agreement between experimental and numerical peak temperatures 37 cm from the heater (i.e., away from inlet and outlet boundary effects). The temperature distribution shows a convex smouldering front, with lower temperatures at the wall, as expected due to radial heat losses [20, 23, 70]. Figure 3.5b also shows a good agreement for the centerline longitudinal temperature distribution between experiments and simulations at three dimensionless times: $DT = 0.25, 0.50, \text{ and } 0.75$. These results show that the model is capable of reproducing: (i) the preheating ahead of the front (which validates the effective thermal properties used), (ii) the position of the smouldering front (which validates the simple one-step oxidation reaction and agrees with [26]), and (iii) the temperature cooling behind the front (which validates the approach used for simulating heat losses).

Figure 3.5: (a) Radial peak temperature distribution at 37 cm comparing experimental (shaded region) and numerical (solid line) results, (b) Centerline temperature distribution along the length of the column at 3 different $DT$: 0.25, 0.50, and 0.75.

### 3.3.3 Model Validation

The robustness of the model in predicting experiments was tested in Figure 3.6. The complete temperature profiles from these simulations and results can be seen in Appendix A, Section A2, which aligns with the results presented above in Figure 3.4. Figure 3.6
compares the average peak temperature ($T_p$) and smouldering front velocity ($\nu_f$) for different GAC concentrations from 0 (i.e., heat transfer-only) to 0.03 kg GAC (kg sand)$^{-1}$. Figure 3.6 represents both the peak temperature and front velocity increase with GAC concentration as more GAC drives hotter, faster smouldering. By increasing GAC concentration from 0 to 0.03, the radial heat transfer coefficient ($H$) increases from 3.0 to 7.0 W/m$^2$K (determined using sensitivity analysis, Appendix A, Section A2). This increase is because (i) the higher temperatures experienced during smouldering with higher GAC concentration should foster greater heat losses due to differences in the thermophysical properties of insulation (e.g., higher thermal conductivity) and (ii) the mechanism of radial heat transfer from column wall to the ambient air is free convection heat transfer, which should also increase with the wall temperature [69]. The model validation was accomplished by comparing the experimental and numerical peak temperatures and smouldering front velocities, respectively, which demonstrate excellent agreement: 658 ± 14 (experimental) and 617 ºC (numerical) and 0.36 ± 0.07 (experimental) and 0.37 cm/min (numerical).

Figure 3.6: Peak Temperature ($T_p$) and smouldering front velocity ($\nu_f$) versus GAC concentration.
3.4 Global Energy

In further understanding the implications of smouldering system behaviour, Figure 3.7 shows a multi-dimensional global energy analysis (see the equations in Table 3.5) considering local processes that play a minor role [19, 29]. During the preheating time \((DT < 0)\), the energy rate leaving the system by radial losses \(\dot{E}_{\text{loss}}\) is less than the rates of energy entering the system through the heater \(\dot{E}_{\text{in}}\) and released by oxidation \(\dot{E}_{\text{oxi}}\), i.e., \(\dot{E}_{\text{loss}} < (\dot{E}_{\text{in}} + \dot{E}_{\text{oxi}})\). Figure 3.7a notes that, while the air supply is off during this period, oxidation is weakly activated by the initial oxygen present inside the pores. Therefore, the net energy rate \(\dot{E}_{\text{net}}\) is positive and energy accumulates \(E_{\text{net}}\) in the system, Figure 3.7b. When the air supply is turned on \((DT = 0)\), the oxidation energy rate \(\dot{E}_{\text{oxi}}\) is fully activated and remains nearly constant until total fuel consumption at end of smouldering \((DT = 1)\). Moreover, \(\dot{E}_{\text{loss}}\) increases due to the increasing length of the cooling zone (hot clean sand), which increases the surface area for radial heat losses (approximately 52 and 70\% of the energy added into the system is lost radially when smouldering with 0.02 and 0.03 GAC concentration, respectively, agreeing with [23]). However, the energy leaving the system through the outlet \(\dot{E}_{\text{out}}\) is negligible when \(DT < 1\) (as the exiting emissions are nearly at ambient temperatures). While \(\dot{E}_{\text{in}}\) is crucial for ignition, the heater is turned off early in the simulation \((DT = 0.08)\); therefore, \(\dot{E}_{\text{in}}\) is negligible throughout most of smouldering. Thus, the global energy balance is governed by a balance between \(\dot{E}_{\text{loss}}\) and \(\dot{E}_{\text{oxi}}\). Since \(\dot{E}_{\text{net}}\) is strongly positive, the system rapidly accumulates energy as smouldering proceeds in a self-sustaining manner. When smouldering is finished \((DT > 1)\), energy starts leaving the system \(\dot{E}_{\text{net}} < 0\) via \(\dot{E}_{\text{out}}\), and \(E_{\text{net}}\) decreases to ambient values. The numerical error associated with spatial and temporal discretization was calculated via the global energy balance and was approximately 2\%. Altogether, these results show expected behaviour, but improve upon previous global energy developments by resolving all terms in a fully-coupled, multi-dimensional model.
Figure 3.7: (a) Energy rate for inlet, outlet, loss, and oxidation, (b) net cumulative energy and energy rate.

3.5 System Energy Efficiency Analysis

Figure 3.8 presents the results from a System Energy Efficiency (SEE) analysis (i.e., previously developed by [26] and presented in Eq. 3.24). In this analysis, the radial heat losses depend on the radius of the column \( R \) and heat loss coefficient \( H \) and approximate all terms when the smouldering front travelled 33 cm (i.e., a propagation distance common to many experimental and numerical smouldering studies). Therefore, a sensitivity analysis with a series of numerical and analytical simulations was performed by changing \( R \) and \( H \).

\( H \) is changing over a wide range of 5.4 (i.e., thick insulation) to 54 (i.e., no insulation) W m\(^{-2}\)K\(^{-1}\), to better understand how the results will change, however \( H \) higher than 27 represents the weak insulation. Figure 3.8 shows that the numerical results are in excellent agreement with the analytical solutions when \( R > 10 \) cm. This provides a robust verification of the numerical model. Additionally, the numerical model predictions are in good agreement with previous experimental and numerical studies, which provides extra confidence in the model’s predictive capacity over these system conditions [19, 20, 23, 26].

Figure 3.8 also reveals that by decreasing \( H \) and increasing \( R \) (decreasing surface-area-to-volume ratio), the SEE improves (agreeing with [26]) due to the diminishing influence of radial heat losses. Moreover, simulations show that for \( R > 40 \) cm (i.e., field scale), the
SEE is insensitive to both $R$ and $H$. However, the analytical model diverges from the numerical simulations with $R < 10$ cm (i.e., the shaded region in Figure 3.8). This divergence is due to different assumptions during quenching, where the numerical simulations more accurately capture the global energy balance terms at conditions near quenching than the approximations embedded in the analytical model [26].

Figure 3.8: System energy efficiency predicted by the calibrated numerical model (coloured circles), analytical model (coloured, dashed lines), and previous studies (symbols) from Rashwan et al. [26], Zanoni et al. [19], Pozzobon et al. [20], and Martins et al. [23]. Different radii (from 4 to 50 cm) and different heat loss coefficients (from 5.4 to 54 W/m$^2$ K$^{-1}$) were considered. Increasing $H$ represents decreasing the quality of insulation. The shaded gray region shows where the analytical predictions are less accurate because of quenching effects.

3.6 Analysis of Multi-Dimensional Contour Maps

2D contour maps and videos of the solid temperature, GAC bulk density, and oxygen mass fraction are presented in Figure 3.9. Figures 3.9a and 3.9b compare 2D contours of the experimental and numerical solid temperatures, respectively, at $DT = 0.5$. These figures
reveal similar temperatures, positions and shapes of the cooling front, smouldering front, and preheating zone. The slight differences are related to the low experimental temperature resolution. Moreover, Figure 3.9b shows the multi-dimensional transfer effect of air flux. This air flow divergence decreases the air mass flux from 0.059 kg m$^{-2}$ s$^{-1}$ at the inlet boundary to ~0.055 kg m$^{-2}$s$^{-1}$ at the centerline, while it increases the air mass flux to 0.082 kg m$^{-2}$s$^{-1}$ near the wall.

Three different zones shown in Figure 3.1 are determined in Figure 3.9a, as previously seen in [30]. Region (I) notes the end of the cooling zone, which is governed by convection heat transfer between hot clean sand and inlet cold air from the inlet. This region grew to ~13 cm in Figs. 3.9a and 3.9b. The shape of the cooling front in this region is concave (i.e., higher temperature at the wall), as a fraction of the energy released from smouldering was transferred quickly downward along the highly conductive wall into this region. Region (II) shows the remaining length of the cooling zone, which grew to ~23 cm in Figs. 3.9a and 3.9b. Similar to Region (I), Figs. 3.9a and 3.9b show that the numerical model captured the major trends in Region (II) observed in the experiment. This region is controlled by the difference between the smouldering and cooling velocities and distorted by radial heat losses. Without radial heat losses, this region would grow indefinitely; however, with heat losses, it would reach a maximum length when the radial heat losses balance the rate of energy released from smouldering. In this region, the temperatures were higher at the centerline due to radial heat losses [13, 26]. Region (III) shows the smouldering front associated with GAC oxidation, which was ~0.15 cm thick at $DT = 0.5$. Figure 3.9c shows that GAC was fully destroyed, and only clean sand remained behind the smouldering front. These smouldering front features agree with many applied smouldering studies, e.g., [11, 20, 23, 45, 71]. Moreover, the smouldering front is convex (higher temperatures at the centerline), which agrees with the simulations from [20] under similar conditions. Unlike the fuel in this region, the oxygen is not fully consumed, i.e., it decreases from 0.23 to 0.06 and 0.12 at the centerline and wall, respectively. Higher oxygen consumption at the centerline fosters more robust chemical reactions, which contributes to higher peak temperatures. Finally, Region (IV) shows the preheating zone, where the temperature of the sand/GAC layer is increased by the hot air passing through the smouldering front. It was hypothesized that there is a super-adiabatic effect associated with the local radial
velocity component that brings heat towards the centre from the wall [22]. A sensitivity analysis on GAC concentration (-), and Darcy air flux (m s$^{-1}$) using a validated model was performed in Appendix A, Section A4, and results were discussed. These numerical results provide quantitative results that substantiate that hypothesis.

Figure 3.9: 2D contours of: (a) experimental temperatures, (b) simulated solid temperature, (c) simulated GAC bulk densities, and (d) oxygen mass fractions.

3.7 Analysis of Multi-dimensional Transfer Effects

3.7.1 Global Quenching

Figure 3.10 shows a model simulation of GAC smouldering with 0.02 kg GAC (kg sand)$^{-1}$ and $H = 28$ W m$^{-2}$K$^{-1}$. The multi-dimensional transfer effects of dimensionless parameters including solid temperature, air mass flux, GAC bulk density, and oxygen mass fraction were investigated (see Table 3.4). The results are shown at three different times including $DT = 0$ (i.e., smouldering initiation), 0.25 (i.e., peripheral extinction), and 0.50 (i.e., global quenching). Figures 3.10b, f, and j show peak temperatures drop near the wall due to radial heat losses in the cooling zone that lead to peripheral extinction at the initial time, agreeing with [12, 72], and global quenching at the latter time (i.e., non-self-sustaining smouldering), agreeing with [28], moreover, peripheral extinction may be enhanced by a parabolic laminar flow pattern entering the system, which may decrease the flow rate close to the wall and create an unburned, cooler crust along the reactor wall that could enhance
air channelling [25]; therefore, air mass flux increases from centerline to the wall, agreeing with experimental data [20, 23, 35]. This multi-dimensional transfer effect is low initially (e.g., 0.78 to 1.43) then increases (e.g., 0.62 to 1.62) and, finally by quenching the smouldering, reduces again (e.g., 0.72 to 1.28); see Figs. 3.10a, e, i. The longitudinal distribution of air mass flux (Figure 3.10m) shows minimum air mass flux at the centerline in the position close to the peak temperature where it tends to move around the hot zone towards the wall that causes a reduction in forward heat transfer at the centerline.

Figures 3.10c, g, and k show 2D contours of the GAC bulk density distributions, which show how chemical reaction multi-dimensional transfer effects develop in less robust smouldering systems (e.g., with lower SEE because of high heat loss coefficient (H) and low radius (R)). Peripheral extinction starts at early time then grows into the reactor center and leads to global quenching. A convex shape of the smouldering front is predicted, agreeing with the field data in [24], which confirms that, in this scenario, the effect of multi-dimensional reactions dominates that of air mass flux [22]. Figures 3.10d, h, and l show 2D contours of the oxygen mass fraction distribution, where the oxygen supply decreases at the centerline because of multi-dimensional transfer effects of air flux that cause lower smouldering robustness. By decreasing the smouldering robustness, oxygen mass fraction consumption at the smouldering front drops, decreasing from 1 to 0.63 and 0.72 at Dt = 0 and 0.25, respectively (see Figure 3.10o). Altogether, Figure 10 demonstrates the powerful capabilities of this novel multi-dimensional model in exploring many complicated and interconnected phenomena.
Figure 3.10: (a, e, and i) and (m, n, and o) show radial and longitudinal distribution of dimensionless parameters, respectively. 2D contours of temperature and air mass flux were shown in (b, f, and j), GAC bulk density (c, g, and k), and oxygen mass fraction (d, h, and l) at Dt = 0.00, 0.25, and 0.50, respectively.
### 3.7.2 Permeability Heterogeneity

The computational domain and list of simulations with Region 1 and 2 in different permeability heterogeneity scenarios were detailed in Appendix A, Section A5 where Simulation # 1 (Figure 3.11a, b, and c) with a permeability ratio \( \left( k_p(1)/k_p(2) \right) \) of 2 shows higher smouldering front velocities and hotter peak temperatures (0.65 cm/min and 716 ºC, respectively) in Region 1 compared to Region 2 (0.60 cm/min and 660 ºC, respectively). These values corresponded to a higher air mass flow rate \( 3.3 \times 10^{-4} \text{ kg/s} \) in Region 1 than Region 2 \( 2.5 \times 10^{-4} \text{ kg/s} \) – note the small air vectors in Region 2 (Figure 3.11a). In comparison to the Base Case (homogeneous domain), the peak temperature was relatively unchanged, and the smouldering front velocity increased in Region 1; although, Region 1 had the same intrinsic permeability as the Base Case. This behaviour is hypothesized to be due to the higher fraction of air mass flow rate redirected from Region 2 (low permeability) towards Region 1 (high permeability). In Region 2, the smouldering front velocity also increased compared to the Base Case, despite the lower air mass flow rate. The fast smouldering velocity in Region 2 is hypothesized to have been driven by lateral heat transfer outward from Region 1 toward Region 2, which agrees with experiments from [45]. Oxygen mass fraction decreased to 0.08 and 0.02 (-) in Region 1 and 2, respectively, which shows lower oxygen mass fraction consumed at the front in Region 1 because of higher air mass flow rate – despite that smouldering was more robust in Region 1 than Region 2. Therefore, the surprisingly fast smouldering front velocity in Region 2 with a low air mass flow rate is due to a key multidimensional heat transfer effect.

Simulation # 2 (Figure 3.11d, e, and f) represents a permeability ratio of 10, where a major fraction of the air was funnelled into Region 1 from Region 2 (i.e., with air mass flow rates of \( 4.9 \times 10^{-4} \text{ kg/s} \) and \( 0.8 \times 10^{-4} \text{ kg/s} \), respectively). Note the absence of air vectors in Region 2 (Figure 3.11d). This strong contrast in air mass flow rates between Regions 1 and 2 resulted in an even higher smouldering front velocity and peak temperature in Region 1 when compared to the homogeneous Base Case. In Region 2, the smouldering front is quenched half-way up the column (see Video S2.b). Though a large fraction of the air mass flow rate in Region 2 was channelled into Region 1, the remaining air flow was above the threshold for smouldering self-propagation observed from laboratory studies [17, 46, 47].
Therefore, it is hypothesized that radial heat losses played a key role in driving Region 2 quenching in this simulation. The oxygen mass fraction ahead of smouldering decreased to 0.08 and 0 (-) in Regions 1 and 2, respectively; this indicates that nearly the same fraction of incoming oxygen was consumed in Simulation # 2 as in Simulation # 1, which drove more robust, faster smouldering through Region 1 in Simulation # 2 than Simulation # 1. Oxygen was fully consumed in Region 2 prior to quenching due to the low air mass flow rate.

Simulation # 3 (Figure 3.11g, h, i) represents a permeability ratio of 100 times where, due to insufficient air mass flow rate in Region 2 \( (0.1 \times 10^{-4} \text{ kg s}^{-1}) \), smouldering quenched quickly at the bottom of the column shortly after a successful ignition. However, the smouldering front velocity and peak temperature in Region 1 increased compared to the homogeneous Base Case, but smouldering in this region was hindered by heat losses outward into the unreactive Region 2. In Appendix A, Section A4, Figure A.9b shows that, with the same air mass flow rate equal to \( 5.6 \times 10^{-4} \text{ kg s}^{-1} \) (i.e., \( 0.098 \text{ m s}^{-1} \)) in a homogenous medium with full smouldering, the smouldering front velocity should be \( 0.93 \text{ cm min}^{-1} \). However, Simulation # 3 shows smouldering front velocity was lower (\( 0.81 \text{ cm min}^{-1} \)) because of heat transfer outward from the reaction zone in Region 1 lost to Region 2. This result aligns with theory [73] and experimental results [45] in the literature.
Figure 3.11: 2D contours of temperature and air flux distribution (a, d, and g), GAC bulk density (b, e, and h), and Oxygen mass fraction (c, f, and i) at $Dt = 0.5$ for simulations #1, 2, and 3. Dashed lines determine the boundary of Region 1 and Region 2.

Figure 3.12 shows the results from Simulations #4-6 where Region 1 modelled fine sand (low permeability) and Region 2 modelled coarse sand (high permeability). Simulations #4-6 investigated the same permeability differences as explored in Simulations #1-3 but in different orientations. These different orientations generally led to similar distributions in air mass flow rate from the low to high permeability regions but exhibited important differences associated with multidimensional heat transfer effects (see Figure 3.9b).

Figure 3.12a shows that only a small fraction of the air mass flow rate in Simulation #4 passed through Region 1 ($1.9 \times 10^{-4} \text{ kg s}^{-1}$) compared to Region 2 ($3.9 \times 10^{-4} \text{ kg s}^{-1}$). Note the small and large air vectors in Regions 1 and 2, respectively. The high air mass flow rate in Region 2 increased the smouldering front velocity that resulted in a concave front shape, i.e., smouldering travelled faster in Region 2 than in Region 1; however, the peak
temperature in Region 2 suffered from radial heat transfer inward to Region 1 and heat losses outward.

Region 1 in Simulation #4 showed a much higher peak temperature (928 °C), lower smouldering front velocity (0.47 cm min\(^{-1}\)), and lower air mass flow rate (1.9 \(\times\) 10\(^{-4}\) kg s\(^{-1}\)) than Region 2, Simulation #1 (660 °C, 0.60 cm/min, and 2.5 \(\times\) 10\(^{-4}\) kg s\(^{-1}\), respectively). These simulations modelled the same intrinsic permeability differences, but different orientations. It is hypothesized that high peak temperature in Simulation #4’s Region 1 was due to heat transfer inward from Region 2 to Region 1, which led to greater preheating in Region 1. This inward preheating aligns with findings from [22]. Oxygen mass fraction after front decreased to 0 and 0.13 (-) in Regions 1 and 2, respectively, which shows the oxygen was fully and partially consumed in Regions 1 (low permeability) and 2 (high permeability), respectively. These results mirror the oxygen consumption differences discussed above in Simulations #1-3 with the alternative orientations.

Simulation #5 represents the permeability ratio of 0.10 where higher smouldering front velocities but lower peak temperatures (0.53 cm/min and 600 °C, respectively) were achieved in Region 1 compared to Region 2 (0.27 cm/min and 767 °C respectively). These smouldering differences corresponded to a higher air mass flow rate (5.1 \(\times\) 10\(^{-4}\) kg/s) in Region 2 than Region 1 (0.7 \(\times\) 10\(^{-4}\) kg/s). The low peak temperature in Region 2, despite high air mass flow rate and fast smouldering front velocity, was again due to radial heat losses outward and heat transfer inward from Region 2 to Region 1. Simulation #5 shows similar trends as observed in Simulation #4, but to a greater degree. That is, though the air mass flow rate redistribution in Region 2 was greater in Simulation #5 than #4, the smouldering front velocities and peak temperatures were similar between both simulations. This similar smouldering performance, despite different airflow patterns, is hypothesized to be due to greater heat transfer from Region 2 to Region 1 and radial heat losses, which both moderated the local energy balance in Region 2. Moreover, Simulation #5’s Region 1 peak temperature was much lower than that of Simulation #4, but still relatively high due to the energy transfer inwards from Region 2. Figure 3.12f shows the oxygen was fully consumed at Region 1, again because of low air mass flow rate and robust smouldering in this region, while it decreased to 0.15 at Region 2. Note that a smaller fraction of Region
oxygen was consumed in Simulation # 5 than # 4 because of the increased air mass flow rate and local energy balance losses described above. Importantly, though Simulations # 5 and # 2 exhibited similar air flow redistributions from the low to high permeability regions, the low permeability Region 1 in Simulation # 5 was self-sustaining, while the low permeability region in Simulation # 2 experienced quenching. This difference between Simulations # 5 and # 2, i.e., with the same permeability differences but different orientations, highlights the complicated interplay between both global heat and mass transfer effects on smouldering performance.

Simulation # 6 revealed that, with a permeability ratio of 0.01, the majority of the air flow rate was funnelled into Region 2. The smouldering velocity and peak temperature in Region 2 of Simulation # 6 were similar to those in Simulations # 5 and # 4, again, because the local energy balance was moderated by heat transfer outwards (i.e., radial heat losses) and inwards (i.e., conductive heat transfer from Region 2 to Region 1). However, Region 1 in Simulation # 6 exhibited global quenching after a successful ignition because of the low air mass flow rate in this region, which aligns with previous predictions [45, 73].
Overall, permeability heterogeneity strongly influences air mass flow rate distribution, smouldering front velocity and robustness, peak temperature, front shape, and oxygen consumption. Air mass flux distribution plays a key role in smouldering systems as it delivers oxygen and drives convective heat transfer to and from the reaction zone; therefore, low air mass flux from severe channelling resulted in global quenching in Simulations # 3, and # 6. Moreover, these simulations also show the important role of lateral heat transfer between adjacent layers, as this redistribution of energy can weaken smouldering in regions with faster smouldering velocities, and strengthen regions with slower smouldering velocities.
3.8 Conclusion

In this study, a 2D numerical model was developed and validated with experimental results quantitatively and qualitatively to investigate the effect of radial heat loss on temperature, air mass flux, oxygen mass fraction and chemistry distribution. For validating the 2D numerical model, a heat transfer model was developed by eliminating the effect of chemical reactions and then validated with heat transfer-only experiments. A simplified chemical model (i.e., global one-step oxidation reaction) achieved from TG/DTG experiments was proposed to describe GAC smouldering in an inert porous medium. Last, a 2D smouldering model was developed combining the heat transfer and chemical models.

The model predictions were in excellent agreement with the experimental results in terms of temperature evolutions in space and time, smouldering velocities, and the shape of the smouldering front. The model also reproduced expected dynamics in multi-dimensional transfer effects of air mass flux and reactions. Moreover, it is perhaps the first model to accurately simulate both local and global extinction of smouldering and permeability heterogeneity effects across a range of scenarios. Therefore, this new model is anticipated to accurately predict smouldering behaviour over a wide range of conditions and is relevant for application and design. Furthermore, a global energy balance revealed evolutions in the overall system behaviour, and the results compared well with other energy balance results from numerical simulations, experiments, and analytical modelling in the literature. This clearly demonstrates the model’s ability to capture the main physics and chemistry of smouldering and their complex interactions which significantly impact the outcomes. Altogether, this validated multi-dimensional smouldering model is anticipated to help better understand, design, and optimize future applied smouldering systems.

3.9 References


[59] É. Clapeyron, Mémoire sur la puissance motrice de la chaleur, Jacques Gabay1834.


Chapter 4

4 Investigation of Applied Smouldering in Different Conditions: The Effects of Oxygen Mass Flux

4.1 Introduction

Applied smouldering systems are operated as a “self-sustaining” process for a variety of applications, including: (i) waste-to-energy [1, 2], (ii) syngas production (e.g., CO and H2) [3-6], (iii) off-grid sanitation [7], (iv) remediation of contaminated soil [8-10], and (v) energy and resource recovery [11, 12]. Smouldering combustion is defined as a flameless form of combustion driven by exothermic oxidation reactions at the surface of porous fuels [13]. In engineering applications, applied oxygen supply, which is often moderated via the air delivery, controls many features including processing rate, peak temperatures, residual fraction of organic compounds and the fate of smouldering in critical cases [13-21]. While smouldering is generally fuel-rich where all supplied oxygen is necessarily consumed. Therefore, the oxygen supply and oxygen consumption rates can be adjusted in applied smouldering systems for process optimization [22].

Applied smouldering systems are often designed to operate in a robust self-sustaining condition (i.e., global net positive energy balance) [22, 23] (Figure 4.1a). Nevertheless, smouldering systems can exhibit a spectrum of conditions depending on oxygen supply and consumption (see Figure 4.1) [24]. Weak smouldering (i.e., global net energy balance still positive but closer to 0) may be unavoidable in systems using low calorific or high moisture contents wastes (Figure 4.1b), and global quenching is a form of system failure (Figure 4.1c) [18, 25]. Conversely, in a fire safety context, smouldering quenching is desired while robust smouldering should be avoided [26]. To quantify whether smouldering is robust, weak, or towards quenching, energy balance analyses can be applied locally across the reaction zone (Figure 4.1d) and globally across the system boundaries (Figure 4.1e) [9, 22]:

\[
\dot{E}_{\text{net}} = \dot{E}_{\text{in}} + \dot{E}_{\text{oxid}} - \dot{E}_{\text{out}} - \dot{E}_{\text{loss}} - \dot{E}_{\text{pyr}}
\]  

(4.1)
The net energy rate ($\dot{E}_{\text{net}}$) (i.e., net rate of energy accumulation) indicates the robustness of smouldering systems, where the global $\dot{E}_{\text{net}}$ is mostly governed only by the balance between the rates of energy released by oxidation ($\dot{E}_{\text{oxid}}$) and lost by lateral heat losses ($\dot{E}_{\text{loss}}$) [27]. The pyrolysis energy rate ($\dot{E}_{\text{pyr}}$) often plays a minor role in applied systems, e.g., bitumen smouldering [22, 26]. The rate of energy added from igniter ($\dot{E}_{\text{in}}$) and lost due to convection at the system outlet boundary ($\dot{E}_{\text{out}}$) are initial- and end-effects, respectively, and negligible when the smouldering front is sufficiently far from the inlet and outlet boundaries [9, 28].

The Damköhler number ($Da$) is defined as the ratio of mass transport ($\tau_f$) to the reaction time scales ($\tau_R$) and used in many combustion science analyses to identify extinction conditions at a critical value ($Da_{\text{cri}}$). This approach can be applied to smouldering [29] using the same definition:

$$Da = \frac{\tau_f}{\tau_R} \quad (4.2)$$

Considering the global $\dot{E}_{\text{net}}$ and $Da_{\text{cri}}$, four different scenarios are possible where the level of robustness is determined by the energy accumulated in the system that acts as a buffer against quenching and stabilizes the reaction [22]. Figure 4.1, for a reactor, using a mixture of sand and GAC, presents all four scenarios. The first scenario is given in Figure 4.1a, (i) $\dot{E}_{\text{net}} \gg 0 \& Da > Da_{\text{cri}}$ represents robust self-sustaining smouldering where energy accumulation increases the system's robustness. (ii-iii) $\dot{E}_{\text{net}} \sim 0 \& Da > Da_{\text{cri}}$ represents either (ii) robust where there is a large energy buffer and a cooling zone is developing at a similar rate as the smouldering front propagation (this will occur theoretically in very tall reactors [30]) or (iii) weak self-sustaining smouldering without or with a small rate of energy accumulation where the energy buffer is relatively small, and it could not completely overcome heat losses, therefore the system is highly sensitive to lateral heat losses. In this condition, some layers of fuel around the reactor wall will remain unburned (i.e., crust formation) which facilitates the air channelling and causes more weakening of the smouldering at the centerline.
In this case, peripheral extinction occurs and generally, the remaining unreacted porous media insulates the centreline [31] allowing for smouldering to persist (Fig 4.1b). (iv) $\dot{E}_{\text{net}} < 0 \& Da < Da_{\text{crit}}$ represents global quenching (i.e., non-self-sustaining smouldering) [22, 32].

Figure 4.1: This figure presents three smouldering regimes for a specific mixture of sand and GAC. (a) multiple distinct zones in a typical applied smouldering reactor, (b) temperature distribution and the position of peak, average, and ambient temperatures performed to determine smouldering and cooling front velocities, respectively. Smouldering propagation in (c) robust condition, (d) weak condition, (e) global quenching. (f) shows the boundaries and terms in the local energy balance and (g) shows the same information for the global energy balance.

In addition to robustness, applied systems foster smouldering that remains self-sustained until all the fuel is consumed at the front [21, 33] and uses oxygen in an efficient manner, i.e. all the oxygen supply is consumed at the front [18]. These characteristics enable applications like soil remediation [8], waste-to-energy [1], off-grid sanitation [34] and syngas production [3].
Oxygen consumption plays a key role in defining smouldering robustness, oxygen- or fuel-rich conditions, and quenching conditions due to dynamics that need to be resolved in space and time [22, 26, 35]. Some dynamics are intuitive, and others are not. For example, a reduction in oxygen consumption can transition a smouldering system from robust to weak conditions with cooler peak temperatures, slower smouldering velocities, peripheral extinction, and global quenching in limiting conditions [16, 18, 33, 36]. Moreover, in fire safety scenarios, oxygen supply is a critical parameter that controls smouldering propagation and transition to flaming. It was found that the oxygen concentration threshold for fire activity on the earth is close to 11% [37]. While these effects are intuitive, oxygen reductions can also lead to unexpected effects due to the interplay between chemical and physical processes. Aldushin et al. [38] theorized that oxygen dilution with an inert gas can slow the smouldering front velocity (i.e., the rate of smouldering propagation, \( v_f \) in Eq. 4.3 [19]) to equal the cooling velocity (i.e., the rate of propagating cooling zone behind the front, \( v_c \) in Eq. 4.4 [39]) where \( v_c \) is largely insensitive to the oxygen concentration [36, 40]. The condition \( v_f = v_c \) leads to a super-adiabatic singularity where almost all energy released from robust smouldering accumulates in a thin reaction region and increase peak temperature towards infinity [38, 41], however in real application, this condition never achieved. Super-adiabatic singularity is equal to combustion process that takes place adiabatically (i.e., no heat losses) with no shaft work where the maximum temperature of the products is referred to as the adiabatic flame temperature [42].

\[
\begin{align*}
\nu_f &= \frac{\Delta Y_{O_2} \rho_g u_g \Delta H - \dot{q}_{loss} \left( \frac{A_l}{A_c} \right) + \dot{q}_{lg}}{(\rho C_p)_{eff} \left( T_p - T_{amb} \right) + \Delta Y_{O_2} \rho_g \Delta H} \quad (4.3) \\
\nu_c &= \frac{\rho_g C_p u_g}{(\rho C_p)_{eff}} \quad (4.4) \\
T_p &= T_{amb} + \frac{m_{fuel}}{m_s} \frac{\Delta H_{fuel}}{C_p s \left( 1 - \frac{v_c}{v_f} \right)} = T_{amb} + \frac{T_{adiabatic}}{\left( 1 - \frac{v_c}{v_f} \right)} \quad (4.5)
\end{align*}
\]
where $q_{\text{loss}}, q_{\text{ig}}, A_L, A_c, m_{\text{fuel}}/m_s, \Delta H_{\text{fuel}},$ and $T_{\text{adiabatic}}$ are defined as radial heat loss, ignition heat flux, lateral and cross-sectional areas, mass fraction of fuel to sand, the heat released by mass of fuel, and adiabatic combustion temperature, respectively, assuming all the heat released from fuel absorbed in the nearby solid (e.g., inert porous medium). While this super-adiabatic singularity is theoretically possible, to the authors’ knowledge, it has not been rigorously achieved in any applied smouldering systems, and only a handful of studies have investigated these effects [36, 43, 44].

Across the smouldering literature, inlet air flux is routinely investigated as a key sensitivity parameter, as it controls both oxygen supply and convective heat transfer rates in smouldering systems [8, 23, 31, 45, 46]. In applied systems, low inlet air flux systems (~0.5 to 1.4 cm s$^{-1}$) foster decreased oxygen supply and convective heat transfer, which therefore results in low peak temperatures and slow smouldering velocities [47, 48]. High inlet air flux systems (~2.5 to 8.3 cm s$^{-1}$) exhibit high temperatures and fast smouldering velocities (up to 0.5 cm min$^{-1}$) [22].

While 1D smouldering models have elucidated some of the phenomena described above [32, 49], weak smouldering leads to numerous multidimensional effects that affect energy redistribution, which are not captured in 1D models [24, 50]. For example, multidimensional models are needed to: (i) capture non-uniformities in temperature, air mass flux, oxygen mass flux, and chemical reactions associated with radial heat losses, which can deteriorate smouldering robustness; (ii) consider the effective radius of smouldering that could shrink due to peripheral extinction, especially if smouldering is weak, which affects energy redistribution and can promote air channelling in the unburned crust; and (iii) quantify the smouldering front deformations that can change across weak to robust conditions. These multidimensional effects are generally poorly understood. Given that the relevant transport processes are affected by buoyancy, the scale has an amplifying effect, therefore without a clear understanding of multidimensional effects, it is difficult to design larger, commercial-scale smouldering systems [51].

In a similar manner, there is even less work completed on the sensitivity of oxygen variations on applied smouldering systems. As mentioned previously, the effects of oxygen
variations may lead to non-intuitive system behaviour, which may constitute a system risk or perhaps be harnessed for improved operation. To the authors’ knowledge, no study has explored the multidimensional transfer effects associated with oxygen variations in applied smouldering systems.

This study tackles these key knowledge gaps by pairing a recently validated multidimensional numerical model [24] alongside smouldering experiments with varying oxygen concentrations and air fluxes. These experiments exhibited robust, weak, and quenched smouldering, and fostered both oxygen- and fuel-rich conditions. Numerical sensitivity analyses were performed to understand the effects of these parameters and fuel concentration on smouldering characteristics. Local and global energy balances were performed to quantify the multidimensional transfer effects on the system energy redistribution over a wide spectrum of conditions from robust to weak smouldering, to global quenching. Altogether, this study illuminated many coupled multidimensional effects, particularly with varying oxygen concentrations, which supports the development of smouldering systems for a wide range of beneficial applications.

4.2 Methodology

4.2.1 Experiments

Eight smouldering experiments were conducted in a laboratory-sized reactor to provide a unique, targeted data set across smouldering robustness and oxygen- or fuel-rich conditions. These experiments were simulated via a validated axis-symmetric (2D) smouldering model [24]. The experiments explored the effects of oxygen mass fraction \(Y_{O_2}\), and inlet air flux \(u_g\). The experimental setup (Figure 4.2a) and methodology are described in detail in [28]; therefore, only the differences are explained here. An air diffuser made of perforated tubes was placed at the bottom of the reactor and connected to two mass flow controllers (FMA5400 Series, 0-80 L min\(^{-1}\), Omega Ltd), which controlled the mass flow rates of: (i) air from an air compressor and (ii) a nitrogen tank (99.99 % purity). These mixed gases were used to control the supplied oxygen mass fraction \(Y_{O_2}\). Granular Activated Carbon (GAC) (McMaster-Carr, CAS Number: 7440-44-0) was used as the model fuel because it minimizes the chemical complexity [27, 30, 52-54]. Moreover, there
is an emerging interest in smouldering spent GAC from adsorption processes, as smouldering has been demonstrated to be a highly effective tool for GAC disposal (e.g., GAC contaminated with per- and polyfluoroalkyl substances [55]). The GAC was mixed with silica sand (K&E Sand and Gravel, WP #2, grain size between 0.118 and 0.200 mm) via an electric mixer (Kitchen Aid) at 0.03 kg\textsubscript{GAC} kg\textsubscript{sand}\textsuperscript{-1}. The mixture was carefully packed in the reactor to ensure good homogeneity. Each experiment heated a localized area with a resistive heater (Watlow, USA, 450 W) until the first thermocouple above the heater (x = 0.12 m) reached 270 °C (for experiments # i, ii, iii), and 400 °C (for experiments # iv, v, vi, and vii). These differences in ignition procedures only led to small differences in initial effects that did not influence the main effects studied. Then, air injection at a fixed rate was supplied at \( t = t_g \), which ignited the smouldering reactions. The heater was then turned off at \( t = t_h \) while the air was maintained until the end of smouldering. The smouldering front propagated upwards until it reached the top of the reactor, leaving behind clean sand. Table 4.1 shows the list of experiments and their corresponding simulations.

Table 4.1: List of the Experiments and their Corresponding Simulation Performed for Model Validation

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Simu</th>
<th>Exp Repeat</th>
<th>( u_{g,m} ) [m/s]</th>
<th>( C_c ) [-]</th>
<th>( Y_{O_2} ) [-]</th>
<th>( \Delta H ) [MJ/kg]</th>
<th>( v_{O_2} ) (kg O\textsubscript{2}/kg GAC)</th>
<th>Air On (( t_g )) [s]</th>
<th>Heater Off (( t_h )) [s]</th>
<th>Self Sustained</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>1</td>
<td>1</td>
<td>0.05</td>
<td>0.03</td>
<td>0.230</td>
<td>32.9</td>
<td>3.1</td>
<td>3660</td>
<td>4380</td>
<td>Yes</td>
</tr>
<tr>
<td>ii</td>
<td>2</td>
<td>3</td>
<td>0.05</td>
<td>0.03</td>
<td>0.115</td>
<td>30.4</td>
<td>2.7</td>
<td>4500 ±70</td>
<td>4980 ±80</td>
<td>Yes</td>
</tr>
<tr>
<td>iii</td>
<td>3</td>
<td>1</td>
<td>0.05</td>
<td>0.03</td>
<td>0.057</td>
<td>21.2</td>
<td>1.9</td>
<td>3660</td>
<td>4980</td>
<td>Yes</td>
</tr>
<tr>
<td>iv</td>
<td>4</td>
<td>1</td>
<td>0.01</td>
<td>0.03</td>
<td>0.230</td>
<td>31.4</td>
<td>2.2</td>
<td>4620</td>
<td>7740</td>
<td>Yes</td>
</tr>
<tr>
<td>v</td>
<td>5</td>
<td>1</td>
<td>0.01</td>
<td>0.03</td>
<td>0.115</td>
<td>26.8</td>
<td>2.0</td>
<td>4500</td>
<td>7560</td>
<td>Yes</td>
</tr>
</tbody>
</table>
The thermocouples (Type K, Inconel, Omega) were placed at the centerline spaced 3.5 cm apart (see the position of the thermocouples, Figure 4.2a) and temperatures were recorded every two seconds using a data logger (Multifunction Switch/Measure Unit 34980A, Agilent Technologies). The heat flux ($\dot{q}$) from the heater towards the reactor inlet boundary was considered based on the previous study [52].

![Figure 4.2: (a) Schematic view of the experimental setup and (b) computational domain](image)

To compare the results between different experimental conditions, the solid temperature ($T_s$), air mass flux ($\rho_g u_g$), GAC bulk density ($\rho_{bgAC}$), and oxygen mass flux ($\rho_g u_g Y_{O_2}$) were normalized in Table 4.2. The time was normalized as a Dimensionless Time (Dt) [9] to account for differences in the smouldering front velocities, fuel bed lengths, and ignition times [56].
Table 4.2: Dimensionless Parameters used in Smouldering Experiments and Simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>$D_t = \frac{(t - t_g) \nu_f}{L}$</td>
</tr>
<tr>
<td>Solid Temperature</td>
<td>$D_{T_s} = \frac{(T_s - T_{amb})}{(T_{p_{max}} - T_{amb})}$</td>
</tr>
<tr>
<td>Air Mass Flux</td>
<td>$D_{\rho_g u_g} = \frac{\rho_g u_g}{(\rho_g u_g)_{in}}$</td>
</tr>
<tr>
<td>GAC Bulk Density</td>
<td>$D_{\rho_{bGAC}} = \frac{\rho_{bGAC}}{(\rho_{bGAC})_0}$</td>
</tr>
<tr>
<td>Oxygen Mass Flux</td>
<td>$D_{\rho_g u_g Y_{O_2}} = \frac{\rho_g u_g Y_{O_2}}{(\rho_g u_g Y_{O_2})_{in{max}}}$</td>
</tr>
</tbody>
</table>

Note that $\nu_f$ is the average smouldering front velocity calculated using the procedure from [57]. $L$ is the length of the packed bed, $t$ is time, and $t_g$ is the air injection time. Time ($t$) was normalized to a Dimensionless Time ($D_t$) to account for differences in smouldering front velocities and ignition times [56] where $D_t < 0$, $D_t = 0$, and $0 < D_t \leq 1$ represent the preheating, smouldering ignition (i.e., air injection initiation), and the smouldering propagation time, which are all explained in detail in [9]. The cooling front velocity ($\nu_c$) was determined by averaging the maximum (peak) and minimum (ambient) temperatures ($T_{avg}$) in the cooling zone (Figure 4.1b). The position of $T_{avg}$ was identified after ignition ($t_1$, $z_1$) and then it was tracked along the reactor over time. As the cooling front propagated to the top of the reactor, the time and position of $T_{avg}$ ($t_2$, $z_2$) was recorded. Finally, $\nu_c$ was calculated by dividing the traveled distance ($z_2 - z_1$) over the time difference ($t_2 - t_1$) between the two positions. The other parameters are also explained in Table 4.3.
4.3 Modelling

An axisymmetric, 2D numerical model was developed previously in COMSOL Multiphysics (Version 6) [24], which was adapted to a different geometry in this study using a high resolution of 0.05 and 0.16 cm discretization axially and radially, respectively. The computational domain used cylindrical coordinates and simulated: (i) a porous medium of clean sand at the bottom and top of the reactor with 10 and 1 cm thicknesses, respectively; (ii) a porous medium composed of clean sand mixed with GAC; and (iii) a surrounding, solid metal sheet representing the reactor stainless steel wall as shown in Figure 4.2 (b). The governing equations (Eqs. 4.10-28) were solved at every node in space and time, where two main phases were considered: (i) solid (i.e., GAC and sand) and (ii) gas. GAC smouldering kinetics followed a global, 1-step oxidation mechanism [52] where pyrolysis reactions were assumed to be negligible [27, 53, 54]. See a robust explanation of this approach in [24]:

\[
\text{GAC} + \nu_{O_2} \text{O}_2 \xrightarrow{R_{\text{GAC}}} \nu_{\text{CO}} \text{CO} + \nu_{\text{CO}_2} \text{CO}_2 \tag{4.10}
\]

Oxidation reaction rate \( R_{\text{GAC}} \) was described by first-order Arrhenius reaction [58]:

\[
R_{\text{GAC}} = A_{\text{GAC}} \exp \left( -\frac{E_{\text{GAC}}}{R_g T_s} \right) (Y_{\text{GAC}})(Y_{\text{O}_2}) \tag{4.11}
\]

where \( A_{\text{GAC}} \) is the pre-exponential factor, \( E_{\text{GAC}} \) is the activation energy, \( T_s \) is the solid temperature, and \( \nu_{O_2} \) is the oxygen stoichiometric coefficient measured from experimental data (see Appendix B, section B.2 and Table 4.1). Experimental results suggested that by diluting the oxygen mass fraction \( (Y_{O_2}) \) from 0.230 to 0.057 [-] (Exp i-iii), peak temperatures decreased from 924 to 698 °C, which resulted in different oxygen stoichiometric coefficients \( (\nu_{O_2}) \). Experimental measurements of CO and CO\(_2\) show that by diluting the oxygen volume fraction, more complete combustion was achieved, increasing CO\(_2\)/CO ratio. This behavior might be associated with i) different oxygen diffusion towards the GAC surface due to oxygen dilution and ii) homogeneous reactions (e.g., between CO and O\(_2\)) in the thick reaction zone (e.g., Exp iii) after the first initial global reaction of GAC and O\(_2\). Investigation of these hypotheses is beyond the scope of
this paper. The GAC and oxygen mass fractions are defined as $Y_{GAC} = m_{GAC}/m_{GAC,0}$ and $Y_{O_2} = m_{O_2}/m_{air}$ while the kinetic parameters ($A_{GAC}$ and $E_{GAC}$) were estimated in the previous study [24]. The conservation of mass for the solid phase is [52]:

$$\frac{\partial (Y_{GAC})}{\partial t} = -R_{GAC} \quad (4.12)$$

and the gas phase is [59, 60]:

$$\frac{\partial \left( \rho_g \phi_g \right)}{\partial t} + \frac{1}{r} \frac{\partial \left( r \rho_g u_r \right)}{\partial r} + \frac{\partial \left( \rho_g u_z \right)}{\partial z} = Q_g \quad (4.13)$$

where $Q_g$ represents the volumetric mass generation rate for the gas phase:

$$Q_g = (\phi_{GAC} \rho_{GAC})(R_{GAC}) \quad (4.14)$$

Darcy’s Law was used to determine the gas velocity in radial and longitudinal directions, Eq. (4.15, 16) [61]:

$$u_r = -\frac{k_p}{\mu} \left( \frac{\partial p}{\partial r} \right) \quad (4.15)$$

$$u_z = -\frac{k_p}{\mu} \left( \frac{\partial p}{\partial z} + \rho_g g \right) \quad (4.16)$$

where $k_p, \mu, \rho_g, p$, and $g$ represent intrinsic permeability, viscosity, gas density, pressure, and gravity respectively. The gas density was calculated via the ideal gas law [62]:

$$\rho_g = \frac{p}{R T_g} \quad (4.17)$$

where $R$ is the gas constant. The bulk transport of oxygen in the gas phase was described by Eq. (4.18) [52]:
\[
\frac{\partial (\rho g Y_{O_2})}{\partial t} + \frac{\partial (\rho g u_r Y_{O_2})}{\partial r} + \frac{\partial (\rho g u_z Y_{O_2})}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \phi_g \rho g D_g \frac{\partial Y_{O_2}}{\partial r} \right) + \frac{\partial}{\partial z} \left( \phi_g \rho g D_g \frac{\partial Y_{O_2}}{\partial z} \right) + Q_{O_2}
\]

(4.18)

where \( D_g \) is the diffusion coefficient and \( Q_{O_2} \) represents the mass per unit volume per unit time for oxygen consumption and was defined by Eq. (4.19):

\[
Q_{O_2} = -\phi_{GAC} \rho_{GAC} \nu_{O_2} R_{GAC}
\]

(4.19)

where \( \phi_{GAC} \) and \( \rho_{GAC} \) is the GAC porosity and density, respectively. The conservation of energy considers local thermal non-equilibrium (LTNE) [28, 39, 52]:

\[
(\rho C_p)_{eff} \frac{\partial T_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r k_{eff} \frac{\partial T_s}{\partial r} \right) + \frac{\partial}{\partial z} \left( k_{eff} \frac{\partial T_s}{\partial z} \right)
\]

(4.20)

\[
+ h_{sg} \left( \frac{A_{s,sp}}{V_{sp}} \right) (T_g - T_s) + Q_{gen}
\]

\[
\phi_g \rho_g C_p g \frac{\partial T_g}{\partial t} + \rho_g C_p g \left( u_r \frac{\partial T_g}{\partial r} + u_z \frac{\partial T_g}{\partial z} \right)
\]

(4.21)

\[
= \frac{1}{r} \frac{\partial}{\partial r} \left( r \phi_g k_g \frac{\partial T_g}{\partial r} \right) + \frac{\partial}{\partial z} \left( \phi_g k_g \frac{\partial T_g}{\partial z} \right)
\]

\[
+ h_{sg} \left( \frac{A_{s,sp}}{V_{sp}} \right) (T_s - T_g)
\]

where \( A_{s,sp} \) and \( V_{sp} \) are the surface area and volume of the sand, respectively, and \( Q_{gen} \) represents the volumetric energy production rate from GAC oxidation (\( \Delta H_{GAC} \)):

\[
Q_{gen} = \phi_{GAC} \rho_{GAC} (\Delta H_{GAC} R_{GAC})
\]

(4.22)

The interfacial heat transfer coefficient \( (h_{sg}) \) was described by Eq. (4.23) [63]:

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

(4.23)
Eq. (4.20) assumes effective thermal properties for the solid phase [52]:

\[
(\rho C_p)_{eff} = \phi_s \rho_s C_{Ps} + \phi_{GAC} \rho_{GAC} C_{P_GAC} \tag{4.24}
\]

\[
k_{eff} = (\phi_s)(k_s + k_{rad}) + (\phi_{GAC})(k_{GAC}) \tag{4.25}
\]

\[
\phi_g = \phi - \phi_{GAC} \tag{4.26}
\]

\[
\phi_s = 1 - \phi \tag{4.27}
\]

where \(\rho, \phi, C_p,\) and \(k\) are the densities, porosities, heat capacities, and thermal conductivities, respectively, and the subscripts \(s, GAC,\) and \(g\) note the sand, GAC, and air constituents, respectively. Radiative heat transfer was embedded in the effective solid conductivity following the Rosseland approximation \((k_{rad} = 16\sigma d_p T_s^3/3)\) [63], where \(\sigma\) is the Stefan-Boltzmann constant [64]. Conductive heat transfer within the metal sheet was also modeled [59]:

\[
\left(\rho_i C_{pi}\right) \frac{\partial T_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r k_i \frac{\partial T_s}{\partial r} \right) + \frac{\partial}{\partial z} \left( k_i \frac{\partial T_s}{\partial z} \right) \tag{4.28}
\]

where \(\rho_i, C_{pi}, k_i\) are density, heat capacity and thermal conductivity of the metal sheet.

The model parameters not described above are presented in Table 4.3 and the initial and boundary conditions are provided in Table 4.4. The heater was simulated by a constant heat flux delivered at the inlet boundary determined in the previous study [28]. The Darcy air flux was initiated at \(z = 0\) cm by a constant \(u_{g,in}\) (measured).
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log(A_{GAC})$</td>
<td>3.79</td>
<td>log(s$^{-1}$)</td>
<td>[24]</td>
</tr>
<tr>
<td>$C_{PGAC}$</td>
<td>1100</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>[65]</td>
</tr>
<tr>
<td>$C_{pi}$</td>
<td>440.8</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>[66]</td>
</tr>
<tr>
<td>$D_g$</td>
<td>4.35×10$^{-5}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>[67]$^1$</td>
</tr>
<tr>
<td>$E_{GAC}$</td>
<td>72.9</td>
<td>kJ mol$^{-1}$</td>
<td>[24]</td>
</tr>
<tr>
<td>$H$</td>
<td>10</td>
<td>W m$^2$ K$^{-1}$</td>
<td>This work, calibrated</td>
</tr>
<tr>
<td>$h$</td>
<td>0.3</td>
<td>Cm</td>
<td>This work, measured</td>
</tr>
<tr>
<td>$k_{GAC}$</td>
<td>0.25</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[65]</td>
</tr>
<tr>
<td>$k_i$</td>
<td>14.7</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[68]</td>
</tr>
<tr>
<td>$k_p$</td>
<td>1.4 ×10$^{-9}$</td>
<td>m$^2$</td>
<td>This work, measured</td>
</tr>
<tr>
<td>$m_s$</td>
<td>8.00</td>
<td>Kg</td>
<td>This work, measured</td>
</tr>
<tr>
<td>$m_{GAC}$</td>
<td>0.240</td>
<td>Kg</td>
<td>This work, measured</td>
</tr>
<tr>
<td>$M_g$</td>
<td>28.97</td>
<td>g mole$^{-1}$</td>
<td>[69]</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.433</td>
<td>-</td>
<td>This work, measured</td>
</tr>
<tr>
<td>$\phi_{GAC}$</td>
<td>0.05</td>
<td>-</td>
<td>This work, measured</td>
</tr>
</tbody>
</table>

$^1$ The diffusivity was extracted from reference [66] nevertheless, this is a calibrated value for polyurethane foam. There are no available estimates of diffusivity for a configuration like the present one. While changing this value will alter the boundaries of the limit states it will not affect the general conclusions of this study, therefore a sensitivity analysis for this value was not conducted.
\[ \rho_{GAC} = 1311 \text{ kg m}^{-3} \]  
\[ \rho_i = 8000 \text{ kg m}^{-3} \]  
\[ \dot{q} = 25000 \text{ W m}^{-2} \]  
\[ R = 8.0 \text{ Cm} \]  
This work, measured
\[ R_g = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \]  
[63]
\[ u_{g, in} = 0.05 \text{ and } 0.01 \text{ m s}^{-1} \]  
This work, measured
\[ \sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \]  
[63]

Table 4.4: Initial and Boundary Condition in Numerical Model

<table>
<thead>
<tr>
<th>Initial Condition</th>
<th>Boundary Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (t = 0) )</td>
<td>( y_{GAC} = 0 )</td>
</tr>
<tr>
<td>( (4.12) )</td>
<td>( \rho_g u_g = \rho_g u_g(t) )</td>
</tr>
<tr>
<td>( z = 0.0 ) &amp; ( 0.0 &lt; r &lt; 8.0 )</td>
<td>( T_g = T_0 )</td>
</tr>
<tr>
<td>( u_g = 0 ) ( \rightarrow ) ( 0 \leq t \leq t_g )</td>
<td></td>
</tr>
<tr>
<td>( u_g = u_0 ) ( \rightarrow ) ( t_g \leq t \leq t_f )</td>
<td></td>
</tr>
<tr>
<td>( Y_{O_2} = Y_{O_2, 0} )</td>
<td></td>
</tr>
</tbody>
</table>

\( z = 10.0 \) & \( 0.0 < r < 8.0 \)

\( (4.12) \) \( y_{GAC} = 1 \)
| \( \rightarrow \) \( (k_s + k_{rad}) \frac{\partial T_s}{\partial z} = \dot{q} \) \( \rightarrow \) \( 0 \leq t \leq t_h \) |
| \( -(k_s + k_{rad}) \frac{\partial T_s}{\partial z} = 0 \) \( \rightarrow \) \( t_h \leq t \leq t_f \) |

\( (4.13) \) \( P = 101375 \text{ Pa} \)
| \( z = 0.0 \) & \( 8.0 < r < 8.3 \) | \( \rightarrow \) \( -(k_i) \frac{\partial T_s}{\partial z} = 0 \) |
\[ z = 37.5 & 0.0 < r < 8.0 \]

\[(4.18) \quad Y_{O_2} = 0.23 \]

\[
\begin{align*}
-(k_s + k_{rad}) \frac{\partial T_s}{\partial z} &= 0 \\
-(k_g) \frac{\partial T_g}{\partial z} &= 0 \\
\rho_g u_g (Y_{O_2,0} - Y_{O_2}) &= 0 \\
D_g \frac{\partial (\rho_g Y_{O_2})}{\partial r} &= H(T_s - T_{\infty})
\end{align*}
\]

\[ r = 0.0 & 0.0 < z < 37.5 \]

\[(4.20-21) \quad T_s = T_g = 295 \text{ K} \]

\[ z = 37.5 & 8.0 < r < 8.3 \]

\[(4.28) \quad T_s = 295 \text{ K} \]

\[ r = 8.3 & 0 < z < 37.5 \]

In this work, the effective radial heat loss coefficient \((H)\) represents the radial heat transfer coefficient at the outer surface of the reactor wall (see Figure 4.2) determined based on a simple calibration [24], and \(h\) is the metal sheet thickness. Table 4.5 shows the equations for global and local energy balances in cylindrical coordinates based on the approach developed by [9, 22]. The energy rates at the inlet (i.e., heat influx, \(E_{in}^i\)), outlet (i.e., convective outlet heat flux, \(E_{out}\)), and loss (i.e., radial heat loss, \(E_{loss}\)) were calculated by integrating the energy fluxes over the reactor radius and relevant outer surfaces, and the oxidation energy rate \((E_{\text{oxid}})\) was integrated over the reactor volume. The net energy rate \((E_{\text{net}})\) corresponds to the sum of these four components (Eqs. 4.29-32).
Table 4.5: The Local and Global Energy Rate

<table>
<thead>
<tr>
<th>Energy Rate of</th>
<th>Eq. (Local)</th>
<th>Eq. (Global)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet ($\dot{E}_{\text{in}}$)</td>
<td>$\int_0^R \rho u C_p \left( T_{\text{in}}(z) - T_\infty \right) 2\pi r , dr$</td>
<td>$\int_0^R \dot{q} 2\pi r , dr$</td>
</tr>
<tr>
<td>Outlet ($\dot{E}_{\text{out}}$)</td>
<td>$\int_0^R \rho u C_p \left( T_{\text{out}}(z) - T_\infty \right) 2\pi r , dr$</td>
<td>$\int_0^R \dot{q} 2\pi r , dr$</td>
</tr>
<tr>
<td>GAC oxidation ($\dot{E}_{\text{oxi}}$)</td>
<td>$\int_{z_1}^{z_2} \int_0^R \rho_g u_g C_p \left( T_{\text{GAC}}(z) - T_\infty \right) R_{\text{GAC}} 2\pi r , dr , dz$</td>
<td>$\int_0^R \int_{z_1}^{z_2} -\Delta H_{\text{GAC}} \rho_{\text{GAC}} R_{\text{GAC}} 2\pi r , dr , dz$</td>
</tr>
<tr>
<td>Radial heat loss ($\dot{E}_{\text{loss}}$)</td>
<td>$\int_{z_1}^{z_2} H \left( T_{s(R+h)} - T_\infty \right) 2\pi (R+h) , dz$</td>
<td>$\int_0^L H \left( T_{s(R+h)} - T_\infty \right) 2\pi (R+h) , dz$</td>
</tr>
<tr>
<td>Net ($\dot{E}_{\text{net}}$)</td>
<td>$\dot{E}<em>{\text{in}} + \dot{E}</em>{\text{oxi}} - \dot{E}<em>{\text{out}} - \dot{E}</em>{\text{loss}}$</td>
<td>$\dot{E}<em>{\text{in}} + \dot{E}</em>{\text{oxi}} - \dot{E}<em>{\text{out}} - \dot{E}</em>{\text{loss}}$</td>
</tr>
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</table>

4.4 Results and Discussion

4.4.1 Experimental Results

Figure 4.3 shows the key experimental data (see Appendix B, Section B.3) and simulated numerical results. That is, the exiting mass fractions of oxygen ($Y_{O_2}$), carbon dioxide ($Y_{CO_2}$), and carbon monoxide ($Y_{CO}$); temperature evolutions and peak temperatures ($T_p$); front velocities of smouldering ($\nu_f$) and cooling ($\nu_c$). Recall that the inlet air fluxes ($u_g$) used in these experiments were 0.01-0.05 m s$^{-1}$, and the incoming $Y_{O_2}$ was diluted from 0.230 (i.e., ambient air) to 0.115 and 0.057 (see Table 4.1).

Figure 4.3b shows results from Exp. $i$, which was a robust smouldering experiment that used undiluted air and exhibited high $T_p$ and $\nu_f$ values of 924 °C and 0.54 cm min$^{-1}$, respectively, and an exiting $Y_{O_2}$ of 0.07 after smouldering (see Figure 4.3a). This result indicates that not all O$_2$ was consumed, though all fuel was. In other words, the fuel content ultimately limited the rate of smouldering propagation in Exp. $i$. 


On the other hand, Figure 4.3c shows the results from Exp. ii, which was a robust fuel-rich experiment with diluted air (i.e., an incoming $Y_{O_2}$ of 0.115, Table 4.1). In this experiment, the diluted air reduced the oxygen flux into the reaction zone, (i.e., similar to the restricted oxygen delivery in [31]). Relative to the undiluted experiment under otherwise the same experimental conditions (i.e., Exp. i, Table 4.1), Exp. ii exhibited a decreased oxygen stoichiometric coefficient ($v_{O_2}$) from 3.1 to 2.7 [-] (i.e., mass of oxygen consumed per mass of GAC) obtained from experimental data. In this experiment, smouldering was sufficiently robust and effectively consumed all oxygen mass flux injected into the reactor (i.e., with an exiting $Y_{O_2}$ of 0.009). Moreover, the $v_f$ was lower in Exp. ii than Exp. i (i.e., 0.33 and 0.54 cm min$^{-1}$, respectively), but the $T_p$ was almost constant between the experiments (i.e., 930 and 924 °C, respectively), which agrees with others [19, 67, 71]. Therefore, smouldering in Exp. ii was robust and fuel-rich, as the oxygen delivery limited the rate of smouldering propagation. Moreover, it is hypothesized that the high peak temperature in Exp. ii, despite the lower oxygen flux, is associated with the reaction zone approaching super-adiabatic conditions. That is, because $v_f$ and $v_c$ approached similar values in Exp. ii, the cooling zone growth rate was slow throughout Exp. ii. Therefore, the produced oxidation energy transferred forward in the reaction and preheating zones and resulted in a high $T_p$, agreeing with [38]. However, these dynamics did not lead to a temperature singularity because of the limiting role of the chemical reaction; therefore, the dynamics are referred to here as quasi-super-adiabatic effects.

Figure 4.3d shows weak fuel-rich smouldering from Exp. iii with low incoming $Y_{O_2}$ (i.e., 0.057), where the $v_f$ (i.e., 0.22 cm min$^{-1}$) and $T_p$ (i.e., 700 °C) were both lower than Exps. i and ii, which used less diluted air but otherwise the same experimental conditions. Moreover, like Exp. ii, effectively all oxygen was consumed. However, the $v_c$ trailing smouldering was nearly the same between Exps. i and ii (i.e., 0.19 and 0.21 cm min$^{-1}$) and lower for Exp. iii (i.e., 0.13 cm min$^{-1}$), as the $v_c$ was controlled by axial heat transfer and largely insensitive to $Y_{O_2}$ differences [30]. In Exp. iii, $v_{O_2}$ decreased to 1.9 kg$_{O_2}$ kg$_{GAC}^{-1}$, which confirms that 63% and 42% lower oxygen was consumed by smouldering in comparison to Exps. i and ii in Figure 4.3b, and c, respectively. Also, by decreasing $Y_{O_2}$,
the produced $Y_{CO_2}$ and $Y_{CO}$ decreased by 64% and 88%, respectively, in comparison to Exp. i.

Figure 4.3g shows the results of Exp. iv, which used undiluted air and a lower incoming $u_g$ than Exps. ii-iii (i.e., 0.01 m s$^{-1}$). Therefore, this experiment used the $u_g$ to lower rate of oxygen mass flux ($\rho_g u_g Y_{O_2}$) relative to Exp. i. Exp. iv fostered robust fuel-rich smouldering, where the $v_f$ and $v_c$ both decreased to 0.20 and 0.11 cm min$^{-1}$, respectively, relative to the values in Exp. i (i.e., 0.54 and 0.19 cm min$^{-1}$, respectively). This result reflects the fact that both velocities are highly sensitive to inlet air flux [21]. Moreover, the $T_p$ in Exp. iv decreased to 790 °C (compared to 924 °C in Exp. i). Together, the lower $T_p$ and $v_f$ in Exp. iv relative to Exp. i demonstrates a lower oxidation energy production rate due to the lowered incoming air flux.

Figure 4.3h shows the results from Exp. v, which coupled with low $u_g$ (i.e., 0.01 m s$^{-1}$) and incoming $Y_{O_2}$ (i.e., 0.115). This experiment fostered weak fuel-rich smouldering (Figure 4.3f) with a slow $v_f$ (i.e., 0.07 cm min$^{-1}$) and all oxygen was consumed by smouldering. Note that $T_p$ is slightly decreasing with time. A global energy balance analysis (see Appendix B, Section B.4) predicted a negative net energy rate ($Dt = 0.57$), indicating the smouldering is moving towards extinction. However, $T_p$ (i.e., 750 °C) was comparable to Exp. iv (i.e., 790 °C) due to quasi-super-adiabatic effects, like in Exp. ii (as discussed above).

Figure 4.3i represents global quenching associated with critically low $u_g$ (i.e., 0.01 m s$^{-1}$) and incoming $Y_{O_2}$ (i.e., 0.057). That is, the rate of local heat losses overwhelmed the rate of local energy production, which drove smouldering towards global quenching and resulted in decreasing $T_p$ values over time – common to non-self-sustaining smouldering.

Overall, Figure 4.3 demonstrates key evolutions due to variations in incoming $u_g$ and $Y_{O_2}$, which can transition smouldering propagation from robust to weak, oxygen- to fuel-rich, and lead to global quenching under limiting conditions.
4.5 Model Comparison

Figure 4.3 confirms the numerical model captured key experimental features over a wide range of conditions, from robust oxygen- (Figure 3b) to fuel-rich (Figure 4.3c, g) conditions, and well-captured weak smouldering dynamics (Figure 4.3d, h) and global quenching (Figure 4.3i). The numerical model predicted the oxygen consumption by smouldering with different inlet air fluxes \(u_g\) and oxygen mass fractions \(Y_{O_2}\). Also, the modelled temperature evolutions, peak temperatures \(T_p\), smouldering and cooling front velocities \(v_f\) and \(v_c\), respectively) were in good agreement with the experimental data. Altogether, Figure 4.3 bolsters confidence in the numerical model’s predictive capabilities across many applied smouldering conditions.
Figure 4.3: Key experimental results from Exp. i-vi in Table 1 and model validation where (a, and f) show a comparison of gas emissions, mass fractions of oxygen ($Y_{O_2}$), carbon dioxide ($Y_{CO_2}$), and carbon monoxide ($Y_{CO}$) after smouldering (note that only $Y_{O_2}$ was modelled, due to the simple degradation chemistry assumed [24]); (b, c, d) inlet air flux ($u_g$) equal to 0.05 m s$^{-1}$ and (g, h, i) inlet air flux ($u_g$) equal to 0.01 m s$^{-1}$, show centreline temperature evolutions from Exps. i-vi and comparisons of temperature evolutions for experimental (dotted lines and shaded regions for three repeats) and numerical results (solid lines). (e and j) show peak temperatures ($T_p$) and the front velocities of smouldering ($v_f$) and cooling ($v_c$) versus incoming $Y_{O_2}$ variations and their comparisons with numerical results.
4.5.1 Multi-Dimensional Transfer Effects

Figure 4.4 explores various multi-dimensional effects from simulating GAC smouldering with 0.03 kg GAC kg sand\(^{-1}\) and \(u_g = 0.05\) m s\(^{-1}\) at \(Dt = 0.5\), where \(Y_{O_2}\) was diluted from 0.230 (i.e., robust oxygen-rich) to 0.115 (i.e., robust fuel-rich), and 0.057 (i.e., weak fuel-rich).

Figures 4.4d, e, and f show the temperature distributions with the higher temperatures at the centerline and lower temperatures near the wall due to radial heat losses, which agrees with [24, 59]. In addition, \(Y_{O_2}\) dilution led to increased non-uniformities in the temperatures from centerline to wall, i.e., as weakening GAC oxidation near the wall (see Figure 4.4a, b, c). Moreover, the cooling zones were shortened, and the preheating zones were lengthened with increased \(Y_{O_2}\) dilution, which both show that less energy was dispersed in the cooling zone and was instead accumulated into the reaction and preheating zones as \(Y_{O_2}\) dilution increased (i.e., due to the quasi-super-adiabatic effect) (see Figure 4.4g).

Figures 4.4d, e, and f show non-uniform air mass flux (white vectors) tended to circumvent the hot zone towards the wall due to thermally-induced air channelling, which agrees with [72, 73], where 33%, 38%, and 59% higher air mass flux was delivered at the wall than the centerline in the simulations with incoming \(Y_{O_2}\) of 0.230, 0.115, and 0.057, respectively. In other words, increased oxygen dilution worsened non-uniform air flux, due to low temperatures near the wall with weak smouldering, which agrees with previous experimental studies [59, 74, 75].

Figures 4.4h, i, and j show the shape of the smouldering front and GAC bulk density distribution radially and longitudinally. The front shape was almost uniform in oxygen-rich condition, and then became more concaved in the fuel-rich condition, associated with non-uniform air and oxygen mass fluxes. However, the shape of the smouldering front near the wall was driven by locally weak smouldering (i.e., local conductive heat transfer quickly transported heat away near the wall, which resulted in lower temperature and slower chemical reaction rates), which agrees with [24, 30].
During global weak smouldering (i.e., with incoming $Y_{O_2} = 0.057$), the heat released from smouldering near the wall was insufficient to overcome heat losses, which led to peripheral extinction and fostered an unburned crust along the reactor wall, which was cooler and exacerbated wall air channelling (Figure 4.4c). Figure 4.4j showed smouldering was self-sustained throughout the process (i.e., with a positive net global energy balance) and the unburnt crust thickness ($R^*$) decreased from 1 cm at $Dt = 0.5$ to $R^* = 0$ cm at $Dt = 1$ (see video S3.b), which confirmed that smouldering robustness increased over time because of accumulating energy in the system.

Figures 4.4l, m, and n, show oxygen mass flux (green vectors) increased from the centerline to the wall because of non-uniform air flux (as described above). Figure 4.4o confirms all the oxygen was consumed at the centerline, while weak smouldering associated with lower temperatures and higher oxygen mass fluxes near the wall caused oxygen leakage, which is in good agreement with experimental results (Figure 4.4a). Overall, Figure 4 provides a better understanding of the key multidimensional effects during smouldering propagation across robust oxygen-rich to weak fuel-rich conditions.
Figure 4.4: Simulation # 1-3, (a, b, c), (g, k, o) radial and centreline longitudinal distributions, respectively, of the 2D contours of simulated: (a, b, c) solid temperatures and air mass fluxes (d, e, f) GAC bulk densities; and (l, m, n) oxygen mass fractions and mass fluxes. The horizontal lines A-A, B-B, and C-C note the cross-sections examined in (a), (b), and (c), respectively.

4.5.2 Energy Analysis

To further understand smouldering robustness, limiting conditions, and quasi-superadiabatic effects, Figure 4.5 shows the results from multidimensional global (i.e., bed) and local (i.e., smouldering front) energy analyses (see equations in Table 4.2) at $Dt = 0.5$ (i.e., when the smouldering front was at the middle of the fuel bed). The comparison between
the global and local energy balances provides valuable insight into the transitions between various smouldering conditions.

In the local energy balances (Figure 4.5a, c), the oxidation energy rate (Oxidation) contributed most to the net energy rate (Net), while the inlet energy rate (i.e., energy delivered by convective heat flux to the reaction zone) \( \dot{E}_{in} \) played an important role as hot air was convected from the clean sand in the cooling zone behind the front. From Simulation # 1 (i.e., \( u_g = 0.05 \text{ m s}^{-1} \) with ambient air, \( Y_{O_2} = 0.23 \)), \( \dot{E}_{in} \) was 14.7% higher than \( \dot{E}_{out} \) (i.e., the rate of energy that left the reaction zone with convective outlet heat flux), which demonstrates a positive contribution to the local net energy rate. By diluting \( Y_{O_2} \) to 0.115 in Simulation # 2, which decreased \( v_f \) (as discussed above), \( \dot{E}_{in} \) contributed a higher portion of the net energy rate (58% versus 31%). This shows, despite weakening the smouldering robustness (i.e., decreasing \( dE_{net}/dt \)), increased energy transfer from the cooling zone accumulated in the reaction zone, which concentrated along the centerline due to the converged air mass flux (Fig 4.5e). Note that the local \( \dot{E}_{out} \) was proportional to the \( T_p \) as hotter emissions corresponded to higher convection rates out of the reaction zone.

In the highly diluted case in Exp # iii, i.e., \( Y_{O_2} = 0.057 \), the \( \dot{E}_{oxid} \) and \( dE_{net}/dt \) dropped dramatically due to the lower \( v_f \) (i.e., rate of oxidation) and heat released from oxidation. Therefore, smouldering was weak under these conditions as \( \dot{E}_{loss} \) drew a large fraction of the released energy (i.e., 46% of \( \dot{E}_{oxid} \)). Consequently, Exp # iii fostered an unburnt crust near the wall that insulated the centreline, like in [8, 50]. Similar dynamics were also observed in polyurethane foam smouldering by Ohlemiller [31]. However, the energy did accumulate in the system and the robustness, therefore, improved throughout propagation (which aligns with the simulated crust shrinkage discussed previously).

By decreasing the inlet air flux \( (u_g) \) with the same GAC concentration (i.e., Simulations #4-6 in Figure 4.5c), the \( \dot{E}_{oxid} \) decreased by \(~3\)-fold compared to Simulations # 1-3, while the local \( \dot{E}_{in} \) and \( \dot{E}_{out} \) nearly balanced each other. Therefore, the local \( dE_{net}/dt \) nearly equalled \( \dot{E}_{oxid} \), as the local \( \dot{E}_{loss} \) was negligible. With low incoming \( Y_{O_2} \), the local
\( dE_{\text{net}}/dt \) became zero, i.e., indicating extinction (Figure 4.4i), which agrees with [22]. This result matches the non-self-sustaining behaviour observed from Simulation #6’s corresponding experiment (Exp. vi).

In the global (bed) energy analyses, the balance between rates provides additional information on system performance. While the \( \dot{E}_{\text{oxid}} \) terms were the same in the local and global analyses, the \( \dot{E}_{\text{in}} \) terms were zero in the global analyses since the heater was off at \( Dt = 0.5 \), and the convective energy loss rate from the bed (\( \dot{E}_{\text{out}} \)) was also small in all simulations; at most, only 5% of the oxidation energy rate left the bed (\( \dot{E}_{\text{out}} \)) in the highly diluted simulation (i.e., Simulation #3, \( Y_{O_2} = 0.057 \)), due to its long preheating zone (see Figure 4.5f). The global energy losses (\( \dot{E}_{\text{loss}} \)) were much higher in global energy balances because the main losses occurred throughout the cooling zone behind the smouldering front, which agrees with [22, 26, 27, 30, 39]. Therefore, the fraction of stored energy in the global energy balances was lower than the local energy balances. The global energy balance is helpful in diagnosing weak experiments. For example, while Simulation # 5’s local \( dE_{\text{net}}/dt \) was slightly positive, its global \( dE_{\text{net}}/dt \) was negative. This discrepancy indicates that Simulation # 5 was weakly smouldering and trending towards quenching. This numerical result matches the observations from Simulation # 5’s corresponding experiment (Exp. v), which was weakly self-sustaining.

Altogether, these analyses demonstrate that diluted \( Y_{O_2} \) decreased the overall cumulative energy, both locally and globally. The increased \( Y_{O_2} \) dilution transitioned the systems from robust oxygen-rich, to robust fuel-rich, to weak fuel-rich, to quenching. The reasons governing this transition were due to energy balance dynamics that were examined in the local and global energy balance analyses.
Figure 4.5: Local and global energy rates for oxidation ($\dot{E}_{\text{oxid}}$), loss ($\dot{E}_{\text{loss}}$), inlet ($\dot{E}_{\text{in}}$), outlet ($\dot{E}_{\text{out}}$), and their net result ($\frac{dE_{\text{net}}}{dt}$) at $Dt = 0.5$ in Simulations # 1-6 (see Table 3).

4.5.3 Sensitivity Analysis

Figure 4.6 further explores the smouldering sensitivities to applied air flux and fuel concentration across a range of conditions, from weak to robust and oxygen- and fuel-rich, where the oxygen stoichiometric coefficient ($\nu_{O_2}$) and heat of oxidation ($\Delta H$) were assumed to be consistent with the values calibrated in Simulations # 1-3 in Table 4.1. Figure 4.6a, b shows the transition from weak fuel-rich to robust oxygen-rich smouldering via increasing inlet air flux ($u_g$) (i.e., from 0.01 to 0.09 m s$^{-1}$), which led to hotter peak temperatures ($T_p$) (i.e., from 786 to 884 °C, respectively, for $Y_{O_2} = 0.230$ and 334 to 830 °C, respectively, for $Y_{O_2} = 0.057$) and faster smouldering front velocities ($\nu_f$) (i.e., from 0.14 to 0.09 cm min$^{-1}$, respectively, for $Y_{O_2} = 0.230$, and quenching to 0.4 cm min$^{-1}$, respectively for $Y_{O_2} = 0.057$). These results demonstrate the improved smouldering
performance due to: (i) enhanced convective heat transfer and (ii) oxygen mass flux \((\rho_g u_g Y_{O_2})\) to the reaction zone, which agrees with [8, 22, 23, 41, 45]. However, with high \(u_g\) (e.g., 0.13 cm min\(^{-1}\)) and \(Y_{O_2} = 0.230\), the \(T_p\) values were insensitive to further increases in \(u_g\). This insensitivity indicates, despite increasing \(v_f\) and \(\dot{E}_{oxid}\), the excess energy did not accumulate in the reaction zone but instead in the cooling zone behind the smouldering front. On the other hand, with lower incoming \(Y_{O_2}\) (i.e., 0.115), a larger fraction of the energy was accumulated in the reaction zone and \(T_p\) values were moderated, despite the lower \(\dot{E}_{oxid}\) and \(dE_{net}/dt\) associated with the lower incoming oxygen. This \(T_p\) moderation was due to the quasi-super-adiabatic effect, which agrees with [31].

A sensitivity analysis on fuel concentration is useful in applied smouldering systems where fuel (e.g., organic waste) is mixed within an inert matrix at a determined concentration [7, 45, 76]. By increasing GAC concentration \((C_c)\) (i.e., from 0.01 to 0.05), \(T_p\) increased from 482 to 1280 °C, respectively, for \(Y_{O_2} = 0.230\); and \(\dot{E}_{out}\) also increased linearly agreeing with [36, 41, 77]. The green line in Figure 6c shows the analytical model \(T_p\) predictions (Eq. 4.5) that confirms very good agreement with the numerical model results under oxygen-rich conditions. By diluting \(Y_{O_2}\), the analytical model over-predicted \(T_p\), as smouldering transitioned to fuel-rich conditions. However, the \(T_p\) values with incoming \(Y_{O_2} = 0.115\), were comparable to the \(Y_{O_2} = 0.230\) results, due to the quasi-super-adiabatic effect. With highly diluted \(Y_{O_2}\), \(T_p\) dropped dramatically (e.g., from 1280 to 975 °C for \(C_c = 0.05\)) due to lower energy released by oxidation under fuel-rich conditions. With a lower GAC concentration (i.e., \(C_c = 0.01\)), which fostered even lower \(\dot{E}_{oxid}\) due to minimal fuel, diluted \(Y_{O_2}\) (i.e., from 0.230 to 0.057) drove smouldering to global quenching, as heat losses overwhelmed local energy production in these conditions, agreeing with [45, 59]. With an increase in \(C_c\) from 0.02 to 0.03, the \(v_f\) increased while smouldering was oxygen-rich; however, beyond oxygen-rich conditions, the oxygen supply governed the smouldering propagation rate (i.e., smouldering became fuel-rich) and \(v_f\) decreased with high GAC concentrations (e.g., \(C_c = 0.04\) and 0.05). Therefore, reductions in \(Y_{O_2}\) under
fuel-rich conditions further decreased $\nu_f$ due to oxygen starvation, which agrees with [31, 41, 77, 78]. Overall, Figure 4.6 clarifies the sensitivity of smouldering systems to $u_g$, $C_c$, and $Y_{O_2}$ under a robust range of conditions that stretch across weak to robust smouldering from either oxygen- to fuel-rich conditions.

Figure 4.6: Local net ($dE_{net}/dt$) and out ($\dot{E}_{out}$) energy rates, peak temperature ($T_p$), and smouldering front velocity ($\nu_f$) sensitivities to fuel concentration ($C_c$), applied air flux ($u_g$), and incoming oxygen concentration ($Y_{O_2}$).

4.5.4 Conclusion

As the applications of smouldering-based technologies are growing, understanding the smouldering characteristics across a wide range of conditions is relevant for engineering
and safety applications. Therefore, a validated 2D smouldering model equipped with heat transfer mechanisms and chemical reactions was compared to new experimental results to quantify the effects of oxygen mass fluxes in different conditions including: (i) oxygen mass fraction \( Y_{O_2} \), (ii) inlet air flux \( u_g \), and (iii) fuel concentration \( C_c \). These simulations explored both oxygen- and fuel-rich smouldering that was robust, weak, and non-self-sustaining. A quasi-super-adiabatic effect was shown to moderate peak temperatures with dilute oxygen mass fractions and slow smouldering front velocities and low oxidation rates. The cooling front velocity was insensitive to oxygen dilution as it was moderated by the heat transfer characteristics of the system. However, with highly diluted oxygen mass fractions, smouldering was very weak with low peak temperatures. By decreasing the inlet air flux, a lower rate of convective heat transfer and oxygen mass flux were delivered to the reaction zone; therefore, smouldering propagation was fuel-rich. A sensitivity analysis showed the smouldering front velocity increased linearly with inlet air flux, where the rate was increased by increasing the oxygen mass fraction; however, the peak temperatures reached a plateau at high inlet air fluxes. Finally, multidimensional effects were investigated via the validated numerical model to compare key physical metrics (e.g., temperature, air flux, oxygen mass flux), chemical indicators (e.g., smouldering front shape), and operational characteristics (e.g., robustness) of applied smouldering systems. Overall, this study provides novel insight into the key system characteristics in different conditions from robust oxygen-rich to weak fuel-rich and global quenching.

4.6 References


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Chapter 5

5 Delineating the Role of Fuel Mobility in Applied Smouldering Systems

5.1 Introduction

Organic liquid wastes from industrial activities (e.g., oil sludge, coal tar, and oil-based drilled cutting) are been produced in large quantities (60 million tons per year) and more than 1 billion tons of this dangerous waste has been stockpiled worldwide [1]. This accumulated waste poses a looming threat to ecosystems and communities through environmental contamination [2]. Common organic liquid waste treatment methods are (i) incineration [3], (ii) pyrolysis [4], and (iii) gasification [5], which all typically require continuous supplies of additional energy, or waste pre-conditioning.

Recently, applied smouldering combustion was introduced as a new treatment approach for these organic liquid wastes, where the waste is mixed with an inert porous medium (e.g., sand) to form a smoulderable mixture for treatment [1, 2, 6]. Smouldering combustion is a flameless form of combustion driven by exothermic oxidation reactions at the surface of condensed fuels [7]. In smouldering applications, initial heat and air are supplied to a small ignition region until the ignition of smouldering reactions. Once smouldering is ignited, the external heat supply is removed, and the smouldering front propagates in a “self-sustaining” manner without further external energy as long as the local rate of energy released overwhelms local heat loss rates [8].

Fuel mobility plays an important role in applied smouldering systems. Mobility affects key characteristics (e.g., temperature and fuel saturation distribution, and smouldering front velocity), which might be desirable (e.g., depositing more fuel in the reaction zone) or undesirable (e.g., upward mobility can accumulate fuel saturation in the preheating zone and decreases the air permeability to the critical point). For example, an experimental smouldering study treating oil sludge identified undesirable fuel mobility effects where mobility led to erratic temperatures and poor process controllability. In this case, the
downward mobility of low viscous fuel from an extended preheating zone (> 10.5 cm) to the reaction zone caused rapid cooling and reigniting events, a stall in the trailing edge of the smouldering front, and a rapid increase in the temperature (i.e., super-adiabatic effects) and thickness of smouldering front [9]. This hypothesis still needs to be further explored (see these zones illustrated in Figure 5.1).

In a similar but separate context, fuel mobility is used in enhanced oil recovery systems to extract high viscous, heavy oil and bitumen from natural geological formations [10]. The high temperatures in the smouldering front decrease the oil viscosity and mobilize the oil toward the extraction wells [11, 12]. In these studies, fuel mobility in the preheating zone caused separate challenges, as fuel accumulates in this zone due to viscous force by progressing the front, which decreases the air permeability and restricts air flow below a critical level where oxidation reactions could not be self-sustained [1, 13-16].

Figure 5.1 illustrates the fuel mobility dynamics for a typical upward-forward smouldering propagation system. Four main zones can be identified: (i) virgin fuel zone, (ii) preheating zone, (iii) reaction zone, and (iv) cooling zone. In the virgin fuel zone, high viscosity fuels are immobile at ambient temperatures, while low viscosity fuels at ambient temperature can either be immobile or mobilize downwards due to gravity effects. In the preheating zone, downward mobility can occur due to gravity and decreased viscosities with elevated temperatures. Moreover, upward mobility can take place due to upward viscous forces caused by the applied air flow. In the reaction zone, fuel is pyrolyzed and oxidized to produce heat and gases. Finally, in the cooling zone, only hot clean sand remains with no or minimal fuel residual.
Figure 5.1: Conceptual model of liquid fuel saturation distribution with forward-upward smouldering propagation. (a) The key distinct zones including virgin fuel, preheating, reaction, and cooling zones are determined, (b) conceptual model, and (c) liquid fuel saturation and temperature distribution.
As many applied smouldering applications treat hazardous organic liquids, fuel mobility effects are routinely observed; however, the governing physics are poorly understood. For example, the interplay between fuel, air, and porous media on mobility and smouldering behaviour has not been well-explained. Lessons from other applications, e.g., enhanced oil recovery, can assist in understanding this phenomenon, but ultimately more research is needed to understand fuel mobility effects in the context of applied smouldering. This is a key knowledge gap and the main motivation for this research.

This study tackled this knowledge gap via equipping a previously developed 1D numerical model [8] with key multiphase flow equations to model fuel mobility in an applied smouldering system. Experimental results from canola oil smouldering (i.e., a low viscosity surrogate fuel) were used to calibrate the model. The calibrated model was used to simulate independent experiments with a fuel mixture of canola oil and viscosity index (VI) improver (i.e., an additive to increase viscosity) to validate the model. As fuel concentrations are not routinely tracked over space and time, temperature histories were used for model calibration and validation. The effects of mobility were explored by simulating the smouldering of high (i.e., non-mobile) and low (i.e., mobile) viscous. Sensitivity analyses were performed to better understand the effects of fuel (e.g., initial saturation, viscosity), air (e.g., Darcy air flux), and porous media (e.g., intrinsic permeability, pore size distribution index, and length of the fuel bed) on key fundamental (e.g., peak temperature, front velocity, saturation leading edge, and oxygen consumption), and practical (e.g., robustness, and global extinction) aspects of applied smouldering systems. Global and local energy analyses were performed to quantify all effects. Altogether, this study provides novel insight into the dynamics and effects of liquid fuel mobilization in applied smouldering systems, which support the improved design, implementation, and optimization of smouldering-based technologies.
5.2 Methodology

5.2.1 Experiments

Three smouldering experiments were conducted by Kinsman et al. [9] in a laboratory-sized reactor using organic liquid fuels with different viscosities to evaluate the effects of fuel mobility on smouldering. First, pure canola oil (non-toxic low viscosity fuel, 0.07 Pa s, Exp. \# i, Table 5.1) was used to demonstrate a smouldering system that was highly affected by fuel mobility. Then, a 1:1 mixture (i.e., with a mass ratio of 0.5 kg kg\(^{-1}\)) of canola oil to viscosity index (VI) improver (V-158, Tempo Canada ULC) was used to increase the mixture viscosity to 1.32 Pa s (Exp. \# ii, iii, Table 5.1). VI improver was used to reduce downward mobility to approximately represent the mobility expected in smouldering systems with oil sludge and coal tar [9]. Surrogated fuel with well defined properties was used in this study to simplify the complicated phenomena, however for using the real fuel (e.g., oil sludge), the thermos-physical and chemical properties of the fuel would be different but the methodology will be the same.

The stainless-steel reactor was 16 cm in diameter and 64 cm tall, where 30 cm tall fuel beds were used. Quartz sand (#12ST, Bell and Mackenzie Co. Ltd., Canada) with a bulk dry density of 1600 kg m\(^{-3}\) and a mean grain size of 0.88 mm was used in all experiments. A mass ratio of 0.06 kg kg\(^{-1}\) of organic liquid mass to sand mass was used in all experiments, with a saturation (\(S_w\)) of 0.30, based on the average measured sand porosity (\(\phi = 0.38\)). Note that there were minor differences between the saturations with and without VI added due to the small impact of the fuel density variations.

The effects of water evaporation and condensation on smouldering systems were not considered in this study due to the negligible initial moisture content of the fuel [17]. The thermocouples (Type K, Inconel, Omega) were placed at the centerline spaced 3.5 cm apart, where the first thermocouple (TC1) was located 1.0 cm above the heater and 11 cm above the gas diffuser (see Figure 5.2 (a)). Temperatures were recorded at two seconds intervals using a data logger (Multifunction Switch/Measure Unit 34980A, Agilent
Technologies). Schematics of the experimental setup and computational domain are shown in Figure 5.2, which were described in detail previously [9].

![Figure 5.2: Schematic view of (a) experimental setup and (b) computational domain.](image)

A standard ignition procedure was used in each experiment [18]. That is, a localized area was heated with an Inconel-sheathed electrical cable heater (Waltow, USA, 450 W), which was coiled into a flat spiral and placed above the gas diffuser. The heater power was increased in 25 W increments every 10 min from an initial power of 290 W to 415 W following [9] until the first thermocouple (x = 0.11 m) reached 360 °C (i.e., the approximate smouldering ignition temperature of canola oil) after approximately 90 min. The air was injected at a fixed rate at \( t = t_g \) to ignite the smouldering reactions using an air diffuser placed at the bottom of the column (x = 0.00 m). The heater was then turned off at \( t = t_h \) after TC1 reached its peak temperature (570 °C), while the air remained on to support the self-sustaining smouldering propagation. The differences in ignition conditions (i.e.,
air/heater on/off times) only led to small differences in initial effects and did not influence the main effects studied. Table 5.1 shows the list of experiments and their corresponding simulations. Note that all experiments supported self-sustaining smouldering propagation.

Table 5.1: List of the Experiments and Simulations Performed in the Sensitivity Analyses

<table>
<thead>
<tr>
<th>Exp. # (repeat s)</th>
<th>Simulation #</th>
<th>Fuel Type</th>
<th>Darcy Air Flux $q_{n,\text{in}}$ ($\text{m s}^{-1}$)</th>
<th>Initial Saturation $S_w$</th>
<th>Intrinsic Permeability $k_i$ ($10^{-10} \text{ m}^2$)</th>
<th>Viscosity $\mu$ Pa s</th>
<th>Pore Size Distribution Index ($\lambda$)</th>
<th>Fuel Bed Length ($L \text{ m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i (3) 1 (Base Simulation)</td>
<td>1</td>
<td>Canola oil</td>
<td>0.058</td>
<td>0.30</td>
<td>5.0</td>
<td>0.07</td>
<td>2.5</td>
<td>0.30</td>
</tr>
<tr>
<td>ii (3)</td>
<td>2</td>
<td>Canola oil with VI improver</td>
<td>0.062</td>
<td>0.27</td>
<td>5.0</td>
<td>1.32</td>
<td>2.5</td>
<td>0.30</td>
</tr>
<tr>
<td>iii (1)</td>
<td>3</td>
<td>VI improver</td>
<td>0.025</td>
<td>0.27</td>
<td>5.0</td>
<td>1.32</td>
<td>2.5</td>
<td>0.30</td>
</tr>
<tr>
<td>-</td>
<td>4</td>
<td>VI improver</td>
<td>0.058</td>
<td>0.30</td>
<td>5.0</td>
<td>31.04</td>
<td>2.5</td>
<td>0.30</td>
</tr>
<tr>
<td>- 5</td>
<td>0.040</td>
<td>0.30</td>
<td>5.0</td>
<td>0.07</td>
<td>2.5</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 6</td>
<td>0.080</td>
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<td>0.07</td>
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<tr>
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<td>- 8</td>
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<td></td>
</tr>
<tr>
<td>- 9</td>
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<td>0.07</td>
<td>2.5</td>
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<td></td>
</tr>
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<td>0.30</td>
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<td></td>
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<td>- 12</td>
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<td>5.0</td>
<td>1.32</td>
<td>2.5</td>
<td>0.30</td>
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<td></td>
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<td>- 13</td>
<td>0.058</td>
<td>0.30</td>
<td>5.0</td>
<td>0.07</td>
<td>1</td>
<td>0.30</td>
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<td></td>
</tr>
<tr>
<td>- 14</td>
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<td>0.30</td>
<td>5.0</td>
<td>0.07</td>
<td>4</td>
<td>0.30</td>
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<tr>
<td>- 15</td>
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<td>0.30</td>
<td>5.0</td>
<td>0.07</td>
<td>2.5</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 16</td>
<td>0.058</td>
<td>0.30</td>
<td>5.0</td>
<td>0.07</td>
<td>2.5</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To compare between experimental results and numerical simulations, time ($t$) was normalized as a dimensionless time ($Dt$) [19] to account for differences in the average smouldering front velocities ($v_f$) calculated using the procedure from [18], fuel bed lengths ($L$), and ignition times ($t_g$) [9, 19]. The length ($z$) was normalized to account for the difference in the fuel bed length (see Table 5.2).

Table 5.2: Dimensionless Parameters used in Smouldering Experiments and Simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>$Dt = \frac{(t - t_g)v_f}{L}$ (5.1)</td>
</tr>
<tr>
<td>Length</td>
<td>$Dz = \frac{z}{L}$ (5.2)</td>
</tr>
</tbody>
</table>

The non-dimensional times and time frames: (i) $Dt < 0$, (ii) $Dt = 0$, (iii) $0 < Dt \leq 1$, and (iv) $Dt > 1$ represent the following: (i) preheating, (ii) smouldering ignition (i.e., start of air injection), (iii) smouldering propagation over the initial fuel bed length, and (iv) when smouldering reached above the initial fuel bed length due to fuel mobility. (i) – (iii) were explained in detail in [20] and (iv) is discussed in detail in Section 5.3.2. The other parameters are explained in Table 5.3.

5.2.2 Modelling

A previously developed 1D numerical model in COMSOL Multiphysics (Version 6) [8] was equipped with multiphase flow equations to simulate the migration of an organic liquid fuel in a porous medium under smouldering conditions. This model used a resolution of 0.05 cm mesh size.

The computational domain simulated: (i) a porous medium of clean sand at the bottom and top of the reactor with 11 and 21 cm thicknesses, respectively, and (ii) a porous medium composed of clean sand mixed with canola oil (or canola oil with VI improver) with 30 cm
thickness. The governing equations (Eqs. 5.3-29) were solved at every node in space and time, where three main phases were considered: (i) solid (i.e., sand and char produced by canola oil pyrolysis), (ii) liquid (wetting phase: canola oil or canola oil with VI improver), and (iii) gas (non-wetting phase: air). Canola oil chemical kinetics followed a global, two-step reaction mechanism (see Appendix C, Section C1) where canola oil was pyrolyzed to char and the char was oxidized.

\[
\text{Canola Oil} \xrightarrow{R_p} \nu_c \text{Char} + (1 - \nu_c) \text{Gas}
\]

\[
\text{Char} + \nu_{O_2} O_2 \xrightarrow{R_c} \text{Gas}
\]

Pyrolysis \((R_p)\) and oxidation reaction rates \((R_c)\) were described by first-order Arrhenius reactions [21]:

\[
R_p = A_p \exp \left( - \frac{E_p}{R_g T_w} \right) (Y_w)
\]

\[
R_c = A_c \exp \left( - \frac{E_c}{R_g T_w} \right) (Y_{\text{char}})(Y_{O_2})
\]

where \(A_p\) and \(A_c\) are pre-exponential factors; \(E_p\) and \(E_c\) are the activation energies for pyrolysis and oxidation reactions, respectively; \(T_w\) is the wetting phase temperature (i.e., canola oil), which was assumed to be in local thermal equilibrium with sand temperature (i.e., see Eq. 5.23); and \(\nu_c\) and \(\nu_{O_2}\) are the char and oxygen mass yields, respectively. The canola oil and oxygen mass fractions were defined as \(Y_w = m_{\text{Canola oil}} / m_{\text{Canola oil,0}}\) and \(Y_{O_2} = m_{O_2} / m_{\text{air}}\), respectively. The subscripts \(s\), \(w\), and \(n\) note the solid (i.e., sand), wetting phase (i.e., canola oil), and non-wetting phase (i.e., air), respectively.

The pressure and saturation distributions were solved as functions of space and time, subject to inertial, gravity, and capillary forces considering the influences of soil intrinsic permeability, relative permeabilities, and temperature-dependent organic liquid viscosity.
The conservation of mass for the wetting phase (i.e., canola oil), char, and non-wetting phase (i.e., air), was defined by Eqs. 5.7, 10, and 11 [22]:

\[
\frac{\partial (\phi S_w \rho_w Y_w)}{\partial t} + \frac{\partial (\rho_w q_w)}{\partial z} = -Q_w \tag{5.7}
\]

where \(\phi, S_w, \rho_w,\) and \(q_w\) are porosity, canola oil saturation, canola oil density, and Darcy flux of canola oil, respectively. \(Q_w\) (i.e., volumetric mass consumption rate from canola oil pyrolysis), and \(Y_w\) were defined by [8]:

\[
Q_w = \phi S_w \rho_w R_p \tag{5.8}
\]

\[
\frac{\partial (Y_w)}{\partial t} = -R_p \tag{5.9}
\]

The char conservation of mass was [8]:

\[
\frac{\partial (Y_c)}{\partial t} = \nu_c R_p - R_c \tag{5.10}
\]

The conservation of mass for the non-wetting phase (i.e., air) was [22]:

\[
\frac{\partial (\phi \rho_n S_n)}{\partial t} + \frac{\partial (\rho_n q_n)}{\partial z} = Q_n \tag{5.11}
\]

Where \(S_n, \rho_n,\) and \(q_n\) are the saturation, density, and Darcy flux of air, respectively. \(Q_n\) represents the volumetric mass generation rate and was defined by [8]:

\[
Q_n = \phi S_w \rho_w ((1 - \nu_c) R_p + R_c) \tag{5.12}
\]

\(R_p\) and \(R_c\) are the pyrolysis and oxidation reaction rates defined by Eqs. 5.5, 6, respectively. Capillary pressure-saturation functions were defined by Eqs. 5.13, 14) [23, 24]:
\[ S_w = \left( \frac{p_c}{p_d} \right)^{-\lambda} (1 - S_r) + S_r \]  
(5.13)

\[ S_n = 1 - S_w \]  
(5.14)

where \( p_c, p_d, S_r, \) and \( \lambda \) represent the capillary pressure, displacement pressure, residual saturation, and pore size distribution index, respectively. Darcy’s Law was used to determine the wetting and non-wetting phase velocities:

\[ q_w = -K_w \frac{dh_w}{dz} = -\frac{k_{rw} k_i}{\mu_w} \left( \frac{\partial p_w}{\partial z} + \rho_w g \right) \]  
(5.15)

\[ q_n = -K_n \frac{dh_n}{dz} = -\frac{k_{rn} k_i}{\mu_n} \left( \frac{\partial p_n}{\partial z} + \rho_n g \right) \]  
(5.16)

where \( K, h, k_r, k_i, \mu, \rho, p, \) and \( g \) represent hydraulic conductivity, fluid head, relative permeability, intrinsic permeability, viscosity, density, pressure, and gravity, respectively. The key factors were (i) phase hydraulic gradients \((dh/dz)\), (ii) temperature-dependent liquid viscosity, (iii) porous medium intrinsic permeability, and (iv) relative permeability. The relative permeability for wetting and non-wetting phases were defined by [22]:

\[ k_{rw} = S_e^{(\frac{2+3\lambda}{\lambda})} \]  
(5.17)

\[ k_{rn} = (1 - S_e)^2 \left( 1 - S_e^{\left(\frac{2+3\lambda}{\lambda}\right)} \right) \]  
(5.18)

where \( \lambda \) is the pore size distribution index and \( S_e \) is the effective saturation [22]:

\[ S_e = \frac{S_w - S_r}{1 - S_r} \]  
(5.19)

The gas density was calculated via the ideal gas law [25]:
\[ \rho_n = \frac{p_n}{R \ T_n} \]  \hspace{1cm} (5.20)

where \( R \) is the gas constant. The bulk transport of oxygen in the gas phase was described by Eq. 5.21 [26]:

\[ \frac{\partial (\phi S_n \rho_n Y_{O_2})}{\partial t} + \frac{\partial (\rho_n \ q_n Y_{O_2})}{\partial z} = \frac{\partial}{\partial z} \left( \phi S_n \ p_n \ D_g \ \frac{\partial Y_{O_2}}{\partial z} \right) + Q_{O_2} \]  \hspace{1cm} (5.21)

where \( D_g \) is the oxygen diffusion coefficient, \( Q_{O_2} \) represents the mass per unit volume per unit time of oxygen consumed via Eq. 5.22:

\[ Q_{O_2} = -\phi \ S_w \ \rho_w \ v_{O_2} \ R_c \]  \hspace{1cm} (5.22)

The conservation of energy considered local thermal equilibrium (LTE) between condensed phases (i.e., sand, canola oil, and char) and local thermal non-equilibrium (LTNE) between the condensed phases and air [26-28]:

\[ (\rho \ C_p)_{eff} \ \frac{\partial T_w}{\partial t} + \rho_w C_{P_w} \left( q_w Y_w \ \frac{\partial T_w}{\partial z} \right) \]
\[ = \frac{\partial}{\partial z} \left( k_{eff} \ \frac{\partial T_w}{\partial z} \right) + h_{nw} \left( \frac{A_{s,sp}}{V_{sp}} \right) (T_n - T_w) - U \ SA \ (T_w - T_0) + Q_{gen} \]  \hspace{1cm} (5.23)

\[ \phi \ S_n \ \rho_n C_{P_n} \ \frac{\partial T_n}{\partial t} + \rho_n C_{P_n} \left( q_n \ \frac{\partial T_n}{\partial z} \right) \]
\[ = \frac{\partial}{\partial z} \left( \phi \ S_n \ k_n \ \frac{\partial T_n}{\partial z} \right) + h_{nw} \left( \frac{A_{s,sp}}{V_{sp}} \right) (T_w - T_n) \]  \hspace{1cm} (5.24)

where \( A_{s,sp} \) and \( V_{sp} \) are the specific surface area and volume of the sand, respectively. \( Q_{gen} \) represents the volumetric energy consumption rate of canola oil pyrolysis (\( \Delta H_p \)) and production rate from char oxidation (\( \Delta H_c \)) defined by Eq. 5.25:
\[ Q_{gen} = \phi S_w \rho_w \left( \Delta H_p R_p + \Delta H_c R_c \right) \] (5.25)

The interfacial heat transfer coefficient \( (h_{sg}) \) was described by Eq. 5.26 [29]:

\[ Nu = \frac{h_{sg} d_p}{k_g} = 0.001 \left( Re^{1.97} Pr^{0.1} \right) \] (5.26)

Eqs. 5.27, and 28 assumed effective thermal properties in the bulk combinations of sand and canola oil [26]:

\[ (\rho C_p)_{eff} = \phi_s \rho_s C_{ps} + \phi S_w \rho_w C_{pw} \] (5.27)

\[ k_{eff} = \phi_s (k_s + k_{rad}) + \phi S_w k_w \] (5.28)

\[ \phi_s = 1 - \phi \] (5.29)

where \( \rho \), \( \phi \), \( C_p \), and \( k \) are the densities, porosities, heat capacities, and thermal conductivities, respectively. Radiative heat transfer was embedded in the effective solid conductivity following the Rosseland approximation \( (k_{rad} = 16\sigma d_p T_s^3 / 3) \) [29], where \( \sigma \) is the Stefan-Boltzmann constant [30]. The model parameters not described above are presented in Table 5.3, and the initial and boundary conditions are provided in Table 5.4. The heater was simulated by a constant heat flux delivered at the inlet boundary, as determined in the previous study [28]. The heat loss coefficient \( (U = 8 \text{[W m}^{-2}\text{K}^{-1}] \) was based on a previous established methodology [20]. Global and local energy balances based on the approach developed by [8, 19] were used and the equations are shown in Table 5.5.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log(A_c)$</td>
<td>6.7560</td>
<td>log(s$^{-1}$)</td>
<td>This work, measured</td>
</tr>
<tr>
<td>$\log(A_p)$</td>
<td>9.3593</td>
<td>log(s$^{-1}$)</td>
<td>This work, measured</td>
</tr>
<tr>
<td>$C_{pn}$</td>
<td>$-3\times10^{-5} T_n^2 + 0.2261 T_n + 940.35$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>[31]</td>
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<tr>
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<td>J kg$^{-1}$ K$^{-1}$</td>
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<td>$5.3054 T_w + 287.56$</td>
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<td>W m$^{-1}$ K$^{-1}$</td>
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<td>[9]</td>
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<td>[28]</td>
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<td>MJ·kg$^{-1}$</td>
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<td>-</td>
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<tr>
<td>$\nu_{O_2}$</td>
<td>2.5</td>
<td>-</td>
<td>This work, calibrated</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>$-9 \times 10^{-12} T_n^2 + 4 \times 10^{-8} T_n + 6 \times 10^{-6}$</td>
<td>Pa·s</td>
<td>[35]</td>
</tr>
</tbody>
</table>
| $\mu_w$ (canola oil) | \[
\begin{align*}
3.23 \times 10^7 \exp(-0.0699 T_w) + \\
6.152 \exp(-0.01833 T_w)
\end{align*}
\] for $70 < T_w < 627$ °C | Pa·s | [9], correlated |
| $\lambda$ | 2.5 | - | [22] |

In this work, correlations were defined for canola oil thermal conductivity ($k_w$), heat capacity ($C_{p_w}$), and viscosity ($\mu_w$).
Table 5.4: Initial and Boundary Conditions in the Numerical Model

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Initial Condition</th>
<th>Boundary Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5.7)</td>
<td>( S_w = S_r \rightarrow 0.00 &lt; z &lt; 0.11) ( z = 0.00)</td>
<td>( \rho_w q_w = 0 )</td>
</tr>
<tr>
<td>(5.9)</td>
<td>( Y_w = 1 )</td>
<td>( \rho_n q_n = \rho_n q_n(t) )</td>
</tr>
<tr>
<td>(5.10)</td>
<td>( Y_c = 0 )</td>
<td>( -(k_{eff}) \frac{\partial T_w}{\partial z} = 0 )</td>
</tr>
<tr>
<td>(5.11)</td>
<td>( P_n = 101375 \text{ Pa} )</td>
<td>( T_n = T_0 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( Y_{O_2} = Y_{O_2,0} )</td>
</tr>
<tr>
<td>(5.21)</td>
<td>( Y_{O_2} = 0.23 )</td>
<td>( -(k_{eff}) \frac{\partial T_w}{\partial z} = 0 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \rightarrow 0 \leq t \leq t_h )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( -(k_{eff}) \frac{\partial T_w}{\partial z} = 0 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \rightarrow t_h \leq t \leq t_f )</td>
</tr>
<tr>
<td>(5.23)</td>
<td>( T_s = T_w = 295 \text{ K} )</td>
<td>( z = 0.64 )</td>
</tr>
<tr>
<td>(5.24)</td>
<td>( T_g = 295 \text{ K} )</td>
<td>( \frac{\partial p_w}{\partial z} = 0 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( p_n = p_0 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( -(k_{eff}) \frac{\partial T_w}{\partial z} = 0 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( -(k_n) \frac{\partial T_n}{\partial z} = 0 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( -D_g \frac{\partial \rho_n Y_{O_2}}{\partial z} = \rho_n q_n(Y_{O_2,0} - Y_{O_2}) )</td>
</tr>
</tbody>
</table>
Table 5.5: Local and Global Energy Equations

<table>
<thead>
<tr>
<th>Energy Rate</th>
<th>Eq. (Local)</th>
<th>Eq. (Global)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet ($\dot{E}_{in}$)</td>
<td>$\rho_n q_n C_p n (T_{n(z1)} - T_\infty) \pi R^2$</td>
<td>$\dot{q}_{in(z=0.11)} \pi R^2$ (from heater)</td>
</tr>
<tr>
<td>Outlet ($\dot{E}_{out}$)</td>
<td>$-\rho_n q_n C_p n (T_{n(z2)} - T_\infty) \pi R^2$</td>
<td>$-\rho_n q_n C_p n (T_{n(z=L)} - T_\infty) \pi R^2$</td>
</tr>
<tr>
<td><strong>Canola oil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pyrolysis ($\dot{E}_{pyr}$)</td>
<td>$\int_{z1}^{z2} \Delta H_p (\phi S_w \rho_w) R_p \pi R^2 dz$</td>
<td>$\int_{0}^{L} \Delta H_p (\phi S_w \rho_w) R_p \pi R^2 dz$</td>
</tr>
<tr>
<td>Char oxidation ($\dot{E}_{oxi}$)</td>
<td>$\int_{z1}^{z2} \Delta H_c (\phi S_w \rho_w) R_c \pi R^2 dz$</td>
<td>$\int_{0}^{L} \Delta H_c (\phi S_w \rho_w) R_c \pi R^2 dz$</td>
</tr>
<tr>
<td>Radial heat loss ($\dot{E}_{loss}$)</td>
<td>$\int_{z1}^{z2} -U (T_w - T_\infty) 2 \pi R dz$</td>
<td>$\int_{0}^{L} -U (T_w - T_\infty) 2 \pi R dz$</td>
</tr>
<tr>
<td>Net ($\dot{E}_{net}$)</td>
<td>$\dot{E}<em>{in} + \dot{E}</em>{oxi} - \dot{E}<em>{out} - \dot{E}</em>{loss}$</td>
<td>$\dot{E}<em>{in} + \dot{E}</em>{oxi} - \dot{E}<em>{out} - \dot{E}</em>{loss}$</td>
</tr>
</tbody>
</table>
5.3 Results and Discussion

5.3.1 Model Calibration and Validation

Figure 5.3 shows a comparison of experimental results and numerical model predictions for different fuels (i.e., canola oil and canola oil with VI improver) and inlet Darcy air fluxes ($q_{n,\text{in}}$). Figure 5.3a highlights the experimental results from canola oil smouldering with $q_{n,\text{in}} = 0.058$ m s$^{-1}$ (i.e., Exp. # i, repeated 3 times). These experiments exhibited a stable average peak temperature ($T_{p,\text{avg}} = 557 \pm 4$ °C) and smouldering front velocity ($v_f = 0.41 \pm 0.01$ cm min$^{-1}$) that progressed up to 46 cm until $Dt = 1.32$; however, after this height, the peak temperatures dropped until all fuel was fully consumed at 53 cm. Note that the initially packed fuel bed was 41 cm tall (i.e., which the smouldering front reached $Dt = 1.00$). The results during $Dt > 1.00$ correspond to smouldering propagation in the originally clean top sand pack. In other words, 19% of canola oil mass (i.e., 118 g of the 637 g added) was mobilized up to the clean sand cap due to upward fuel mobility and smouldering propagated up to 12 cm in the newly fuel bed.

To minimize fuel mobility and better represent smouldering high viscous organic liquid waste (e.g., oil sludge), VI improver was added to canola oil at a mass ratio of 1:1 (Figure 5.3b, c). The temperature-dependent viscosity of the homogeneous mixture increased by 19 times, agreeing with [9]. Experimental results of canola oil with VI improver (Exp. #ii-#iii) show that, by increasing the viscosity of the fuel, more robust smouldering was achieved with higher $v_f = 0.52$ cm min$^{-1}$ and $T_p = 570$ °C. Experimental results confirmed self-sustaining smouldering until $z = 41$ cm (i.e., the initial fuel bed height). However, after this height, experimental global extinction was achieved at $z = 42.5$ cm for $q_{n,\text{in}} = 0.025$ m s$^{-1}$, but smouldering remained self-sustained for $q_{n,\text{in}} = 0.062$ m s$^{-1}$. Altogether, upward fuel mobilization was minimized with the addition of VI improver.

Figure 5d shows that, by increasing $q_{n,\text{in}}$ from 0.025 to 0.062 m s$^{-1}$, the experimental $T_p$ was nearly constant around 570 °C; however, the smouldering front velocity ($v_f$) increased
from 0.45 to 0.52 cm min\(^{-1}\). The trends in Figure 5.3d are routinely found in applied smouldering studies \([8, 36-39]\).

The model was calibrated by adjusting the chemistry parameters \(\nu_c, \nu_{O_2}, \Delta H_c,\) and \(\Delta H_p\) to match experimental data from smouldering canola oil. The calibrated model results in Figure 5.3a show good agreement with experimental data, with the error between temperatures of 8\%, calculated via the methodology from [20]. The numerical \(\nu_f\) and \(T_p\) at these calibrated conditions were 0.37 cm min\(^{-1}\) and 574 °C, respectively, which match well with experimental results (Figure 5.3d).

Figs. 5.3b, c show the robustness of the calibrated model in predicting independent experimental results (Exp. # ii-iii, Table 5.1) conducted using canola oil with VI improver at two different \(q_{n,in}\) (i.e., 0.025 and 0.062 m s\(^{-1}\)). The calibrated model accurately predicted the key experimental metrics, i.e., ignition temperature (360 °C), \(T_p\) (620 °C), and \(\nu_f\) (0.46 cm min\(^{-1}\)) with an average error of 14\%. Moreover, the model predicts upward fuel mobility in low \(q_{n,in}\) where it is globally extinct at \(z = 42.5\) cm. This is the first time fuel mobility has been simulated in applied smouldering systems.

The experiments and simulations with pure VI improver (i.e., \(\mu_w = 31.04\) Pa s at ambient temperature, which represents no mobility) at two different Darcy air flux of 0.025 and 0.062 m s\(^{-1}\) confirms almost uniform \(T_p\) and \(\nu_f\). Therefore, these results demonstrate that fuels with ambient viscosities higher than 1.33 Pa s do not exhibit noticeable mobility effects (see Appendix C, Section C2).

These results demonstrate the model validation at different experimental conditions without further calibration. Overall, the model reproduced key experimental trends that govern the complex interplay between coupled heat and mass transfer, multi-phase flow, and chemical reactions in these smouldering experiments with different fuel viscosities, saturations, and air fluxes.
Figure 5.3: Temperature evolutions comparing experimental (dashed line) and numerical (solid line) results for: (a) canola oil at Darcy air flux ($u_g$) equal to 0.058 m s$^{-1}$; (b) and (c) canola oil with VI improver at Darcy air fluxes of 0.025 and 0.062 m s$^{-1}$, respectively; (d) shows the experimental and numerical smouldering front velocities ($v_f$) and peak temperatures ($T_p$).

5.3.2 Mobility versus Non-Mobility

Figure 5.4a shows a comparison between smouldering numerical simulations using: (i) canola oil (i.e., with mobility due to canola oil’s low $\mu_w$ of 0.07 Pa s at 20°C, Simulation # 1) and (ii) VI improver (i.e., effectively without mobility due to pure VI improver’s high $\mu_w = 31.04$ Pa s at 20°C, Simulation # 4). These results demonstrate that, without mobility, smouldering progressed more robustly with a higher average $T_p = 662$ °C and $v_f = 0.46$ cm min$^{-1}$. 
Figure 5.4b shows saturation histories at different positions in the simulation during smouldering propagation for canola oil (solid line) and VI improver (dotted line) with the initial saturation, $S_{w,0} = 0.30$. The simulations for canola oil show downward mobilization with a decrease in $S_w$ during the air-off period for the positions (i) near the heater, where temperature effects on the canola oil viscosity are high (i.e., at $z = 14.5$ cm, $S_w$ decreased from 0.30 to 0.20), and (ii) at the top of the fuel bed due to gravity (i.e., at $z = 35.5$ cm, $S_w$ decreased from 0.30 to 0.22). Conversely, VI improver did not migrate during the same time period and $S_w$ remained unchanged.

Upon igniting smouldering, changes in temperature distributions and upward viscous force associated with air pressure gradients caused further canola oil redistribution. This pressure redistribution is illustrated in Figure 5.5e, where the main trends agree strongly with routine experimental observations [40]. For example, mobile fuel is routinely found in the initially clean sand caps in experiments as documented in [15]. As smouldering progressed, the canola oil was pushed ahead of the chemical reactions. Figure 5.4b shows that this accumulation of canola oil by progressing the smouldering front increased the magnitude and location of the peak saturation ($S_{w,peak}$) from 0.23 to 0.53 at $z = 14.5$ to 35.5 cm, respectively. When the smouldering front reached the top of the fuel bed, canola oil was pushed into the initially clean sand and the final $S_{w,peak}$ values decreased to 0.36 at $z = 46.0$ cm. The canola oil was finally consumed at $z = 53$ cm (see Figure 5.3a). Conversely, the VI improver saturation was constant ahead of the smouldering front over time. That is, the VI improver saturation was either 0.30 (i.e., before smouldering) or 0.00 (i.e., after smouldering), agreeing with [15, 41]. The results for VI improver therefore represent typical smouldering using non-mobile fuel. Overall, the model results provide previously unseen insights into the effects of fuel mobility on temperature and saturation distributions.
Figures 5.4: (a and b) numerical simulation of temperature evolution comparing canola oil (solid line) and VI improver for $q_{n,in} = 0.058 \text{ m s}^{-1}$.

5.3.3 Dynamic of Mobility

To better understand the dynamics of fuel mobility in smouldering systems, the distributions of different parameters including canola oil temperature ($T_w$), saturation ($S_w$), oxygen mass fraction ($Y_{O2}$), Darcy flux of canola oil ($q_w$), air pressure ($P_n$) and reaction rates ($R$) at different times ($Dt = -0.20, 0.40, 0.80, 1.20$) are shown in Figure 5.5.

At $Dt = 0$, canola oil was at an initial saturation of 0.30 while the entire domain was at ambient temperature (i.e., 20 °C). During the preheating period, ($Dt = -0.20$), the heater was turned on, $T_{w,peak}$ increased to 620 °C (Figure 5.5a) and canola oil migrated downward to the initially clean sand region below the heater due to gravity force (Figure 5.5b), confirmed with $q_w < 0$). A weak oxidation reaction was detected due to the initial oxygen mass fraction ($Y_{O2,0}$) in the pores, which depleted the oxygen locally before ignition (Figure 5.5c).

From $0.00 < Dt < 1.00$, the smouldering front progressed through fuel bed with consistent $T_p = 570$ °C (Figure 5.5a); however, $S_{w,peak}$ increased up to 0.51 (Figure 5.5b) due to the accumulation of fuel in the preheating zone. For example, at $Dt = 0.40$ (smouldering front position at $z = 0.22$ m), canola oil was pushed upward ($q_w > 0$ m s$^{-1}$, Figure 5.5d) in the
preheating zone due to viscous forces (associated with air pressure gradients, Figure 5.5e), which decreased the saturation in the reaction zone ($S_w = 0.23$). This mobility ultimately decreased $T_p$, compared to high viscous fuel with minimal mobility (see Figure 5.4a). Above the preheating zone, canola oil was at ambient temperature where gravity dominated downward mobility and $S_w$ decreased to 0.27 ($S_{w,0} = 0.30$). At this time, the pressure at the bottom of the reactor increased to 3.7 kPa (Figure 5.5e).

At $Dt = 0.80$, the cooling zone grew; therefore, the overall pressure drop across the system increased over time, due to the increased flow resistance from the high temperature and high viscosity air [40] and the peak pressure at the reactor base increased to 3.9 kPa. In addition, the relative air permeability ($k_{rn}$) decreased in preheating zone due to the accumulation of fuel, which resulted in higher pressure drop locally in this zone. This pressure trend is common across applied smouldering systems with a constant air mass flux [26, 27]. Moreover, the reaction zone shows that the two-step canola oil pyrolysis and char oxidation took place within a thin, 7.0 mm region that coincided with the peak temperature and maximum oxygen consumption rate ($dY_{O2}/dt = 0.004 \text{ [s}^{-1}]$). Again, this reaction zone thickness is commonly observed in many comparable smouldering systems [39, 42, 43].

At $Dt > 1.00$ (e.g., $Dt = 1.20$), a slightly higher oxygen mass fraction ($Y_{O2}$) was consumed and $T_p$ increased slightly as the smouldering front accelerated in this region due to end-effects. However, $S_{w,peak}$ decreased as it was consumed by the front, which resulted in decreasing $q_w$ (i.e., from 7.2 to $3.3 \times 10^{-6} \text{ m} \text{s}^{-1}$) associated with decreasing relative canola oil permeability ($k_{rw}$) (see Eq. 5.14 and 16). After smouldering reached the top of the reactor ($z = 53 \text{ cm}$), all canola oil was consumed, and only hot clean sand remained behind. Low viscous fuel increases the time of smouldering remediation, as fuel is transferred to the area that was previously clean.

Overall, Figure 5.5 illustrates many key dynamics of fuel mobility in applied smouldering systems where the model reproduces the experimental temperature along the height of the
column well (Figure 5.5a). These results provide critical insight and clarity into the key trends routinely observed in experiments.
Figure 5.5: Distribution of various key parameters: (a) temperature ($T_w$), (b) saturation ($S_w$), (c) oxygen mass fraction ($Y_{O_2}$), (d) Darcy flux of canola oil ($q_w$), (e) air pressure ($P_n$), (f) reaction rates ($R_p$ and $R_c$) and oxygen consumption rate ($dY_{O_2}/dt$), at four different times: $Dt = -0.20$, 0.40, 0.80, and 1.20. Dashed vertical blue lines show the position of the reaction zone at $Dt = 0.80$. 
5.3.4 Sensitivity Analyses

Figure 5.6 and 7 illustrate the sensitivity analyses of inlet Darcy air flux \(q_{n,in}\), initial saturation \(S_{w,0}\), intrinsic permeability \(k_i\), fuel viscosity \(\mu_w\), pore size distribution index \(\lambda\), and the fuel bed length \(L\) on \(T_w, S_w, Y_{O2}\) distributions, and \(T_p\) and \(\nu_f\) at \(Dt = 0.50\).

5.3.4.1 Inlet Darcy Air Flux \(q_{n,in}\)

Darcy air flux \(q_{n,in}\) is one of the most effective parameters in controlling smouldering characteristics (e.g., robustness, \(T_p\), and \(\nu_f\)), as it determines the rate of convective heat transfer and oxygen mass flux \(\rho_n q_{n,in} Y_{O2}\) delivered to the reaction zone. All scenarios in Table 5.1 show by increasing \(q_{n,in}\) from 0.040 to 0.080 m s\(^{-1}\) (in Simulation \# 5 to 6, respectively), (i) saturation leading edge position progressed from \(z = 0.28\) to \(z = 0.36\) m, respectively, due to higher viscous forces, (ii) a lower \(Y_{O2}\) was consumed due to higher \(\rho_n q_{n,in} Y_{O2}\) delivered to the front (see Figure 5.6a, b), (iii) \(\nu_f\) increased from 0.32 to 0.44 cm min\(^{-1}\), respectively. However, \(T_p\) and fuel mobilization below the heater during the air-off period remained almost constant (i.e., \(575 \pm 6^\circ C, S_w = 0.18\) (see Figure 5.7a).

With a low \(q_{n,in} = 0.025\) m s\(^{-1}\), \(T_p\) increased to 625 \(^\circ C\) (i.e., relative to 575 \(^\circ C\) at 0.040 m s\(^{-1}\)), while \(\nu_f\) decreased to 0.20 cm min\(^{-1}\) (i.e., relative to 0.28 cm min\(^{-1}\) at 0.040 m s\(^{-1}\)). While the \(\nu_f\) trend is expected, the \(T_p\) trend is not. Both trends reflect that, by decreasing \(q_{n,in}\), a higher \(S_w\) was fostered in the reaction zone, which resulted in higher \(T_p\), agreeing with [9, 44]. This redistribution is a key phenomenon unique to mobile liquid fuels. That is, this effect is not seen in smouldering immobile fuels (e.g., GAC) [45]. Figure 5.7a also shows that, with a very low \(q_{n,in} = 0.015\) m s\(^{-1}\), smouldering was not self-sustaining, as the radial heat losses dominated over the produced oxidation energy and the global net energy rate was negative (see further discussion in Section 5.3.5).
5.3.4.2 Initial Saturation ($S_{w,0}$)

Figure 5.6c shows that by increasing $S_{w,0}$ from 0.20 to 0.40 (in Simulation # 8 to 9, respectively), more fuel was mobilized downward below the heater during the air-off period ($S_w = 0.25$ for $S_{w,0} = 0.40$). $T_p$ and oxygen consumption remained uniform ($T_p = 570 \, ^\circ C, \Delta Y_{O2} = 12\%$) in comparison to the base case ($T_p = 574 \, ^\circ C, \Delta Y_{O2} = 12\%$), which shows that in this saturation range almost the same amount of $S_w$ was consumed in the reaction zone. This finding qualitatively agrees with Section 5.3.4.6 and experimental data from [46], which both hypothesize that a high $q_{n,in} = 0.058 \, m \, s^{-1}$ caused sufficient upward viscous force to drive the fuel into the preheating zone (i.e., ahead of the smouldering front). In these conditions, no fuel leaked from the preheating zone to the reaction zone. The $\nu_f$ slightly dropped (from 0.38 to 0.35 cm min$^{-1}$) due to accumulation of fuel in the preheating zone, which also decreased the relative air permeability ($k_{rn}$) and Darcy air flux ($q_n$).

Figure 5.7b confirms that by decreasing the saturation below 0.20, both $T_p$, and $\nu_f$ dropped, as lower $S_w$ was deposited in the reaction zone, therefore smouldering was weak. For $S_w < 0.05$, smouldering is not self-sustaining as energy losses overwhelmed the oxidation energy production rate (see additional discussion in Section 5.3.5).

5.3.4.3 Intrinsic Permeability ($k_i$)

Figure 5.6e shows key sensitivities to intrinsic permeability ($k_i$). When $k_i$ was halved (i.e., from $k_i = 5 \times 10^{-10} \, m^2$ in Simulation # 1 to 10, respectively), less fuel was mobilized downward below the heater during air-off period ($S_w = 0.12 \, vs. \, S_w = 0.19$, respectively). Moreover, the saturation leading edge in the low $k_i$ Simulation # 10 was located at $z = 41$ cm (base case, $z = 33$ cm), which indicates that fuel (upward) mobilization carried a large fraction of fuel further ahead into the preheating zone. This upward mobilization resulted in less fuel deposited in the reaction zone, where deposited $S_w$ decreased from 0.23 (base case) to 0.15. This decreased saturation deteriorated the reaction robustness $T_p = 506 \, ^\circ C$ and $\nu_f = 0.28 \, cm \, min^{-1}$ (base case, $T_p = 574 \, ^\circ C$ and $\nu_f = 0.37 \, cm \, min^{-1}$). Ultimately, these
effects were due to a large viscous force against gravity, driven by higher air pressures in the low \( k_l \) Simulation # 10. Conversely, doubling \( k_l \) (i.e., from \( k_l = 5 \) to \( 10 \times 10^{-10} \) m\(^2\) in Simulation # 1 to 11, respectively), increased downward mobilization during the air-off period and lowered upward fuel mobilization (i.e., as the saturation leading edge was located close to the reaction zone at \( z = 0.29 \) m). Thus, more fuel is deposited in the reaction zone, i.e., \( S_w \) increased from 0.23 (base case) to 0.27 (high \( k_l \) Simulation # 11). This increase in deposited \( S_w \) resulted in a high \( T_p = 645 \) °C and increased oxygen consumption (final \( Y_{O_2} \) from 0.11 to 0.02), relative to the base case (Simulation # 1).

5.3.4.4 Temperature-dependent Viscosity of Fuel (\( \mu_w \))

Figure 5.6g illustrates the effects of \( \mu_w \) on \( T_w \) and \( S_w \) distributions for three different fuels: (i) Canola oil (Simulation # 1, base case simulation), (ii) Canola oil with VI at a mass ratio of 1:1 (i.e., Simulation # 12), and VI improver-only (i.e., Simulation # 4). For (i), \( \mu_w \) decreased from 0.070 to 0.009 Pa s when temperature increased from ambient (20 °C) to ignition temperature (360 °C), respectively. This temperature dependency strongly affects fuel downward mobilization below the heater during the air-off period and upward mobilization to the preheating zone. Downward mobilization resulted in \( S_w = 0.19 \) below the heater.

For (ii), the addition of VI in the canola oil increased \( \mu_w \) to 1.32 Pa s (ambient temperature) and 0.017 Pa s (ignition temperature), i.e., approximately 19 and 2 times more viscous than canola oil alone at the respective temperatures. Practically, these higher viscosities resulted in a slight downward mobilization below the heater during the air-off period. However, upward mobility was the highest in the preheating zone reaching \( S_w = 0.75 \) at \( z = 0.30 \). Slightly more fuel (\( S_w = 0.24 \)) remained in the reaction zone when compared to the base case and resulted in \( T_p = 590 \) °C and \( v_f = 0.42 \) cm min\(^{-1}\). Between \( z = 0.31 \) and \( z = 0.39 \), saturation distribution remained uniform (\( S_w = 0.30 \)), as this region experienced near-ambient temperatures with high-viscosity fuel.
For (iii), $\mu_w$ increased to 31.04 (ambient temperature) and 5.00 Pa s (ignition temperature), i.e., 444 and 556 times more viscous than canola oil at the respective temperatures. Downward and upward mobility was not observed due to the high viscosities of VI. Therefore, $S_w$ remained uniform as smouldering progressed to the top of the reactor. In this case, the smouldering front consumed the entire fuel (i.e., $S_w = 0.30$) in the reaction zone, which resulted in the highest $T_p = 650$ °C (see Figure 5.7d), and greatest oxygen consumption (final $Y_{O_2} = 0.11$ to 0.01).

5.3.4.5 Pore Size Distribution Index ($\lambda$)

Figure 5.6i and j illustrate the effects of $\lambda$ on $T_w$ and $S_w$ distribution in the reactor. $\lambda = 2.5$ represents a normal pore size distribution performed in the base case simulation, while a lower $\lambda = 1$ represents a wider pore size distribution (i.e., poorly sorted material), and a higher $\lambda = 4$ represents a narrower pore size distribution (i.e., well-sorted material such as glass beads, see Eq. 5.12). By decreasing $\lambda$ to 1 (Simulation # 13), downward and upward fuel mobilization through the porous medium was limited; gravity and viscous force were less effective, therefore higher fuel ($S_w = 0.32$) was concentrated in the reaction zone when compared to the base case Simulation # 1 ($S_w = 0.23$), which caused higher $T_p = 675$ °C, and faster $\nu_f = 0.47$ cm min$^{-1}$, with entire oxygen consumption, relative to the base case. This is the only scenario in which $S_w$ was concentrated in the reaction zone more than $S_{w,0}$ and oxygen was entirely consumed. By increasing $\lambda$ to 4 (Simulation # 14), fuel easily migrated through the porous medium, which resulted in more fuel mobilization below the heater during the air-off period and in the preheating zone away from the reaction zone (i.e., only $S_w = 0.13$ remained in the reaction zone). Therefore, $T_p$ and $\nu_f$ decreased to 527 °C and 0.30 cm min$^{-1}$, respectively, relative to the base case. As $\lambda$ and displacement pressure ($P_d$) are interconnected, a sensitivity on $P_d$ was performed in Appendix C section C4.
5.3.4.6 Fuel Bed Length ($L$)

Figure 5.6k and l illustrate the effects of $L$ on $T_w$, and $S_w$ distributions. Decreasing $L$ from 30 (base case Simulation # 1) to 15 cm (Simulation # 15), decreased the peak saturation ($S_{w,peak}$) to 0.33 (in comparison to 0.53 in the base case), and $T_p$ to 567 °C (compared to 574 °C in the base case) as less fuel remained in the reaction zone due to mobility ($S_w = 0.15$). However, $v_f$ (0.37 cm min$^{-1}$) and oxygen consumption were nearly the same as the base case. These simulations showed that by decreasing $L$, a comparable amount of fuel was mobilized downward below the heater during the air-off period. Moreover, $S_{w,peak}$ decreased, however almost uniform $v_f$ with the base case was achieved.

By increasing $L$ to 90 cm (Simulation # 17), canola oil accumulated in the preheating zone and $S_{w,peak}$ increased to 0.57; however, $T_p$ was nearly the same as the base case, as deposited $S_w$ in the reaction zone remained uniform. This finding is consistent with the experimental results from [9] where high $q_{n,in}$ prevented fuel migration from preheating zone to the reaction zone, which moderated the $T_p$.

Overall, a sensitivity analysis of the key parameters associated with the air, fuel, porous medium on $T_w$ and $S_w$ was performed. These results show that higher $T_p$, $v_f$, and $Y_{O2}$ consumption were all associated with conditions that led to higher fuel saturations in the reaction zone, which in turn led to more robust oxidation reactions (see Section 5.3.5).
Figure 5.6: Sensitivity analyses of (a, b) inlet Darcy air flux ($q_{n, in}$), (c, d) initial saturation ($S_{w0}$), (e, f) intrinsic permeability ($k_i$), (g, h) fuel viscosity ($\mu$), (i, j) pore size distribution index ($\lambda$), and (k, l) contamination length ($L$) on temperature and fuel saturation distributions in the reactor.
Figure 5.7: Sensitivity analyses of (a) inlet Darcy air flux \(q_{n,in}\), (b) initial saturation \(S_{w,0}\), (c) intrinsic permeability \(k_i\), (d) fuel viscosity \(\mu\), (e) pore size distribution index \(\lambda\), and (f) fuel bed length \(L\) on peak temperatures \(T_p\) and smouldering front velocities \(v_f\).
5.4 Sensitivity of Energy Analysis

To verify the model and quantify the effects of liquid mobility on smouldering systems, local (i.e., across the smouldering front) and global (i.e., across the entire system) energy analyses were conducted for the cases presented in Section 5.3.4 at \( \text{D}t = 0.5 \) (Appendix C, Section C3). In all the cases for the local energy balance, the oxidation energy rate \( (\dot{E}_{\text{oxid}}) \) mostly contributed to the net energy rate \( (\dot{E}_{\text{net}}) \), while the inlet and outlet energy rate (i.e., energy delivered to and from the reaction zone by the convective heat flux of air) \( (\dot{E}_{\text{in-air}}, \dot{E}_{\text{out-air}}) \) almost balanced each other across the cases. \( \dot{E}_{\text{in}} \) and \( \dot{E}_{\text{out}} \) did not impact the global energy balance in any case, as the analysis was performed in the middle of smouldering propagation, when the system was not affected by initial- or end-effects, respectively. By increasing \( q_{\text{n,in}} \), \( \dot{E}_{\text{out-air}} \) increased, which promoted pyrolysis and oxidation reactions and increased \( v_f \) (see Figure 5.7a). However, due to decreased \( S_w \) remaining in the reaction zone during upward mobility, \( \dot{E}_{\text{oxid}} \) and \( \dot{E}_{\text{pyr}} \) decreased (see Figure 5.6b). Inlet energy convected by canola oil to the reaction zone \( (\dot{E}_{\text{in-Canola oil}}) \) was negligible, which confirms the low viscous fuel was in the preheating zone and moved upward due to high \( q_{\text{n,in}} \) and a negligible amount moved into the reaction zone.

Figure 5.8c shows the minimal local energy rate changes by increasing \( S_{w,0} \) from 0.20 to 0.40. The previous study [8] showed that, without the effect of mobility, \( \dot{E}_{\text{oxid}} \) increased linearly with \( S_{w,0} \), which resulted in higher \( T_p \) and \( \dot{E}_{\text{out}} \). However, by considering the effect of mobility and a relatively high \( q_{\text{n,in}} = 0.058 \text{ m s}^{-1} \), the fuel was mobilized upward away from reactions into the preheating zone which resulted in a constant \( S_w \) remains in the reaction zone therefore a nearly uniform \( \dot{E}_{\text{oxid}} \) and \( T_p \) values. Similar behaviour was found in the global energy balance (Figure 5.8d).

Figure 5.8e shows that by increasing \( k_i \), more \( S_w \) remained in the reaction zone; therefore, \( \dot{E}_{\text{oxid}} \) and \( T_p \) increased and more energy was convected \( (\dot{E}_{\text{out}}) \) to the virgin fuel in the preheating zone, which provided more energy for pyrolysis \( (\dot{E}_{\text{pyr}}) \). Similar behaviour was found in the global energy balance, Figure 5.8f.
Figure 5.8g shows the effects on the local energy balance from increasing the fuel bed from 15 to 90 cm, which fostered more fuel accumulation in the preheating zone, as the front took longer to reach the middle of the fuel bed. The $\dot{E}_{\text{oxid}}$ increased slightly as a higher $S_w$ remained in the reaction zone; however, $\nu_f$ remained nearly uniform across all $L$ cases. Figure 5.8h confirms that the global $\dot{E}_{\text{net}}$ decreased with increasing $L$ was an expected tendency in the longer systems and reflects the growing contribution of heat losses from a longer cooling zone in a taller system; therefore, the system robustness remained almost uniform for all of these systems.

Overall, these analyses reveal the impacts of key fuel mobility sensitivities on smouldering systems’ energy balances. These results also verify that $\dot{E}_{\text{in-canola oil}}$ was negligible in all scenarios, as $q_{n,\text{in}}$ was sufficient to move fuel upward in the preheating zone and a negligible amount of fuel moved to the reaction zone. Moreover, this energy analysis confirms the prominent role of mobility in determining the system's robustness, i.e., by decreasing $S_w$ within the reaction zone due to mobility, the $\dot{E}_{\text{oxid}}, \dot{E}_{\text{net}},$ and system robustness also decreased.
Figure 5.8: Local and global energy rates for oxidation ($\dot{E}_{\text{oxid}}$), loss ($\dot{E}_{\text{loss}}$), inlet ($\dot{E}_{\text{in}}$), outlet ($\dot{E}_{\text{out}}$), and their net results ($\dot{E}_{\text{net}}$) at $\Delta t = 0.5$. 
5.5 Conclusion

In this study, a previously developed 1D numerical model was equipped with multiphase flow equations, calibrated with experiments using canola oil (low viscosity, mobile), and validated with experiments using canola oil mixed with VI improver (medium viscosity, mobile) and VI improver alone (high viscosity, non-mobile). The model predictions were in excellent agreement with experimental results in terms of temperature evolutions in space and time, and smouldering front velocities. A higher peak temperature and smouldering front velocity were achieved with the non-mobile fuel as higher fuel remained in the reaction zone and less fuel was moved upward into the preheating zone.

The dynamics of fuel mobility were investigated. During the progress of the smouldering front, despite constant peak temperatures, the peak saturation increased initially due to the accumulation of fuel in the preheating zone and then decreased as canola oil was consumed by smouldering.

A sensitivity analysis of saturation, viscosity, Darcy air flux, intrinsic permeability, and pore size distribution index on saturation distribution, peak temperature, front velocity, and oxygen consumption was performed. In all the scenarios, fuel saturation distribution was affected. Fuel viscosity, porous medium permeability, and pore size distribution index had the strongest impacts on temperatures.

Local and global analyses were conducted to quantify the effects of mobility on the system energy balance. The oxidation energy rate was highly dependent on the saturation of fuel within the reaction zone and was affected by fuel, porous medium, and air flux characteristics. In all cases with a sufficiently high Darcy air flux, negligible fuel saturation leaked from the preheating zone into the reaction zone. Therefore, oxidation energy rate and system robustness mainly depended on the initial fuel deposition and smouldering front velocity. Altogether this study provides novel insight into key fuel mobility dynamics that often affect applied smouldering systems. Many dynamics have not been previously investigated. The insight provided from this study will tool engineers and researchers with new information to design improved applied smouldering systems for environmentally beneficial purposes.
5.6 References


Chapter 6

6 Conclusions

6.1 Summary

The goal of this thesis was to better understand the complicated interplay between multiphase flow, heat and mass transfer, and chemistry through porous media in applied smouldering systems. This goal was achieved by developing novel 1D and 2D numerical models to investigate multi-dimensional transfer effects, the effects of oxygen mass flux, and fuel mobility.

The first objective was to develop and validate a 2D numerical model with experimental results to then quantitatively and qualitatively to investigate the multi-dimensional transfer effects associated with radial heat losses (e.g., non-uniformities in temperature, air mass flux, oxygen mass fraction, and chemistry distribution). This was achieved as: (i) a heat transfer model was first developed by eliminating the effect of chemical reactions and validated with heat transfer-only experiments; (ii) a simplified chemical model was developed for granular activated carbon GAC (i.e., GAC, following global one-step oxidation reaction) based on thermogravimetry and derivative thermogravimetry (TG/DTG) experiments; and (iii) a 2D smouldering model was developed by combining the heat transfer and chemical models.

The 2D numerical model captured the main physics and chemistry of smouldering and its complex interactions, reproduced expected dynamics in multi-dimensional transfer effects of air mass flux and reactions, and provided accurate simulations of key local and global phenomena (e.g., temperature histories and smouldering extinction). This model was also used to explore the consequences of permeability heterogeneity across a range of modelling scenarios. Last, a global energy balance revealed evolutions in the overall system behaviour, and the results compared well with other energy balance results from numerical simulations, experiments, and analytical modelling in the literature.

The second objective was to compare the validated 2D smouldering model to new experimental results to quantify the effects of oxygen mass fluxes in different conditions,
including: (i) oxygen mass fraction \(Y_{O_2}\), (ii) inlet air flux \(u_g\), and (iii) fuel concentration \(C_c\). These simulations explored both oxygen- and fuel-rich smouldering that was robust, weak, and quenching. A quasi-super-adiabatic effect was shown as an increased energy efficiency by diluting oxygen mass fractions. However, with highly diluted oxygen mass fractions, smouldering was very weak with low peak temperatures. By decreasing the inlet air flux, the chemical reactions decreased to the point that smouldering quenched globally. Sensitivity analyses showed that by increasing the inlet air flux, the smouldering front velocity increased linearly, and peak temperatures reached a plateau at high inlet air fluxes. Finally, multi-dimensional transfer effects were investigated across the \(Y_{O_2}\), \(u_g\), and \(C_c\) conditions via the validated numerical model.

The third objective was to better understand the dynamics of fuel mobility in applied smouldering systems by equipping a previously developed 1D numerical model with multiphase flow equations. This new model was calibrated to experiments using canola oil (low viscosity, mobile), and validated with experiments using (i) canola oil mixed with viscosity index (VI) improver (medium viscosity, mobile) and (ii) VI improver alone (high viscosity, non-mobile). During smouldering propagation, despite constant peak temperatures, the peak saturation increased initially due to the accumulation of fuel in the preheating zone, and then decreased as canola oil was consumed by smouldering. Higher peak temperatures and faster smouldering front velocities were achieved with the non-mobile fuel than the mobile fuel, as more fuel remained in the reaction zone and less fuel was mobilized upward into the preheating zone. Sensitivity analyses were performed where fuel viscosity, porous medium permeability, and pore size distribution index had the strongest impacts on the temperature distribution. Local and global analyses showed the oxidation energy rate was highly dependent on the saturation of fuel within the reaction zone and was affected by the fuel, porous medium, and air flux characteristics. In all cases with a sufficiently high Darcy air flux, negligible fuel mobilized away from the preheating zone into the reaction zone. Therefore, oxidation energy rate and system robustness mainly depended on the fuel deposition and smouldering front velocity.

Altogether, this study provides novel insight into key smouldering system characteristics and their effects on system performance. Many dynamics were investigated using multi-
dimensional and multiphase modelling, and the insight provided from this study will provide engineers and researchers with new information to design improved applied smouldering systems for many environmental engineering purposes. However, the main limitation of the multi-dimensional model for the field application may be understanding the real-world porous media characteristics (e.g., heterogeneities in permeability) and thermophysical and chemical properties of contaminants.

6.2 Novelty and Implications

This research provides new knowledge on how multi-dimensional transfer effects, oxygen mass flux, and fuel mobility affect applied smouldering systems.

First, the validated 2D smouldering model is a novel tool to (i) clarify the interconnected nature of non-uniformities (e.g., temperature, air mass flux, and chemistry) across a wide range of smouldering systems; (ii) capture peripheral extinction that affects the thermal efficiency (i.e., from by-passing airflow into cold regions; therefore, decreasing the oxygen transport and convective heat transfer at the center), and remediation efficiency (i.e., as the contamination in the outer cool region may not be remediated); (iii) investigate smouldering behaviour near quenching; and (iv) explore the effects of intrinsic permeability heterogeneity on smouldering propagation.

Second, applied smouldering systems work in a “self-sustaining” manner where exothermic oxidation reaction provides a net positive energy balance against the losses. Therefore, oxygen transport to the front plays a vital role in these systems, and a robust understanding of this phenomenon is needed. By diluting the oxygen concentration, smouldering moves toward weakening; however, the heat transfer efficiency increases and moderates the peak temperature almost constant before declining into very weak conditions. These dynamics are relevant in both applied smouldering and fire safety scenarios; however, it was not investigated rigorously in the past. The implications in better understanding the impacts of oxygen delivery sensitivities findings can be used for both applied smouldering engineering and fire safety scenarios.
Finally, fuel mobility impacts applied smouldering systems in many ways, which were previously not well-understood. This knowledge gap is highly relevant as most applied smouldering systems treat hazardous organic liquids (e.g., crude oil sludge). Fuel saturation is not routinely tracked over space and time in smouldering systems; therefore, a validated 1D numerical model is needed to understand the effects and dynamics of fuel mobility. It was shown that fuel mobility has a strong impact on the system's robustness.

In conclusion, this thesis clarified a wide range of challenging aspects in applied smouldering systems via rigorous numerical modelling. Beyond applied smouldering systems, the results and implications from this thesis are expected to be beneficial to others investigating and designing similar technologies (e.g., thermal energy storage), or engaged in smouldering fire safety problems.

6.3 Recommendations for Future Work

While this study revealed some aspects of smouldering that were not investigated before, it also asked new questions. These new questions stem directly from the completed studies and are related to the main objectives. Therefore, some recommendations are:

- As the local processes in the reaction zone determine smouldering behaviour and fate, developing a smouldering model at the micro-scale would provide a better understanding of (i) the heat transfer mechanisms between solid, liquid, and gas phases; (ii) chemical reactions; (iii) oxygen diffusion from bulk phase to the surface of condensed phase; and (iv) multi-phase flow that determines the fuel deposition. These local processes are currently poorly understood.

- Investigation of decreasing CO/CO₂ (i.e., a key metric of combustion completeness) by weakening the smouldering is warranted. The experiments discussed showed increasing CO/CO₂ with smouldering robustness, which is the reverse trend of other combustion systems (e.g., those that are flaming-based). This trend was observed in many other experimental smouldering studies, but the reasons behind this trend are not yet understood.
Investigation of the heat loss coefficient \((H)\) and clarifying its relation to the temperature-dependent thermophysical properties of insulation around the reactor and convective heat transfer to the surrounding atmosphere would be beneficial. Currently, this term needs to be calibrated to experiments, which limits its application.

Developing and validating a 2D smouldering model equipped with multiphase flow equations for investigating of multi-dimensional transfer effects associated with fuel mobility.

Investigating pore-blocking and super-adiabatic effects in smouldering systems with liquid fuel. These phenomena are poorly understood and may decrease remediation efficiency.

Developing a 3D smouldering model to better understand the effects of full heterogeneity in real applications would be beneficial. This 3D model would be beneficial in clarifying the dynamics that cannot be captured in 2D (e.g., 3D bed heterogeneity for oil sludge treatment in large commercial applications). However, the computational costs might be very high.

Quantifying smouldering contaminant remediation efficiency (e.g., of PFAS) using multi-dimensional numerical modelling. As peripheral extinction associated with radial heat losses decreases the remediation efficiency, this effect has not been quantified before.

Emissions from smouldering systems are important; therefore, efficient capturing and treatment techniques are required to control pollution. Simulating more complicated chemical reactions and emissions production would provide a richer understanding of these important dynamics and help engineers improve future designs.
Appendices


A.1 Pneumatic Conductivity, Permeability, and Porosity Measurement

The bed intrinsic permeability was measured following a previous methodology [1] based on ASTM D6539 00 [2]. The packed bed was subjected to cold air injection at several air fluxes (i.e., 5.00, 10.0, 15.0, 20.0, 27.5, and 30.0 L/min) before smouldering (i.e., the permeability of the sand/GAC mixture) and after smouldering (i.e., the permeability of clean sand-only). Pneumatic conductivity was determined by Eq. A.1 [3]:

\[ K = \frac{k_p \rho_g g}{\mu} \]  

(A.1)

where \( k_p \), \( \mu \), \( \rho_g \), and \( g \) represent the intrinsic permeability, viscosity, density, pressure, and gravity, respectively. Experimental results show that the average pneumatic conductivity increased from \( 5.4 \times 10^{-4} \) to \( 1.2 \times 10^{-3} \) m/s when the permeability increased from \( 8.7 \times 10^{-10} \) m\(^2\) to \( 1.95 \times 10^{-9} \) m\(^2\), which corresponds to before and after smouldering. Because these differences are small, an average permeability of \( 1.4 \times 10^{-9} \) m\(^2\) was used in the numerical model for computational efficiency.
Figure A.1: Measurements of pneumatic conductivity and intrinsic permeability before and after smouldering for two different experiments.

The GAC particle density was measured based on the mass of each grain divided by its volume. 109 particles were investigated using a digital calliper (Tritan) to measure the particle diameters and a high-precision scale (METTLER TOLEDO, Balance XSR205DU) to weigh the GAC particles. This resulted in an average GAC particle density of $1311 \pm 190$ kg/m$^3$. The GAC porosity, which corresponds to the pore volume occupied by GAC, was calculated by:

$$
\phi_{GAC} = Y_{GAC} C_{GAC} (1 - \phi) \rho_{sand} \cdot \frac{1}{\rho_{GAC}}
$$

(A.2)

where $Y_{GAC}$ and $C_{GAC}$ are the GAC mass fraction and concentration, respectively. This resulted in a GAC porosity equal to $0.05 \pm 0.006$ for a GAC concentration of $0.03$ kgGAC kg$^{-1}$ sand.
A.2 Experimental Results, Inverse Modelling, and H Sensitivity Analysis

Figure A.2 shows the temperature evolution at the centerline for heat transfer-only and smouldering with 0.03 kg\(GAC\) kg\(sand\)^\(-1\) experiments where the centreline TCs were placed 1 to 70 cm from the plenum. For heat transfer-only and smouldering experiments, the air was turned on when the TC at \(z = 1\) and 4 cm reached 300 °C (i.e., at \(t_g\)) and the heater was turned off when the TC at \(z = 4\) and 7 cm peaked (i.e., at \(t_h\)) (see Table 3.4). Note that the peak temperature in Figure A.2b was nearly constant throughout smouldering (i.e., \(T_p = 732 \pm 6 \, ^\circ C\)), which shows how the oxidation energy rate compensates for local losses in the reaction zone (i.e., at the smouldering front).

![Figure A.2: Experimental temperature evolution for a) heat transfer-only, b) smouldering at the centerline at different heights from 1 to 70 cm.](image)

The heat influx delivered at the bottom boundary (\(\dot{q} (W/m^2)\)) was determined using inverse modelling in which the error between model-predicted temperatures and heat transfer-only experimental results (average of three repeats) of the first centerline thermocouple at \(Z = 1\) cm was minimized. The rest of the thermocouples at the centerline and wall were used for determining the radial heat loss coefficient (\(H\)) via a sensitivity analysis. The objective function for the heat flux optimization takes into account both the temperature evolution (\(T(t)\)) and peak temperature (\(T_p\)) as shown in [4]:

\[
\text{Objective function} = \sum \left( T(t) - T_{model}(t) \right)^2 + \left( T_p - T_{model,p} \right)^2
\]
\[
\text{Error} \ [\%] = (0.5 \times \text{NRMSD}_{T(t)}_{Z=1 \text{ cm}} + 0.5 \times \left| \frac{T_{p\exp} - T_{p\num}}{T_{p\num}} \right|_{Z=1 \text{ cm}}) \times 100
\]

where \( T_{p\exp} \) and \( T_{p\num} \) are the peak temperature in the experiment and numerical simulation, respectively. NRMSD is the Normalized Root-Mean-Square Deviation between experimental \( (T_s,exp) \) and numerical sand temperature \( (T_s,num) \) [5]:

\[
\text{NRMSD}_{T(t)} = \frac{\sqrt{\sum_{i=1}^{n}(T_{s,exp} - T_{s,num})^2/n}}{(T_{s,max} - T_{s,min})}
\]

The data logger measured the temperature every 2 s during the experiment where \( n \) is the number of measurements taken by the data logger. \( T_{s,max} \) and \( T_{s,min} \) are the maximum and minimum temperatures of sand. \( T(t) \) shows that NRMSD is defined based on the difference in temperature changing with time. The “pattern search optimization algorithm” was used to minimize the error calculated by Eq. A.3 built into MATLAB. The algorithm found a sequence of points that approach an optimal point [6]. The value of error either decreased or remained the same from each point in the sequence to the next iteration; the optimal point was that with the lowest value after 100 iterations. The optimal value for \( \dot{q} \) was equal to 35000 (W/m\(^2\)) with an error equal to 6\% providing an excellent agreement (see thermocouple at \( Z = 1 \text{ cm} \) in Figure A3.a). Figure A.3 also shows a sensitivity analysis of \( H \) where the numerical temperatures from \( Z = 13 \text{ cm} \) to \( Z = 61 \text{ cm} \) were used to compare with the experiment. This sensitivity analysis shows that \( H = 3 \text{ W/m}^2 \text{ K} \) results in the best estimation of experimental data with errors equal to 6\% and 5.7\% at the centerline and wall, respectively.
Figure A.3: Various heat transfer simulations. The shaded region represents 95% confidence interval of three repeats of experimental results; the dashed-dot, solid, and dashed lines represent numerical model predictions with $H$ equal to 1, 3, and 5 W/m$^2$K, respectively, along the a) centerline and b) wall.

Figure A.4 shows the sensitivity analysis of $\dot{q}$ for smouldering at 0.03 GAC concentration. By increasing $\dot{q}$ from 23080 to 35000 (W m$^{-2}$K$^{-1}$), a negligible difference in the cooling zone was observed due to boundary effects that are propagated along the system. Moreover, the energy rate of GAC oxidation ($\dot{E}_{ox}$) is much higher than the energy rate of the heater ($\dot{E}_{in}$). Therefore, $\dot{q} = 23080$ (W m$^{-2}$K$^{-1}$) was considered for the smouldering simulation in this research.
Figure A.4: Temperature evolution at multiple radial positions: (a) centerline, (b) wall, (c) $r = 1.5$ cm, and (d) $r = 2.8$ cm. The solid and dashed-dot lines represent numerical results with $\dot{q} = 23080$, and $35000$ (W m$^{-2}$). The shaded region shows three repeats of experimental results.

The sensitivity of the heat loss coefficient ($H$) on the temperature evolutions for smouldering 0.03 and 0.02 GAC concentrations is presented in Figs. A.4 and A.5, respectively. $H$ determines the rate of radial heat loss between the column wall and ambient air, which includes the effect of insulation; therefore, $H$ is a complicated parameter that requires a separate sensitivity analysis for each GAC concentration. In fact, $H$ is expected to change under different smouldering conditions with different temperature profiles because $H$ is affected by the thermal properties of the insulation (e.g., $C_p$ and $k$) and the convection conditions just outside of the column, which are both temperature-dependant.

For 0.03 kg$_{\text{GAC}}$ (kg$_{\text{sand}}$)$^{-1}$, $H$ values between 2 to 14 W m$^{-2}$ K$^{-1}$ were explored, where the best match with the experimental results was achieved using $H=7$ W m$^{-2}$ K$^{-1}$ with an overall error equal to 6%. Note that a higher $H$ indicates poor insulation quality and higher radial
heat losses. The numerical model predicts the peak and cooling zone temperatures near the wall were cooler than those near the centreline due to radial heat losses, which agrees with the experimental results and similar studies, e.g., [7]. In addition, by increasing $H$ from 2 to 14 W m$^{-2}$ K$^{-1}$, $T_p$ at the centerline and wall dropped from 723 to 708 °C and 550 to 405 °C, respectively.

![Diagram](image)

Figure A.5: Various smouldering simulations with a concentration of 0.03 kg$_{GAC}$ (kg$_{sand}$)$^{-1}$. The shaded region represents three repeats of experimental results; the dashed-dot, solid, and dashed lines represent numerical model predictions with $H$ equal to 2, 7, and 14 W m$^{-2}$ K$^{-1}$, respectively, along the a) centerline and b) wall.

Like Figure A.4, Figure A.5 further illustrates the model’s reliability in reproducing key smouldering metrics (e.g., temperatures and front velocities). By exploring $H$ between 1 to 5 W m$^{-2}$ K$^{-1}$, the best match with experimental results was achieved for $H$=3.2 W m$^{-2}$ K$^{-1}$ (with the error equal to 5 and 6.1 % at the centerline and wall, respectively). As highlighted above, the increased $H$ from 3 to 7 W m$^{-2}$ K$^{-1}$ with increasing GAC concentration from 0.02 to 0.03 is associated with higher temperatures that foster a greater rate of heat losses. The main reasons are associated with the temperature dependencies in: (i) the thermophysical properties of insulation that are embedded in $H$ (e.g., the thermal conductivity increases with temperature and leads to a higher $H$ value) and (ii) free-convection heat transfer dynamics between the column wall and ambient air (e.g., free-convection increases with increasing surface temperature, which also leads to a higher $H$ value [8]).
Figure A.6: Various smouldering simulations with a concentration of $0.02 \text{ kg}_{\text{GAC}} (\text{ kg}_{\text{sand}})^{-1}$. The shaded region and dashed line represent three and one repeats of experimental results; the dashed-dot, solid, and solid-dot lines represent numerical model predictions with $H$ equal to 1, 3.18, and 5 W m$^{-2}$ K$^{-1}$, respectively, along the a) centerline and b) wall.

A.3 GAC Kinetic Analysis

A.3.1 TG/DTG/DSC Experiments

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) experiments (Figure A.7) were performed in a Simultaneous Thermal analyzer (NETZSCH STA 449 F3 Jupiter) under air and N$_2$ atmospheres from 30 to 900 °C at four different heating rates ($\beta = 5, 10, 15, 20$ °C/min) and a gas flow of 100 ml min$^{-1}$. A small sample mass ($5.55 \pm 3.5$ mg) was used to avoid thermal gradients in the sample. Under air, the TG data shows two steps in the mass loss (Figure A.7a) followed by two peaks in the DTG (Figure A.7c), which correspond to water evaporation and char oxidation, respectively. However, only one exothermic peak for the char oxidation is observed in the DSC (Figure A.7e). Complete fuel consumption was achieved at all heating rates, except for $\beta=5$ °C min$^{-1}$, which shows some residue (Figure A.7a). Under N$_2$, only one peak is observed in the DTG, which represents water evaporation (Figure A.7d). As found by other researchers, these TGA/DSC results indicate that GAC does not undergo significant pyrolysis reactions [3, 7].
Thus, a one-step oxidation mechanism was defined as the simplest mechanism for GAC combustion:

\[
\text{GAC} + \left( \frac{Fr_{co}}{2} + (1 - Fr_{co}) \right) O_2 \xrightarrow{R_{GAC}} Fr_{co} CO + (1 - Fr_{co}) CO_2
\]  

(A.5)

where \( Fr_{co} \) is the mole fraction of produced CO and is equal to 0.27, following previous experimental studies [9]. \( Fr_{co} \) strongly affects \( \Delta H_{GAC} \), e.g., as \( Fr_{co} \) decreases from 1 to 0, \( \Delta H_{GAC} \) increases from 110.5 to 393.5 kJ mol\(^{-1}\) [9]. While pure carbon with \( Fr_{co} = 0.27 \) results in \( \Delta H_{GAC} = 26.4 \text{ MJ kg}^{-1} \), this value was corrected for the 2.2% unreactive and 3.2% water content measured in the GAC (which lowered \( \Delta H_{GAC} \) by 1.5 MJ kg\(^{-1}\)); therefore, \( \Delta H_{GAC} = 24.9 \text{ MJ kg}^{-1} \) was used in the numerical model, agreeing with [9]. By considering the molar mass of GAC (12 kg kmol\(^{-1}\)), \( O_2 \) (32 kg kmol\(^{-1}\)), CO (28 kg kmol\(^{-1}\)), and CO\(_2\) (44 kg kmol\(^{-1}\)) Eq. (A.6) was converted to a mass fraction:

\[
\text{GAC} + v_{O_2} O_2 \xrightarrow{R_{GAC}} v_{co} CO + v_{co_2} CO_2
\]  

(A.6)

where \( v_{O_2} \), \( v_{co} \), \( v_{co_2} \) are the mass yields of oxygen (i.e., consumption of oxygen mass per mass of the GAC), carbon monoxide, and carbon dioxide and are equal to 2.304, 0.63, and 2.67, respectively. Eq. A.6 was used as the governing equation for GAC oxidation.
Figure A.7: (a, c, e) GAC Normalized TG, DTG, and DSC under air at four different heating rates; (b, d, f) GAC Normalized TG, DTG, and DSC under N₂ at three different heating rates.

**A.3.2 Inverse Modelling**

The kinetic parameters (log (A) and E) in the Arrhenius equation were determined by inverse modelling via a Genetic Algorithm (GA) optimization method and TG experiments.
[10]. A GA code was developed in MATLAB and used in this study with a population size of 100 and maximum generations of 300. The best solution was determined by maximizing the fitness function ($\phi$), which was defined as the inverse of the error between calculations (“calc”, i.e., the solution proposed by Arrhenius equation) and experimental measurement (“exp”, i.e., TG and DTG experiments), via considering all heating rates at the same time:

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

(A.7)

where $\dot{Y}$ and $Y$ represent normalized mass loss rate (DTG) and mass loss (TG) considering the effect of both at the same time. The constant $\gamma$ was equal to 100 to scale the relative impact on the fitness of the TG over the DTG. The algorithm stopped when $\phi$ reached its maximum value or limit number of generations. Figure A.8 shows the comparison of experimental TG and DTG with the predictions. Note that the differences between experiments and predictions are primarily because water evaporation was not captured by the one-step oxidation reaction (Eq. A.6).
Figure A.8: Genetic Algorithm (GA) optimization for a one-step oxidation reaction. Dashed line shows the experimental data for TG and DTG, and shaded region shows the prediction of Arrhenius equation using the range of optimized kinetic parameters (see Table 3.2).

Table A.1 shows the optimized range of log (A) (1/s) and E (kJ/mol) that fits all heating rates at the same time. Within this range, log (A)=3.79 (1/s) and E=72.9 kJ/mol were implemented in the numerical model.

Table A.1: Range of Optimized Value for log (A) (s\(^{-1}\)) and E (kJ mol\(^{-1}\)) for Heating Rate (\(\beta\))

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Rate ((\beta))</td>
<td>°C min(^{-1})</td>
<td>5-20</td>
</tr>
<tr>
<td>log (A)</td>
<td>(s(^{-1}))</td>
<td>3.21-3.80</td>
</tr>
<tr>
<td>E</td>
<td>kJ mol(^{-1})</td>
<td>72.90-80.18</td>
</tr>
</tbody>
</table>
A.4 Sensitivity Analysis

Figure A.9 represents a sensitivity analysis of GAC concentration and Darcy air flux on peak temperature ($T_p$) and smouldering front velocity ($\nu_f$). Figure A.9a shows that increasing GAC concentration from 0.01 to 0.05 increased $T_p$ from 255 to 1145 °C, respectively, because of the increased oxidation energy rate, agreeing with [11-14]. With low GAC concentration ($C_c < 0.01$), radial heat losses dominated over the oxidation energy rate, which resulted in a negative global net energy rate and global quenching. With a high GAC concentration ($0.04 \leq C_c \leq 0.05$), $\nu_f$ decreased from 0.54 to 0.50 cm/min, respectively, because, the increased GAC concentration shifted the process toward oxygen-limited conditions, i.e., all of the oxygen mass fraction ($Y_{O_2}$) was consumed by the smouldering front [14].

Figure A.9b shows that increasing the Darcy air flux from 0.01 to 0.09 m/s increased $\nu_f$ linearly from 0.13 to 0.84 cm/min, associated with increasing the convective heat transfer and oxygen mass flux to the reaction zone, agreeing with [11, 14-17]. By increasing $\nu_f$, the oxidation energy rate also increased, but $T_p$ reached a plateau (740 °C) at high Darcy air flux ($u_g > 0.07$ m/s). This result indicates that the released oxidation energy accumulated in the cooling zone length (which grew from 11 to 26 cm with applied air fluxes increasing from 0.01 to 0.09 m/s, respectively, at $Dt = 0.5$) and did not affect the peak temperatures.
Figure A.9: Sensitivity analysis on (a) GAC concentration (-), and (b) Darcy air flux (m/s).

A.5 Permeability Heterogeneity

Figure A.10 represents the computational domain with the inclusion of a second region perpendicular to the airflow direction (i.e., an outer concentric cylinder) that represents a separate porous medium with a different intrinsic permeability ($k_p$). $R_1$ and $R_2$ are 3.81 and 1.58 cm, respectively, which each provide the same cross-section area of $4.58 \times 10^{-3}$ m$^2$. A sensitivity analysis on the position of layers and the ratio of intrinsic permeabilities were performed to provide insight into the effects of permeability heterogeneity on smouldering system performance, e.g., peak temperature, smouldering velocity, front curvature, and global quenching.
Table A.2 shows a list of simulations with Regions 1 and 2 in different permeability heterogeneity scenarios. For simulations # 1-3, Region 1 represents coarse sand with high permeability and Region 2 represents fine sand with low permeability, and both contain a GAC concentration of 0.03. For simulations # 4-6, these conditions are reversed. $\dot{m}_{(1)}$ and $\dot{m}_{(2)}$ represent the air mass flow rate at $Dt = 0.5$ that passed through Regions 1 and 2, respectively.
Table A.2: Applied Smouldering Characteristics in Different Permeability Heterogeneity Scenarios

<table>
<thead>
<tr>
<th>Sim #</th>
<th>$u_g$</th>
<th>$C_c$</th>
<th>$k_p(1)$</th>
<th>$k_p(2)$</th>
<th>$k_p(1)/k_p(2)$</th>
<th>$T_p(1)$</th>
<th>$T_p(2)$</th>
<th>$\dot{m}_{(1)}$</th>
<th>$\dot{m}_{(2)}$</th>
<th>$v_f(1)$</th>
<th>$v_f(2)$</th>
<th>Self-Sustained Regi (1)</th>
<th>Regi (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>0.05</td>
<td>0.03</td>
<td>$1.4 \times 10^{-9}$</td>
<td>$1.4 \times 10^{-9}$</td>
<td>1</td>
<td>718</td>
<td>645</td>
<td>2.5</td>
<td>3.2</td>
<td>0.54</td>
<td>0.54</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.03</td>
<td>$1.4 \times 10^{-9}$</td>
<td>$7.0 \times 10^{-10}$</td>
<td>2</td>
<td>716</td>
<td>660</td>
<td>3.3</td>
<td>2.5</td>
<td>0.65</td>
<td>0.60</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.03</td>
<td>$1.4 \times 10^{-9}$</td>
<td>$1.4 \times 10^{-10}$</td>
<td>10</td>
<td>737</td>
<td>616</td>
<td>4.9</td>
<td>0.8</td>
<td>0.75</td>
<td>-</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>0.03</td>
<td>$1.4 \times 10^{-9}$</td>
<td>$1.4 \times 10^{-11}$</td>
<td>100</td>
<td>746</td>
<td>450</td>
<td>5.6</td>
<td>0.1</td>
<td>0.81</td>
<td>-</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.03</td>
<td>$7.0 \times 10^{-10}$</td>
<td>$1.4 \times 10^{-9}$</td>
<td>0.5</td>
<td>928</td>
<td>617</td>
<td>3.9</td>
<td>0.47</td>
<td>0.53</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>0.03</td>
<td>$1.4 \times 10^{-10}$</td>
<td>$1.4 \times 10^{-9}$</td>
<td>0.1</td>
<td>767</td>
<td>600</td>
<td>0.7</td>
<td>5.1</td>
<td>0.27</td>
<td>0.54</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>6</td>
<td>0.05</td>
<td>0.03</td>
<td>$1.4 \times 10^{-11}$</td>
<td>$1.4 \times 10^{-9}$</td>
<td>0.0</td>
<td>627</td>
<td>613</td>
<td>5.7</td>
<td>-</td>
<td>0.56</td>
<td>-</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

\[ \dot{m}_{(1)} = \int_{0}^{R(1)} (\rho_g u_g) 2\pi r dr \times 10^{-4} \text{ kg/s} \]

\[ \dot{m}_{(2)} = \int_{R(1)}^{R(2)} (\rho_g u_g) 2\pi r dr \times 10^{-4} \text{ kg/s} \]
A.6 References


Appendix B: Supplementary Material for Chapter 4, “Investigation of Applied Smouldering in Different Conditions: The Effects of Oxygen Mass Flux”

B.1 Heat of Oxidation (ΔH) and Radial Heat Transfer Coefficient (H) Sensitivity Analyses

The sensitivity of heat of oxidation (ΔH) on temperature evolution for smouldering 0.03 GAC concentration is presented in Figure B.1a where ΔH represents the amount of energy released by smouldering 1 kg of GAC. As ΔH is determined based on the enthalpy of the produced gases (e.g., CO, CO₂) during the smouldering process; therefore, it varies from centerline to wall, because of various smouldering robustness associated with radial heat loss. An average value was determined using sensitivity analysis for each smouldering with different oxygen mass fractions (Y₀₂). For Y₀₂=0.230 [-], by changing ΔH from 28 to 38 [MJ kg⁻¹], the best match to the experimental temperature history was achieved for ΔH = 32.9 [MJ kg⁻¹]. Note that the selected ΔH is in the range of experimental results of the heat of oxidation. Decreased ΔH under-predicts peak temperature and cooling zone temperature; however, high ΔH over-predicts the cooling zone temperature. In actuality, the ΔH may vary across the reactor space and time, but this sensitivity was not explored. Furthermore, constant ν₀₂ values were measured from each experiment and used in the simulations; however, this value could also vary throughout space and time. Ultimately, these chemistry variations are currently not well-understood in smouldering systems and warrant further study [1].

The sensitivity of the heat loss coefficient (H) on the temperature evolutions for smouldering 0.03 GAC concentrations is presented in Figure B.1b where H is a complicated parameter that determines the rate of radial heat loss between the column wall and ambient air, and includes the effect of insulation and dynamic convective currents outside the column [2]. The sensitivity analysis shows, while increasing H has negligible effects on the centerline peak temperatures, it decreases the temperatures in the cooling zone, as this zone is most sensitive to radial heat losses. Figure B.1b Shows H = 10 [W m⁻²] provides a good match under robust and weak conditions; therefore, it was selected for
all the simulations from robust fuel-limited to weak oxygen-limited conditions by decreasing oxygen mass transfer ($Y_{O_2}$).

Figure B.11: Various smouldering simulations with a concentration of 0.03 kg$_{GAC}$ kg$_{sand}$

$^{-1}$. The dot line represents experimental results; a. dashed, solid, and line with square represent numerical model predictions with a. $\Delta H$ equal to 28, 32.9, and 38 [MJ kg$^{-1}$], b. with $H$ equal to 20, 10, and 1 [W m$^{-2}$] respectively, along the centerline.

B.2 Oxygen Stoichiometric Coefficient

For determining the oxygen stoichiometric coefficient ($\nu_{O_2}$), a multi-gas analyzer (MGA-3000 Series, ADC) was performed at the top of the reactor to measure the emissions volume fraction (X) of oxygen (O$_2$), carbon monoxide (CO), and carbon dioxide (CO$_2$), continuously. The mass of O$_2$ consumed and CO, CO$_2$ produced are defined by Eq. B. 1-3.

$$m_{O_2-Consumed} = \int_{t_1}^{t_2} \rho_{O_2} \ u_g \ (X_{O_2-In} - X_{O_2-Out}) \ A \ dt \quad (B.1)$$

$$m_{CO-Produced} = \int_{t_1}^{t_2} \rho_{CO} \ u_g \ (X_{CO-Out}) \ A \ dt \quad (B.2)$$

$$m_{CO_2-Produced} = \int_{t_1}^{t_2} \rho_{CO_2} \ u_g \ (X_{CO_2-Out}) \ A \ dt \quad (B.3)$$
where $A$ is the surface of the reactor, $u_g$ is the inlet air velocity, $t_1$ and $t_2$ determine the initial and final time of measurement, and volume fraction of $O_2$, CO, and CO$_2$ defined by Eq. B. 4-6:

$$X_{O_2} = \frac{V_{O_2}}{V_{air}} \quad \text{(B.4)}$$

$$X_{CO} = \frac{V_{CO}}{V_{air}} \quad \text{(B.5)}$$

$$X_{CO_2} = \frac{V_{CO_2}}{V_{air}} \quad \text{(B.6)}$$

where $V$ determines the volume of gas. The column rested on a mass balance (KCC 150, Mettler Toledo) to provide real-time mass loss that determines the mass of the GAC that was consumed. Figure B.2 shows the experimental data for Exp ii, air (~20 vol. %) was diluted with nitrogen (N$_2$), resulting in an oxygen volume fraction ($X_{O_2}$) of 10 % (i.e., $Y_{O_2} = 0.115 \ [-]$) at smouldering ignition ($t = t_g$). Smouldering propagation was stabilized from 7980 s to 9720 s and gas emissions were measured during this time. The mass of GAC consumed was determined by the mass balance (Figure B.2c) and the results were used to determine the oxygen stoichiometric coefficient ($\nu_{O_2}$). The mass of $O_2$, and GAC consumed and CO and CO$_2$ produced for Exp i-iii are provided in Table B.1.
Figure B.12: (a) Temperature evolution of self-sustained smouldering propagation for Exp ii (dashed lines determine a time period of 7980 to 9720 s); (b) volume fraction of O₂, CO, and CO₂; (c) mass loss of the reactor.
The oxygen stoichiometric coefficient ($\nu_{O_2}$) and error associated to this calculation are defined by:

\[
\nu_{O_2} = \frac{m_{O_2-Consumed}}{m_{GAC-Consumed}} \quad (B.7)
\]

\[
Error = \frac{(m_{produced} - m_{consumed})}{m_{consumed}} \quad (B.8)
\]

The average error is 7.5 %, which indicates a good match of mass balance between reactants (i.e., GAC, and $O_2$) and products (i.e., CO and $CO_2$). Experimental measurements of CO and $CO_2$ show that by diluting the oxygen volume fraction, more complete combustion was achieved, increasing $CO_2/CO$ ratio. This behavior might be associated with i) different oxygen diffusion towards GAC surface due to oxygen dilution and ii) homogeneous reactions (e.g., between CO and $O_2$) in the thick reaction zone (e.g., Exp iii) after the first initial global reaction of GAC and $O_2$. Investigation of both of these hypotheses is beyond the scope of this paper.
B.3 Experimental Results

Figure B.3.a represents key experimental data where exiting mass fractions of oxygen ($Y_{O_2-out}$), carbon dioxide ($Y_{CO_2}$), and carbon monoxide ($Y_{CO}$), peak temperatures ($T_p$); front velocities of smouldering ($v_f$) and cooling ($v_c$) as a function of the inlet mass fraction of oxygen ($Y_{O_2-in}$); and also temperature evolutions are determined. Results show a range of robust fuel-limited where all the fuel was consumed to weak oxygen-limited where all the oxygen mass flux was consumed at the front and peripheral extinction appeared. A detailed discussion of the results can be found in Section 4.3.1.
Figure B.13: (a) Key experimental results from Exp. i-vi in Table B1. (a, f) show the average exiting mass fractions of oxygen ($Y_{O_2}$), carbon dioxide ($Y_{CO_2}$), and carbon monoxide ($Y_{CO}$) after smouldering; (b, c, d) and (g, h, i) show centerline temperature evolutions from Exps. i-vi. (e and j) show peak temperatures ($T_p$) and the front velocities of smouldering ($v_f$) and cooling ($v_c$) versus incoming $Y_{O_2}$ variations.
B.4 Energy Analysis

Further explanation on the multi-dimensional global energy analysis was provided in [2]. For Simulations # 1-3, the global net energy rate \( (dE_{\text{net}}/dt) \) was positive and energy \( (E_{\text{net}}) \) accumulated in the system. However, the oxidation energy rate \( (\dot{E}_{\text{oxi}}) \) was almost constant for Simulations #1 and 2, and it increased over time in Simulation # 3 where the smouldering was weak and oxygen-limited conditions. Simulation #3 also showed that, by increasing the length of the cooling zone, the smouldering front velocity increased \( (v_f) \) and the thickness of the unburnt crust \( (R^*) \) decreased. Simulation #4 was self-sustained and Simulation #5 was weakly self-sustained as the net energy rate \( (dE_{\text{net}}/dt) \) during propagation was almost zero. Simulation # 6 shows global quenching; even despite the long duration of time that the heater was turned on after starting the air \( (Dt = 0.56 [-]) \), the net global energy rate \( (dE_{\text{net}}/dt) \) became negative. Figure B.4 shows the global energy balance results from these simulations.
Figure B.14: Global energy balance analyses for Simulations #1 (circles), 2 (diamonds), 3 (+), 4 (triangles), 5 (x), 6 (stars). See Table 1 for additional details.

Figure B.5 compares local and global energy analyses of smouldering propagation in and weak oxygen-limited conditions at three different times where oxygen mass fraction ($Y_{O_2}$) = 0.115 and inlet air flux ($u_g$) was 0.05 and 0.01 m s$^{-1}$ (i.e., Simulations # 2, and 5, Table B.1). Figure B.5 shows a nearly constant $\dot{E}_{oxid}$ associated with a constant $v_f$. The local $\dot{E}_{loss}$ rates are negligible (Figure B.5a, and c); however, global $\dot{E}_{loss}$ rates are 15% and 30% of $\dot{E}_{oxid}$ at the initial ($D_t = 0.25$) and late times ($D_t = 0.75$), respectively. This result shows that, as the cooling zone grew, more surface area was exposed to losses and $\dot{E}_{loss}$ increased; therefore, the global $dE_{net}/dt$ decreased over time, which agrees with other previous analyses [3]. Over time, the local $\dot{E}_{in}$ from Simulation # 2 increased and was always larger than the local $\dot{E}_{out}$ (i.e., 22% and 27% at $D_t = 0.25$ and 0.75, respectively), which exemplified robust smouldering, where a fraction of the local $\dot{E}_{in}$ from the cooling...
zone accumulated in the reaction zone in these robust conditions. On the other hand, during weak smouldering (Figure B.5c), the local \( \dot{E}_{\text{in}} \) and \( \dot{E}_{\text{out}} \) nearly balanced, and local \( dE_{\text{net}}/dt \) was almost equal to the local \( \dot{E}_{\text{oxid}} \). Figure B.5d shows, during weak smouldering, the global \( \dot{E}_{\text{loss}} \) decreased over time as the global \( dE_{\text{net}}/dt \) was negative (i.e., energy depleted from the system), and the average temperatures also decreased. These results indicate smouldering robustness deteriorated over time as it transitioned towards global quenching. This behaviour is indicative of non-self-sustaining smouldering.

Figure B.15: Local and global energy rates for oxidation (\( \dot{E}_{\text{oxid}} \)), loss (\( \dot{E}_{\text{loss}} \)), inlet (\( \dot{E}_{\text{in}} \)), outlet (\( \dot{E}_{\text{out}} \)), and their net result (\( dE_{\text{net}}/dt \)) from (a) Simulation # 2 and (b) Simulation # 5 at three different times, \( Dt = 0.25, 0.50, \) and 0.75.

B.5 References


Appendix C: Supplementary Material for Chapter 5, “Delineating the Role of Fuel Mobility in Applied Smouldering Systems”

C1. TG/DTG Analysis of Canola Oil

Figure C1 shows experimental data of Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were performed to determine the chemical kinetics of canola oil. Experiments were performed in a Simultaneous Thermal Analyzer (NETZSCH STA 449 F3 Jupiter) under oxidizer (air) and inert (N_2) atmospheres from 20 to 700 °C at three different heating rates (β = 10, 20, 40 °C min\(^{-1}\)) and gas flow rates of 50 and 100 [ml min\(^{-1}\)], respectively. The data were used to determine the chemical reactions of canola oil smouldering, agreeing with [2]. A small mass of the sample (14.5 ± 3.363 mg) was performed to avoid thermal gradients in the sample. For the temperature range of 293.15 (20 °C) to 550 K (276.85 °C) under the air, and 293.15 (20 °C) to 638 K (364.85 °C) under N_2, TG data did not show a significant mass loss which confirms small quantities of both the water content and light hydrocarbons (see Figure C1.a and b), also DSC data under air and N_2 did not capture any significant heat rate absorbed during this temperature range except the energy that absorbed by the heat capacity of the canola oil under the air and N_2 (see Figure C1.e and f).

Under the air, TG data shows three steps in the mass loss (see Figure C1.a) followed by three peaks in the DTG data (see Figure C1.c) which corresponds to canola oil oxidation (at 716 K (442.85 °C)), canola oil pyrolysis to char (at 780 K (506.85 °C)) and char oxidation (at 850 K (576.85 °C)), respectively. Competition between canola oil oxidation and pyrolysis reactions occurs in TG under the oxidizer atmosphere (air) where canola oil pyrolysis to char is followed by char oxidation, therefore no mass remains behind.

Between 638 to 775 K (364.85 to 501.85 °C), TG data under N_2, confirms pyrolysis reactions under N_2 (i.e., a rapid mass loss) where all the mass was consumed at 775 K that shows canola oil pyrolyzed to volatile material where no hydrocarbon residue remained behind (see Figure C1.b).
Figure C1.d shows DTG under N\textsubscript{2} with one large and unique peak in the temperature of 688.15 K (415 °C), 703.15 K (430 °C), and 723.15 K (450 °C) for the heating rate of 10, 20, and 40 °C min\textsuperscript{-1} where DSC shows a representative endothermic behaviour in this temperature range (638-775 K (364.85 – 501.85 °C)) (see Figure C1. f). Two exothermic peaks for canola oil and char oxidation were observed in the DSC under air (Figure C1.e) where exothermic behaviour suggested that net heat released by canola oil and char oxidation was higher than the net heat absorbed by pyrolysis reactions. Complete fuel consumption was achieved at all heating rates under air and N\textsubscript{2} after 843 (569.85 °C) and 779 K (505.85 °C), respectively. The temperature in which these reactions were taking place may change depending on the heating rates (\(\beta\)). As smouldering took place in a high heating rate, a two-step global pyrolysis and oxidation mechanism was proposed as the simplest mechanism for canola oil smouldering, therefore, Eqs. C1, 2 define two-step kinetic mechanisms developed for canola oil smouldering based on TG, DTG, and DSC results presented in Figure C1.

\[
\text{Canola Oil} \overset{R_p}{\rightarrow} v_c \text{ Char} + (1 - v_c) \text{ Gas} \tag{C1}
\]

\[
\text{Char} + v_{O_2} O_2 \overset{R_c}{\rightarrow} \text{ Gas} \tag{C2}
\]

where \(v_c\) and \(v_{O_2}\) are the mass yields of char and O\textsubscript{2} are equal to 0.9 [kg char kg canola oil\textsuperscript{-1}] and 2.5 [kg O\textsubscript{2} kg char\textsuperscript{-1}] determined using sensitivity analysis of the numerical model. Competing reactions are not considered since their influence on the observed smouldering behaviour is expected to be minor.
Figure C.16: (a, c, e) Canola oil normalized TG, DTG, and DSC under air; (b, d, f) canola oil normalized TG, DTG, and DSC under N\textsubscript{2} at three different heating rates (\(\beta\)) of 10, 20 and 40 °C min\textsuperscript{-1}.

where reaction rates (\(R_p\) and \(R_c\)) are determined using first-order Arrhenius reactions.
\[ R_p = (A_p) \exp \left(-\frac{E_p}{R_g T_s}\right)(Y_{\text{Canola oil}}) \]  
\[ (C3) \]

\[ R_c = (A_c) \exp \left(-\frac{E_c}{R_g T_s}\right)(Y_{\text{Char}})(Y_{O_2}) \]  
\[ (C4) \]

The Arrhenius parameters \((A_i\) and \(E_i\)) for each reaction \((i)\) (presented in Table C1) obtained by using Kissinger method [3].

\[
- \frac{E}{R_g} = \frac{d \left( \ln \frac{\beta}{T_p^2} \right)}{d \left( \frac{1000}{T_p} \right)} \]  
\[ (C5) \]

\[
A = \frac{\beta E}{R T_p^2} \exp \left( \frac{E}{R T_p} \right) \]  
\[ (C6) \]

Figure C2 describes a plot of \(\ln(\beta T_p^{-2})\) versus \((1000 T_p^{-1})\) under N\(_2\) and air at different heating rates \((\beta)\) where \(T_p\) represents the temperature at which the reaction rate for each reaction in the DTG curve is maximum. \(E_i\) was calculated using the slope of linear fit for three experimental points.
Figure C.17: correlation between heating rate ($\beta$) and peak temperature ($T_p$) for pyrolysis under $N_2$ and oxidation under air.

Table C.1 provides value for $A_p$, $A_c$ and $E_p$, and $E_c$, also heat of the reactions ($\Delta H$) for pyrolysis and oxidation were determined using the sensitivity analysis of the numerical model.
Table C.4: Shows $A_t$, $E_t$, and $\Delta H_t$ for Pyrolysis and Oxidation

<table>
<thead>
<tr>
<th>Pyrolysis (N₂)</th>
<th>Oxidation (Air)</th>
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</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>$T_p$ [K]</td>
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<tr>
<td>10</td>
<td>688.15</td>
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<tr>
<td>20</td>
<td>703.15</td>
</tr>
<tr>
<td>40</td>
<td>723.15</td>
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</table>

C2. Comparison of Smouldering Propagation for Canola Oil with VI Improver and Pure VI Improver

Figure C.3a, b. show a comparison of temperature distribution for smouldering propagation with canola oil with VI improver (i.e., $\mu_w = 1.32$ Pa s at ambient temperature that represents mobility in the preheating zone) and pure VI improver (i.e., $\mu_w = 31.04$ Pa s at ambient temperature that represents no mobility) at two different Darcy air fluxes of 0.025 and 0.062 m s$^{-1}$.

An almost uniform temperature distribution was achieved, however peak temperature ($T_p$) increased slightly by increasing viscosity, associated with higher fuel deposition in the reaction zone, therefore mobility in the preheating zone did not affect the temperature distribution in the reactor, however, it caused a huge difference in the saturation distribution, especially in the preheating zone.
Figure C.18: (a, b) Temperature evolution of smouldering propagation with canola oil: VI improver (solid line) and pure VI improver (dot line) in comparison to experimental results (dashed line) with canola oil: VI improver, c. comparison of peak temperature ($T_p$) and smouldering front velocity ($v_f$).

C3. Energy Analysis

Figure C4 shows global energy analysis which confirms the progress of smouldering in a self-sustaining manner as energy accumulated in the system due to a positive net energy rate, agreeing with [1]. During the preheating time ($Dt < 0$), the energy left the system by radial heat losses ($\dot{E}_{\text{loss}}$) and pyrolysis ($\dot{E}_{\text{pyrolysis}}$) where 8.3% of canola oil weight leaked below the heater and pyrolyzed to char before initiating the air injection.

The energy rate entering the system through the heater ($\dot{E}_{\text{in}}$) was higher than the energy rate leaving the system by radial heat losses ($\dot{E}_{\text{loss}}$) and consumed by pyrolysis ($\dot{E}_{\text{pyrolysis}}$), therefore net energy rate ($\dot{E}_{\text{net}}$) was positive during this period of time and net energy ($E_{\text{net}}$) was accumulated in the reactor. At $Dt = 0$, by injecting the air, the oxidation energy rate was fully activated and peaked at 2 kJ s$^{-1}$, as the produced char at a high temperature (770 °C) was oxidized and the heater was turned on, however by turning off the heater (i.e., $\dot{E}_{\text{in}} = 0$ kJ s$^{-1}$) at $Dt = 0.06$, Oxidation energy rate dropped to 1.07 kJ s$^{-1}$ and remained nearly constant until $Dt = 1$.

For the time duration of $Dt > 1$, the oxidation energy rate ($\dot{E}_{\text{oxidation}}$) peaked again, because of accelerating the smouldering front velocity associated with end effects, and then at $Dt = 1.15$ it turned to 0 kJ s$^{-1}$, as all of the canola oil was consumed by the front. Radial heat losses ($\dot{E}_{\text{loss}}$) increased over time ($-0.93 < Dt < 1.15$) because of increasing the length
of the cooling zone and peripheral surface area for radial heat losses by progressing the smouldering front. The energy leaving the system through the hot gas at the top of the reactor ($\dot{E}_{\text{out}}$) was negligible for $Dt < 1.15$, however, it maximized at $Dt = 2.5$ when the hot air reached the top of the reactor. Pyrolysis energy rate ($\dot{E}_{\text{pyrolysis}}$) was initiated by starting the heater ($\dot{E}_{\text{in}}$) and peaked by injecting the air at $Dt = 0.06$ as high oxidation energy was released in a short duration of time, and then it dropped to $0.25 \text{ kJ s}^{-1}$ for the time duration of $0.06 < Dt < 1.00$, and then at $Dt = 1.15$, pyrolysis energy rate turned to zero as the canola oil in the reactor was fully consumed. The numerical error associated with spatial and temporal discretization was calculated via the global energy balance was $9\%$.

Figure C.19: (a) energy rates for inlet, outlet, loss, oxidation, and pyrolysis, (b) net cumulative energy and net energy rate.

C4. Sensitivity analysis on Displacement Pressure ($P_d$)

Figure C.20a and b clarify the effects of $P_d$ on $T_w$ and $S_w$ distribution in the reactor. $P_d = 200 \text{ [Pa]}$ represents the base case simulation, while a lower $P_d = 100 \text{ [Pa]}$ represents a higher diameter of the pore space (i.e., course sand), and a higher $P_d = 400 \text{ [Pa]}$ represents a lower diameter of the pore space (i.e., fine sand). By decreasing $P_d$ to 100 [Pa], downward fuel mobilization in high viscous force was limited therefore lower fuel saturation ($S_w = 0.19$) was concentrated in the reaction zone when compared to the base
case Simulation #1 ($S_w = 0.23$), which caused lower $T_p = 546$ °C, and slower $\nu_f = 0.32$ cm min$^{-1}$ with $\Delta Y_{O_2} = 0.09$. By increasing $P_d$ to 400 [Pa], fuel toughly migrated through the porous medium, which resulted in more fuel concentrated in the reaction zone (i.e., $S_w = 0.25$). Therefore, $T_p$ and $\nu_f$ increase to 600 °C and 0.40 cm min$^{-1}$, respectively, relative to the base case ($T_p = 570$ °C and $\nu_f = 0.37$ cm min$^{-1}$).

![Figure C.20](image)

Figure C.20: (a) Temperature distribution, (b) saturation and oxygen mass fraction distribution.

C5. References


Curriculum Vitae

Name: Seyed Ziaedin Miry

Post-secondary Education and Degrees:

Islamic Azad University – Central Tehran Branch
Tehran, Iran
2006-2010 B.Sc.

University of Tehran
Tehran, Iran
2011-2014 M.Sc.

The University of Western Ontario
London, Ontario, Canada
2019-2023 Ph.D.

Related Work Experience:

Teaching Assistant
The University of Western Ontario
2019-2023

Research Assistant
The University of Western Ontario
2019-2023

Publications:
