THE SPONTANEOUS COMBUSTION OF RAILWAY TIES AND ASPHALT SHINGLES

by

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Abstract

Many Low Carbon Fuels (LCFs) present unknown spontaneous combustion risks, which must be quantified before their use as fossil fuel replacements. Wood and coal spontaneous combustion is well understood; however, LCFs weather, and subsequent chemical changes could affect their spontaneous combustion properties. LCF spontaneous combustion could lead to accidental fires with possible loss of life, limb and property. The spontaneous combustion risks of two LCFs, discarded creosote-treated wooden railway ties and roofing asphalt shingles, were investigated with calorimetry and heat transfer experiments. Chemical changes due to weathering were studied with pyrolysis-Gas Chromatography/Mass Spectrometry (py-GC/MS).

Creosote-treated wooden railway tie dust, roofing asphalt shingle particles, poplar wood pellets, and petroleum coke self-heating were studied with isothermal calorimetry. Railway tie dust and asphalt shingle heat transfer were characterized with a guarded hot plate. Petroleum coke self-heating was consistent with coal, while both poplar pellets and railway tie dust were found to be more reactive compared to oven test results of similar materials. The observed increase in reactivity was probably a result of significant moisture content in the pellet and railway tie dust. Critical conditions for spontaneous combustion were evaluated with the Frank-Kamenetskii parameter, assuming an ambient temperature of 40°C and constant moisture content.
Kamenetskii calculations indicate that a 1.6 m cube of railway tie dust, or a 58 m cube of asphalt particles, would be unstable and combust.

LCF chemistry may have been affected by weathering, which would cause chemical changes that affect their spontaneous combustion properties. Therefore, railway tie wood and roofing asphalt shingle chemistry were investigated by identifying products of 250° and 550°C pyrolysis with py-GC/MS. Railway tie wood pyrolyzates did not show signs of weathering; in contrast, asphalt pyrolysis produced sulfur dioxide and many oxygenated species, which indicated that the asphalt was extensively oxidized.

Calorimetry showed that self-heating was primarily oxidative — the oxygen content of asphalt probably reduced its self-heating capacity. The railway tie wood was not extensively oxidized and it self-heated in a similar manner to “fresh” wood.
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Nomenclature

**Acronyms**

FKP  Frank-Kamenetskii parameter
LCF  low carbon fuel
HDPE high-density polyethylene
py-GC/MS  pyrolysis-gas chromatography/mass spectrometry
TG-FTIR  thermogravimetric-fourier transform infrared spectroscopy
TG-MS  thermogravimetric-mass spectroscopy

**Dimensionless Numbers**

δ, δ_C  Frank-Kamenetskii parameter and critical Frank-Kamenetskii parameter
Θ  dimensionless temperature
ξ  dimensionless diffusion constant
z  dimensionless distance
Bi  Biot number
Raf  filtration Rayleigh number

**Latin Symbols**

a  area [m²].
A  Arrhenius kinetic pre-factor [s⁻¹]
c_p  heat capacity [J/g·K]
k  rate of reaction [s⁻¹]
d  particle size [in or µm]

x
\( E/R \)  
activation energy [K]

\( h \)  
heat transfer coefficient [W/m\(^2\)-K]

\( L \)  
guarded hot plate sample thickness [m]

\( m \)  
mass [g]

\( M \)  
molecular mass [u]

\( MC \)  
moisture content [wt% of dry mass]

\( M/z \)  
mass-to-charge ratio [u/e]

\( q \)  
volumetric heat generation [W/m\(^3\)]

\( q_m \)  
mass-based heat generation [mW/g]

\( q_0 \)  
onset heat generation [mW/g]

\( \dot{q} \)  
calorimetric heat generation [\( \mu \text{W} \)]

\( \bar{q} \)  
heat flux [W/m\(^2\)]

\( \bar{q}' \)  
heat flux per unit length [W/m]

\( \bar{q} \)  
heat flow [W]

\( \bar{q}_P \)  
heater plate power [W]

\( \bar{q}_S \)  
stray heat flows [W]

\( Q \)  
heat of reaction [J/g]

\( r, r_C \)  
radius or side length, and critical radius or side length [m]

\( R \)  
contact resistance [K-m\(^2\)/W]

\( t \)  
time [s, min or ks]

\( T_0 \)  
maximum temperature in a self-heating volume [K]

\( T_A, T_C \)  
ambient and critical ambient temperature [°C]

\( T_{CP} \)  
cold plate temperature [°C]

\( T_{HP} \)  
guard and heater assembly ("hot plate") temperature [°C]
$T_S$ surface temperature of a self-heating volume [K]

$V_{DTC}$ differential thermocouple output [mV]

$x$ distance/position [m]

$X, Y, Z$ lumped Frank-Kamenetskii parameters \([1/m^2, K^2/m^2, K]\)

**Greek Symbols**

$\alpha$ thermal diffusivity \([m^2/s]\)

$\beta$ volumetric thermal expansion coefficient \([m^3/K]\)

$\gamma$ Euler’s constant [no unit]

$\Delta T$ temperature difference [K]

$\kappa$ permeability [m$^2$]

$\lambda$ thermal conductivity, or effective thermal conductivity \([W/(m-K)]\)

$\nu$ kinematic viscosity \([m^2/s]\)

$\rho$ density or bulk density \([g/m^3]\)

$\sigma_y$ error in $y$ [same unit as $y$]

$\phi$ porosity [no unit]
Chapter 1

Introduction

Low Carbon Fuels (LCFs) decrease carbon emissions when burned as a coal or pet-coke replacement. The North American cement industry provides a particularly good opportunity for fossil fuel substitution. Some European cement producers have achieved a 65% fuel replacement, while Canada has replaced only 11% [1]. Lafarge, Canada intends to co-fire LCFs, coal and petroleum coke (pet-coke) at their Bath, Ontario cement plant, and thus decrease their carbon footprint. Large quantities of LCFs will therefore be stored on-site — LCF spontaneous combustion risks should therefore be quantified.

Spontaneous combustion occurs when self-heating processes in a stored fuel exceed heat dissipation to the storage environment [2]. This results in increased internal temperatures, and eventually fuel ignition. Spontaneous combustion therefore depends on fuel self-heating, heat transfer, and ambient conditions. LCFs will likely self-heat, and thus they present unknown spontaneous combustion risks.

A fuel is considered to be an LCF if it provides an environmentally sound coal alternative, is socially responsible, and is economically viable [3]. Lafarge has concluded that waste creosote-treated wooden railway ties and discarded asphalt roofing
1.1. OBJECTIVE

shingles satisfy all three criteria. Waste ties and shingles have substantial chemical differences from materials considered in other spontaneous combustion studies (*e.g.* coal or wood chips). In particular, they will have weathered while in use. Chemical changes that result from weathering may in turn affect self-heating, and thereby affect spontaneous combustion.

Lafarge, Canada intends to store LCFs on-site at their Bath facility, in walking floor bins with a capacity of 80 tonnes. The bins are comparatively small — for instance, wood pellet silos may have a capacity of 4500 tonnes [4]. Nonetheless, Lafarge’s bins are sufficiently large to present spontaneous combustion risks. Better understanding LCF spontaneous combustion will facilitate their use, both by Lafarge and in other industries.

1.1 Objective

This thesis has two objectives:

1. Quantify LCF spontaneous combustion risks

2. Analyze LCF chemistry

As discussed above, Lafarge, Canada intends to store LCFs at their Bath facility, in walking floor bins (50’ × 17’ × 20’ (15 m × 5 m × 6 m), length by width by height). Quantifying tie and shingle spontaneous combustion risks will minimize fuel handling hazards. Simultaneously analyzing their chemistry will reveal how these fuels have weathered, and also how spontaneous combustion risks are affected by weathering.
1.2 Organization

This thesis is written in manuscript style. Chapter 2 presents a review of commonly cited spontaneous combustion and fuel chemistry literature. Chapters 3 and 4 are research articles, and both include a topic-specific literature review.

Chapter 3 examines LCF spontaneous combustion risks, and has been accepted for publication in *The Journal of Loss Prevention in the Process Industries*. Two experiments were conducted: the self-heating of railway tie dust, asphalt shingle particles, poplar pellets and petroleum coke were measured using an isothermal calorimeter, and the heat transfer of railway tie dust and asphalt particles were characterized with a guarded hot plate. Spontaneous combustion risks were then evaluated with the Frank-Kamenetskii parameter and these data. Appendix A discusses the design, construction and validation of the guarded hot plate used in this chapter to measure thermal conductivity. Similarly, Appendix B discusses the calorimetric system used to measure self-heating.

Chapter 4 presents an analysis of LCF chemistry, which will be submitted for publication in *Bioresource Technology*. The chemistry of railway tie wood, asphalt shingle particles and hybrid poplar was studied with pyrolysis-Gas Chromatography/Mass Spectrometry (py-GC/MS). Py-GC/MS heats a sample to the point of pyrolysis, and then identifies pyrolysis products or pyrolyzates with GC/MS. Sample pyrolyzates were examined for signs of degradation or oxidation, *i.e.* weathering.

The concluding chapter summarizes the findings of Chapters 3 and 4 in order to answer the research objectives defined above. Chapter 5 also discusses some of the questions raised by this research.
Chapter 2

Common Literature Review

This chapter presents a review of the science of spontaneous combustion, fuel chemistry and a method of studying fuel chemistry. Spontaneous combustion risks are material specific, and depend on self-heating and heat transfer behaviour, as well as the storage system and ambient conditions. Materials self-heat at low temperatures; if this heat is not dissipated, the temperature of the storage interior will rise. As both heat dissipation and self-heating increase with temperature, the material may either reach a steady state below self-ignition temperatures where self-heating equals heat dissipation, or self-heating may lead to combustion. Section 2.1 summarizes the fundamental self-heating and heat and mass transfer processes that cause spontaneous combustion. Section 2.2 presents a theory, the Frank-Kamenetskii theory, that considers many of these processes as well as ambient conditions. Section 2.2 further presents experimental methods based on the Frank-Kamenetskii theory and discusses numerical spontaneous combustion models. Finally, as self-heating depends on fuel chemistry, Section 2.3 summarizes the chemistry, structure and self-heating of creosote-treated railway tie wood and roofing asphalt. Pyrolysis-gas chromatography/mass spectrometry — a method of studying the chemistry of non-volatile solids
2.1. SPONTANEOUS COMBUSTION PROCESSES

— is also discussed in Section 2.3.

2.1 Spontaneous Combustion Processes

As noted above, spontaneous combustion depends on several interdependent processes, namely, self-heating, heat transfer and mass transfer; they are discussed in this section. Section 2.1.1 discusses the chemical, biological, and physical processes that generate heat at low temperatures (0°-200°C). Section 2.1.2 discusses heat and mass transfer, and some of the material properties which affect transfer processes.

2.1.1 Self-Heating

There are many self-heating processes, which can be broadly classified as chemical, biological or physical [5]. Chemical self-heating includes gas-solid reactions such as oxidation or hydrolysis. The cellular metabolism of microbes or living cells within biomass cause biological heating. Finally, effects related to moisture transport (e.g. condensation) generate heat, and are classified as physical heating mechanisms.

Chemical Heating — Oxidation and Hydrolysis

Fuels such as coal [6], wood [7, 8], and hay [9] oxidize at low temperatures, and polymers — particularly cellulose and hemicellulose — react with water, in a reaction known as hydrolysis [10]. Both of these reactions generate heat.

Coal oxidation demonstrates low-temperature oxidation. Specific reaction pathways are not entirely understood. Global reaction studies indicate that coal oxidizes by either “direct burnoff” or sorption reactions [6]. Burn-off reactions appear similar to combustion, in that they obey first-order Arrhenius kinetics and produce carbon
2.1. SPONTANEOUS COMBUSTION PROCESSES

\[
\begin{align*}
RH + M & \rightarrow R \cdot + H \cdot + M \\
R \cdot + O_2 & \rightarrow ROO \cdot + M \\
ROO \cdot + HR' & \rightarrow ROOH + R' \\
ROOH & \rightarrow RO \cdot + OH \\
ROOH + \cdot R' & \rightarrow ROR' + \cdot OH \\
RH + \cdot OH & \rightarrow R \cdot + H_2O \\
RO \cdot + \cdot R' & \rightarrow ROR' \\
R \cdot + \cdot OH & \rightarrow ROH \\
R \cdot + \cdot R' & \rightarrow RR'
\end{align*}
\]

Figure 2.1: Coal-oxygen chemadsorption mechanism. Adapted from [12] In this mechanism, \( R \) and \( R' \) represent two hydrocarbons, and \( M \) represents an unspecified, unconsumed extra body (e.g. \( H_2O \) or \( O_2 \)).

dioxide. In contrast, sorption is a complex, multi-step process [11, 12]: first, oxygen is chemadsorbed to active sites on the coal surface or within a coal pore, and forms an unstable oxygenated complex. Next, this oxygenated complex decomposes, and produces stable solids and gaseous species. Finally, the solid remnant decomposes and produces a new active site (Figure 2.1). The sorption mechanism is not completely understood, and alternative and supplementary reactions have been suggested; its gross effect is to produce heat, carbon dioxide, carbon monoxide, and water [13].

The oxidation rate, and thus oxidative heat generation, depends on the surface density of active sites, the mass transport of oxygen to a reactive particle (and therefore, local oxygen concentration), and then mass transport to an active site on the particle surface [14]. Generally, smaller particles of compact materials have larger surface areas compared to similar masses or volumes of larger particles. Smaller particles therefore have more available active sites and will oxidize faster. Porous materials — particularly coal — have a large surface area, somewhat independent of their particle size [6]. In that case, over certain particle size ranges, oxidation kinetics may depend more on porous oxygen transport than particle size.
Oxidation also depends on moisture content — volumetric experiments show that the rate of oxygen sorption increases with water content [15] and calorimetric experiments show that coal self-heating is maximized at 5-10 wt% moisture content [16]. The mechanism by which moisture content affects self-heating is poorly understood. Some authors have suggested that water catalyzes or activates oxidation, implying a link between oxidation activation energies and moisture content [17, 18]. However, Nordon et al. [19] observed that the activation energy of coal oxidation was not affected by moisture content. Instead, moisture content increased either the heat of oxidation or oxidation pre-factor.

Water may also react with polymers such as cellulose through hydrolysis, a depolymerization reaction [20]:

$$ROR' + H_2O \rightarrow ROH + HOR'$$

Hydrolysis occurs at high temperatures, or with acid catalysts [21]. Studies have shown that hydrolysis also occurs in biomass at low temperatures. For instance, wet cotton generates more heat than dry cotton [22], and sugarcane bargasse self-heating increases rapidly after wetting; this increase is not related to oxidation or biological processes [10, 23].

Some self-reactive materials undergo exothermic decomposition without exposure to air or water. For instance, asphalt-salt mixtures have ignited after several hours in sealed storage [24]. However, carbonaceous fuels are not likely to be self-reactive, and therefore such processes will not be discussed in detail in this thesis.
2.1. SPONTANEOUS COMBUSTION PROCESSES

Biological Activity

Biological processes in living cells produce heat [9, 25]. Fuels may contain living cells, either because cells in biomass fuels may survive for a short period following harvest [26], or because the fuel is susceptible to bacterial and fungal degradation. In some materials — for example, compost or refuse derived fuels — biological processes generate more heat than chemical or physical processes [27, 28]. Biological activity may also sufficiently raise interior temperatures as to lead to runaway oxidation and spontaneous combustion [29].

Wood and other cellulosic biomass are digested by several types of micro-organism. For instance, blue-stain, mold and soft-rot fungi act on minor wood components, whereas cellulose, hemicellulose and lignin are digested by “brown rot” and “white rot” fungi [30]. Aerobic organisms tend to have more efficient digestion and therefore generate more heat than anaerobic organisms and cause comparatively larger spontaneous combustion risks [31, 32].

The Frank-Kamenetskii theory, as will be discussed in Section 2.2, assumes that self-heating obeys a first-order Arrhenius equation, i.e. the theory considers chemical self-heating. There have been efforts to develop similar theories for biological heating. As bacteria are most active between 20° and 70°C (bacterial metabolisms shut down above 70°C), bacterial heating models include a temperature-related extinction factor. For instance, Nelson et al. [27] developed a spontaneous combustion theory that exclusively considers biological heating. They assumed that digestion rates followed an activation/deactivation law,
2.1. SPONTANEOUS COMBUSTION PROCESSES

\[ k(T) = \frac{A_1 \exp \left( \frac{-E_1}{T} \right)}{1 + A_2 \exp \left( \frac{-E_2}{T} \right)} \]  (2.1)

where \( E_1 \) is an activation energy, \( E_2 \) is a de-activation energy (\( E_2 > E_1 \)) and \( A_1 \) and \( A_2 \) are kinetic pre-factors. Similar digestion rate equations have been used in numerical studies of compost self-heating [33]. Tremier et al. [34] developed a more sophisticated model that considered available oxygen and biomass digestibility. Tremier et al.’s model has been used in numerical studies of wood chip self-heating [5].

Biological heating is typically most active in the first days or weeks of storage. During that period, the interior temperature of the stored biomass increases to 60°-70°C; if this temperature increase does not lead to spontaneous combustion, the biomass temperature remains stable and eventually drops as a result of drying [35]. As will be discussed in Section 2.1.2, high internal temperatures causes fuels to dry. As microbial digestion cannot proceed without moisture [36] — for instance, wood does not rot if \( MC < 20\% \) [37] — fuel drying prevents further biological heating.

Physical Effects

The physical processes of condensation and water sorption, or wetting, releases heat as water undergoes a phase change or is bound to a fuel surface [38, 39]. Condensation occurs when moist air cools — condensation is important in cooler regions of a self-heating volume. Sorption is a result of intermolecular forces or chemical bonds binding water to a solid surface, and continues until surface moisture content reaches thermodynamic equilibrium with its surroundings [40]. Wetting therefore occurs at high temperatures — hot (90°C) oven-dried fibreboard has ignited as a result of moisture sorbing to bone-dry wood fibres [41].
2.1. SPONTANEOUS COMBUSTION PROCESSES

Conversely, evaporation and desorption increase heat dissipation, as both processes absorb heat as water enters a gas phase. Self-heating causes raised internal temperatures, which in turn cause local evaporation or desorption. Gas-phase water may then be transported to either cooler areas of a fuel store, or to the fuel environment. The net effect increases heat transfer away from hot spots, and may lead to an ignition delay as fuel dries [42]. If self-heating continues after the material has dried, however, internal temperatures will subsequently increase and spontaneous combustion may occur [43].

2.1.2 Heat and Mass Transfer

As discussed above, spontaneous combustion occurs when heat generation within a stored material exceeds heat dissipation to the environment. Heat dissipation is affected by both fuel heat transfer properties and ambient conditions, especially wind and temperature. Many self-heating processes depend on mass transfer (e.g. oxidation). Mass transfer depends on ambient conditions, fuel permeability, and temperature gradients within a fuel store.

As many fuels are stored after grinding, mass and heat transfer may be diffusive, conductive or convective. Conduction and diffusion follow either Fourier’s or Fick’s law, respectively. Conduction in granular materials is affected by many factors, and may be measured by either steady- or unsteady-state techniques. Diffusion is affected by similar factors as conduction [44].
Conduction

Thermal conductivity is an empirically defined material property. Fourier’s law posits that heat flux follows and is proportional to a negative temperature gradient:

\[ \bar{q} = -\lambda \nabla T \]  

(2.2)

Thermal conductivity depends on temperature and moisture content [45]; the thermal conductivity of a granular bulk further depends on porosity, particle-to-particle contact resistances and contact area, free water (i.e. droplets) and particle size. As the effective thermal conductivity of granular media depends on many factors, it is difficult to predict [46]. This section discusses the above-mentioned factors.

Porosity decreases thermal conductivity, as interstitial voids are often filled with a thermally insulative fluid (e.g. air). The conductivity of both the interstitial substance and solid fraction establish a theoretical conductivity maximum. If contact resistances are neglected, and all heat transfer occurs in parallel between solid and void fractions (Figure 2.2), then conductivity is given by

\[ \lambda_{\text{max}} = (1 - \phi) \lambda_S + \phi \lambda_V \]  

(2.3)

where \( \phi \) is porosity, \( \lambda_S \) is the conductivity of the solid, and \( \lambda_V \) is the conductivity of the interstitial substance [46]. However, heat transfer in granular materials rarely meets the assumptions of eqn. 2.3, and eqn. 2.3 drastically overestimates the conductivity of most materials.

At a microscopic level, all surfaces are rough; the mechanical contact of two surfaces results in point contacts and fluid-filled gaps distributed across the apparent
contact area. Heat flow across these gaps results in a temperature discontinuity or contact resistance:

\[ R = \frac{T_1 - T_2}{\tilde{q}} \]  

(2.4)

where \( T_1 \) and \( T_2 \) are the temperatures of the two surfaces, \( \tilde{q} \) is the heat flux, and \( R \) is the contact resistance. \( R \) depends on surface roughness, elasticity, contact pressure and the conductivity of the interstitial fluid [47].

In granular materials, particle-to-particle heat flows are affected by contact resistances [48] as well as apparent contact area [49]; granular materials with high contact resistances and small contact areas have low thermal conductivity. However, the impacts of contact resistance and contact area are mitigated by water droplets. Droplets may fill interstitial voids in mechanical contacts (\( \lambda_{\text{water}} \gg \lambda_{\text{air}} \)), and also form bridges around contacts and increase contact area [50].

Particle size also affects conductivity, though its impact is material-dependent. Masamune and Smith [51] and Tavman [46] observed that the thermal conductivity of glass beads and sand, respectively, increased with particle size. In contrast, Ahn et al. [52] found that the thermal conductivity of ground organic materials (e.g. wood) decreased with particle size. Gertrude [53] made similar observations investigating the conductivity of ground organic materials available in Uganda. This discrepancy is probably due to contact resistances — organic materials are softer than sand or
It should be noted that the above discussion presupposes the effective medium assumption, e.g. that conductive volumes act as continua. A bulk particulate volume acts as an effective continuum if the length scale of the volume is sufficiently large to average microscopic inhomogeneities, and the volumes do not exhibit macroscopic inhomogeneities [54]. Over sufficiently large length scales, randomly packed particulate volumes exhibit constant and isotropic thermal conductivity, though shear stresses can introduce significant anisotropies [55]. As fuel stores are unlikely to undergo strong shear stresses, spontaneous combustion studies often presuppose the effective medium assumption [5, 56, 57]. Nonetheless, experiments that measure the thermal conductivity of granular materials must establish large enough length scales to create an effective continuum.

**Conductivity Measurement**

Thermal conductivity in granular media depends on many factors, and models are frequently inaccurate by an order of magnitude or more [48]. Measurement is therefore essential. Thermal conductivity may be measured by steady- or unsteady-state techniques. This section reviews two commonly used measurement techniques, though there are many other methods.

Guarded hot plates measure one-dimensional steady-state conduction. Thermal conductivity is defined by

\[
\tilde{q} = -\lambda \frac{dT}{dx}
\]  

(2.5)

where \( \tilde{q} \) is heat flux, \( \lambda \) is thermal conductivity (or, in granular media, the bulk
2.1. SPONTANEOUS COMBUSTION PROCESSES

thermal conductivity), and $\frac{dT}{dx}$ is the temperature gradient [58]. A guarded hot plate establishes a one-dimensional temperature gradient through a wide, flat sample, and measures the heat flux required to maintain that temperature gradient [59].

The guarded hot plate (Figure 2.3) consists of several layers. The cold plate (outer layer) is controlled by a resistive heater or thermal fluid — it is held to a constant cold temperature, $T_{CP}$. The guard and heater plates (middle layer) are isothermal, and heated by separate resistive elements to a hot temperature, $T_{HP}$. As the two plates are isothermal, no stray heat flows can occur between the heater and the guard. The width of the sample layer ensures that no lateral heat flows occur between the heater and cold plates [60]. Therefore, all of the heat from the heater plate flows directly across the sample into the cold plate, i.e. the heat flow is effectively lossless and the temperature profile is one-dimensional.

Figure 2.3: Guarded Hot Plate schematic. The sample layers (diagonal fill) sit between the guard plate (gray), heater plate (dark gray) and cold plates (white). The guard and heater plates are separately heated by resistive heaters, and are controlled such that they are isothermal. The guard minimizes stray heat flow from the heater (dashed arrows) as well as lateral heat flows in the sample (solid arrows).

The heat flux through the sample may then be found from the heater plate power.
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and area, while the temperature gradient may be found from the thickness of the sample layer \((L)\) and the cold and hot temperatures:

\[
\lambda = \frac{L}{\tilde{q} T_{HP} - T_{CP}}
\]  

(2.6)

The transient hot-wire method measures thermal conductivity by measuring the change in temperature of a heating element — it is an unsteady technique. A hot-wire apparatus holds a test sample in a cylindrical shell, the axis of which is an electrically powered wire heater (Figure 2.4). A thermocouple or some other sensor establishes the temperature of the wire. The system is initially isothermal; a DC voltage is applied to the central heater, and as the wire increases in temperature, heat flows into the sample. Thermal conductivity may then be calculated from the wire temperature change,

\[
\Delta T(r, t) = \frac{\tilde{q}'}{4\pi\lambda} \ln \frac{4\alpha t}{r^2\gamma}
\]  

(2.7)

where \(\tilde{q}'\) is the heat flux per unit length, \(r\) is the radius of the wire, \(t\) is time, \(\gamma\) is Euler’s constant, \(\alpha\) is the thermal diffusivity, and \(\lambda\) is thermal conductivity [61].

The hot-wire method is often inappropriate for measuring the conductivity of granular materials. Beds of granular materials have constant thermal conductivity [57]; however, hot-wire thermal conductivity tests of large granular materials require a more extensive mathematical treatment than that described by eqn. 2.7 [62]. Further, conductivity may be inhomogeneous in transient conditions [63]. Guo et al. nonetheless measured the thermal conductivity of wood pellets using a modified hot-wire device [56] — their apparatus used multiple temperature sensors, and
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they calculated thermal conductivity by comparing measured temperature profiles to numerical solutions of the time-varying heat equation.

Convection and Mass Transfer

Convective flows occur in permeable self-heating materials. These flows increase heat and mass transfer, and therefore may increase self-heating and heat dissipation. Convection in a self-heating volume may be caused by internal temperature gradients, or driven by wind or ventilation.

Self-heating may cause large temperature gradients within a stored material — large temperature gradients cause convective flows [64]. Many materials are stored in open, extended triangular or trapezoidal piles. Natural convective flows tend to be strongest (i.e. have greatest flow speed) near the sides and top of such piles (Figure 2.5) [37, 65].

These flows may either increase or decrease spontaneous combustion risks. Self-heating is often oxidative — mass transfer limitations can decrease oxygen concentrations (and oxidative self-heating) near the centre of a pile of oxidizing material.
As convective flows increase mass transfer [37], oxidative self-heating may therefore be enhanced in regions with convective flows. As a result, maximum storage temperatures may occur close to the surface of a stored fuel. Convection also increases heat dissipation, both because of evaporation (as will be discussed below) and heat transfer effects. If this cooling effect is strong enough, maximum temperatures may occur near the middle-bottom of a pile, or in areas with reduced permeability [35, 66].

Piles have sometimes been ventilated to take advantage of convective heat dissipation effects [67]. Insufficient ventilation may lead to spontaneous combustion [68]. Studies show that wind causes flows of similar or greater magnitude as flows caused by internal temperature gradients [69, 70]. Increased oxygen transfer caused by such flows has presumably led to fires in “stable” piles of coal; coal piles have been known to ignite in strong winds [71].

Convective flows additionally affect self-heating and heat dissipation through interactions with water. Internal temperature gradients cause the convective and diffusive transfer of water. Water may evaporate and desorb in high-temperature areas and enter the gas phase. Convective flows can then carry gas-phase water into cooler...
regions, and the water may re-condense \[64, 72\]. Water transport from a moist environment may increase the moisture content of the entire pile \[65\]. As discussed in the previous section, water affects chemical and biological heating, as well as itself generates or absorbs heat through condensation or evaporation. It has been claimed that moisture content does not ultimately affect whether coal self-ignites or remains stable \[70\]; this will not be true for materials which undergo significant biological heating.

As mentioned above, mass transfer limitations sometimes limit self-heating in the centre of piles of oxidizing materials. Some spontaneous combustion prevention methods decrease self-heating by further decreasing mass transfer. Piles of self-heating materials are sometimes compacted or covered in ash-water slurry, minimizing diffusion and convection \[70, 71\]. However, if stable compacted or covered piles are disturbed, mass transfer can increase and the pile may spontaneously combust.

**2.2 Spontaneous Combustion Theory and Experiments**

Section 2.1 discussed qualitative information regarding spontaneous combustion; this section focuses on theories and models that quantify spontaneous combustion risks. Section 2.2.1 summarizes the Frank-Kamenestkii theory, an analytical theory that determines if a self-heating volume has stable, non-combustion states. Section 2.2.2 presents some of the experimental implementations of the Frank-Kamenetskii theory. Finally, Section 2.2.3 discusses some of the numerical methods that have been used to study spontaneous combustion.
2.2. SPONTANEOUS COMBUSTION THEORY AND EXPERIMENTS

2.2.1 The Frank-Kamenetskii Theory

The Frank-Kamenetskii theory is an ignition theory, similar to the Semenov theory. Both assume that self-heating follows Arrhenius kinetics, and that the system undergoes convective heat losses to its environment. However, the theories assume different behaviour. The Semenov theory assumes that the system under consideration is isothermal, as would occur in small particles or highly conductive objects. In contrast, the Frank-Kamenetskii theory enforces a temperature gradient by assuming that the boundaries of a self-heating volume approach environmental temperatures. Therefore, the Frank-Kamenetskii theory describes a large, self-heating volume with low thermal conductivity, and is frequently used to study spontaneous combustion.

The Frank-Kamenetskii theory considers an infinite, self-heating slab immersed in an isothermal gaseous environment (Figure 2.6) [2]. Using a simplified self-heating and heat dissipation model, the Frank-Kamenetskii theory establishes whether or not such a slab has a steady-state with a finite maximum temperature \( T_0 \). If no steady state exists, then the slab would be unstable and combust.

\[
x = -r \quad x = 0 \quad x = r
\]

\[
\begin{align*}
T_0 & \\
\frac{dT}{dx} \bigg|_0 &= 0 \\
T_S & \quad T_A \\
\lambda \frac{dT}{dx} \bigg|_r &= h(T_S - T_A)
\end{align*}
\]

Figure 2.6: Self-heating slab, as considered by the Frank-Kamenetskii theory, showing internal temperature profile and boundary conditions

The Frank-Kamenetskii theory models self-heating with a volumetric, Arrhenius
equation (eqn. 2.8). It is assumed that the slab self-heats via a chemical reaction, the rate of which is determined by the Arrhenius equation. If this reaction is not limited by reagent consumption or mass transfer, then self-heating only depends on temperature,

\[ q = \rho Q A \cdot \exp \left[ -\frac{E}{RT} \right] \]  

(2.8)

where \( Q \) is the heat of reaction, \( A \) and \( E \) are the Arrhenius pre-factor and activation energy, \( \rho \) is density and \( q \) is volumetric heat generation.

The theory considers heat dissipation with a similarly simplified model. It is assumed that the slab is immersed in an isothermal gaseous environment, and that heat transfer within the slab occurs by conduction only. Taking both the self-heating and heat-dissipation model into account, the steady-state internal temperature of the slab follows a differential equation,

\[ -\lambda \frac{d^2T}{dx^2} = QA\rho \cdot \exp \left[ -\frac{E}{RT} \right] \]  

(2.9)

subject to the boundary conditions,

\[ \frac{dT}{dx} \bigg|_{x=0} = 0 \]  

(2.10)

\[ \lambda \frac{dT}{dx} \bigg|_{x=\pm r} = \pm h (T_S - T_A) \]  

(2.11)

Eqn. 2.9 and its boundary conditions can be made dimensionless using a dimensionless temperature \( \theta = (T - T_A) \frac{E}{RT_A} \) and dimensionless distance \( z = \frac{x}{r} \),
2.2. SPONTANEOUS COMBUSTION THEORY AND EXPERIMENTS

\[ \frac{d^2 \theta}{dz^2} = -\delta e^\theta \]  \hspace{1cm} (2.12)

\[ \frac{d\theta}{dz} \bigg|_{z=0} = 0 \]  \hspace{1cm} (2.13)

\[ -\frac{d\theta}{dz} \bigg|_{z=1} = \alpha \theta_S \]  \hspace{1cm} (2.14)

where \( \alpha \) is the Biot number \( (\alpha = hr/\lambda) \) and \( \delta \) is the Frank-Kamenetskii parameter,

\[ \delta = \frac{E}{RT_A^2} \frac{r^2 Q A \rho}{\lambda} \cdot \exp \left[ - \frac{E}{R T_A} \right] \]  \hspace{1cm} (2.15)

As stated above, if the slab had no steady state, than it would combust. The slab is described by eqns. 2.10–2.14; if this system has a solution, than the slab has a steady state. The existence of a solution depends on \( \alpha \) and \( \delta \). The Frank-Kamenetskii theory considers materials with large \( \alpha \) (e.g. low thermal conductivity, high convective heat losses). In that case, the existence of steady states is determined by \( \delta \); if \( \delta > \delta_C \), then no steady states exist and the slab is unstable and would spontaneously combust.

The FKP can thus be used to find the self-ignition thresholds of real fuel stores, as \( \delta_C \) only depends on the shape of a self-heating volume. Frank-Kamenetskii initially considered three ‘canonical’ or one-dimensional geometries, namely the infinitely long and infinitely wide slab, the infinitely long cylinder and the sphere (\( \delta_C = 0.88, 2.00, \) and 3.32, respectively). \( \delta_C \) has since been determined for many other geometries. For instance, for a rectangular prism or ‘brick’,

\[ \delta_C(a) = 0.840 \left( 1 + \frac{1}{p^2} + \frac{1}{q^2} \right) \]  \hspace{1cm} (2.16)
where $2a$, $2b$ and $2c$ are the side lengths of the prism, $p = b/a$ and $q = c/a$.

As discussed above, the Frank-Kamenetskii theory is based on a simplified model of self-heating and heat-dissipation. As was mentioned in Section 2.1.2, there have been efforts to develop equivalent theories that are more appropriate for compost or other biologically active media [27]. The theory has also been modified to consider diffusion-limited self-heating, by calculating $\delta_C$ as a function of $\xi$,

$$\xi = \frac{E}{RT_A^2} \cdot \frac{Q_g DC_o}{\lambda}$$  \hspace{1cm} (2.17)

However, it has proven difficult to modify the theory to account for physical heating or convective heat and mass transfer. The relationship between convection and oxidative flows is particularly complicated — convective flows may be driven by temperature gradients, which are a result of self-heating, which is affected by mass transfer. These factors have typically been studied with numerical methods, which will be briefly discussed in Section 2.2.3.

### 2.2.2 Oven Tests and Calorimetric Methods

The FKP may be used to predict spontaneous combustion. Eqn. 2.15 may be rearranged:

$$r_C = \sqrt{\frac{\delta_C T_A^2}{E/R} \cdot \frac{\lambda}{\rho QA}} \exp \left[ \frac{E/R}{T_A} \right]$$  \hspace{1cm} (2.18)

In this form, $r_C$ defines the maximum stable size of a self-heating volume at ambient temperature $T_A$, the shape of which is considered by $\delta_C$. The FKP has been used to make spontaneous combustion predictions for many materials, including charcoal,
2.2. SPONTANEOUS COMBUSTION THEORY AND
EXPERIMENTS

fertilizer and milk powder [73]. This section discusses two methods of measuring material properties relevant to eqn. 2.18 — isothermal oven tests and calorimetry.

Isothermal oven tests rely on a further manipulation of the FKP — the logarithm of eqn. 2.15 yields

\[
\ln [XT_C^2] = \ln [Y] - \frac{Z}{T_C}
\]  

(2.19)

where \( X = \delta_C/r^2 \), \( Y = (E/R)\rho Q A/\lambda \), \( Z = E/R \), and \( T_C \) is a critical ignition temperature. Oven tests measure \( Y \), \( Z \) and \( T_C \) — material samples are placed in baskets, then immersed in various constant-temperature environments. Note that \( r_C \) decreases with ambient temperature; a fuel sample in an oven will ignite if the oven temperature exceeds \( T_C \). \( T_C \) is thus determined by the average of the lowest oven temperature where the sample combusts, and the highest oven temperature where the sample undergoes stable self-heating. The critical temperature of at least four differently sized baskets of material is thereby obtained. If the material obeys the assumptions of the Frank-Kamenetskii theory, a plot of \( \ln [XT_C^2] \) vs. \( 1/T_C \) is linear with a slope of \(-Z\) and intercept \( Y \).

These parameters may be substituted into eqn. 2.18:

\[
r_C = \sqrt{\frac{\delta_C T_A^2}{Y} \cdot \exp \left[ \frac{Z}{T_A} \right]}
\]

(2.20)

Note that \( X \) is a geometric factor — \( \delta_C \) and \( r \) depend on the basket. Thus, \( Y \) and \( Z \) are independent of shape [57], and eqn. 2.20 may be used to calculate critical sizes of differently shaped storage situations.
The isothermal oven test has been used to make spontaneous combustion predictions, and is the basis of some standard spontaneous combustion risk assessment methods [74]. However, oven tests are performed at high temperatures (T > 90°C); they therefore do not account for moisture effects or biological heating. Gray et al. found that oven tests significantly overestimated the safe size of a pile of sugarcane bargasse [23]. Oven tests have also under-estimated the spontaneous combustion risks of hay [75] and wood chips [76]. Self-heating has also been studied with calorimetry, to account for the observed discrepancies between oven tests and low-temperature spontaneous combustion behaviour.

Heat flow calorimeters are commercially available, and are frequently used to measure both the heat and rate of chemical reactions [77]. Heat flow calorimeters record heat production as a function of time, and some models (microcalorimeters) are sufficiently sensitive to measure oxidation and biological heating at low temperatures (20-90°C) [78].

Calorimetric studies often show greater self-heating at low temperatures than would be expected from extrapolations of oven tests. For instance, Guo measured the self-heating of wood pellets with both isothermal calorimetry and oven tests, as described above; pellets from the same source showed faster oxidation kinetics in the calorimeter than in the oven [4]. Jones [79] and Lonnermark et al. [80], studying peat moss and wood pellets, respectively, found similar results when comparing isothermal calorimetry to oven tests.

Scanning calorimetry has also been used to measure low-temperature self-heating, for instance, coal oxidation [81]. Scanning calorimeters measure heat production while linearly increasing sample temperature, *i.e.* scanning calorimetry measures
2.2. SPONTANEOUS COMBUSTION THEORY AND EXPERIMENTS

self-heating as a function of time and temperature. Kinetic information can then be inferred by assuming first-order Arrhenius kinetics [82].

2.2.3 Numerical Methods

As discussed in Section 2.1, spontaneous combustion is affected by many interdependent processes. There is — to the author’s knowledge — no equivalent to the Frank-Kamenetskii parameter that incorporates convective effects or biological heating, in addition to conduction, diffusion and chemical heating. These effects have instead been studied with numerical or computational methods.

Similar to how coal oxidation demonstrates typical low-temperature oxidation behaviour, coal spontaneous combustion models are similar to biomass fuel models. Coal spontaneous combustion has been simulated with finite-element or finite-difference models, which may be one-, two- or three-dimensional [70, 83, 84]. Models may solve flow and temperature fields simultaneously, or enforce a flow or temperature profile [85]. The specific formulation of each model varies, depending on solution method, approximations, etc. In general, they consider: conductive flow patterns caused by forced or natural convection; diffusive and convective mass transfer, of oxygen, water, carbon dioxide, etc.; conductive and convective heat transfer; heat of condensation/wetting and evaporation/desorbtion; heat of oxidation, and oxidation products; and, occasionally, reactant consumption.

Biomass spontaneous combustion models account for biological heating in addition to the above factors. Biomass models can therefore be unwieldy — two models, for wood chips [5] and compost [86], used over 40 parameters. Despite their complexity, both coal and biomass models have accurately described self-heating behaviour,
such as the formation of hot spots [83] or the temperature profiles of large wood chip piles [5]. They have also contributed to the understanding of natural and forced convection — many of the convective effects discussed in Section 2.1.2 were investigated computationally.

2.3 The Chemistry of Railway Ties and Asphalt

Self-heating, and by extension, spontaneous combustion, depends on fuel chemistry and structure. This section discusses the chemistry of two materials. Section 2.3.1 discusses the structure, chemistry and self-heating processes of creosote-treated railway tie wood, and Section 2.3.2 discusses the same subjects for roofing asphalt. Section 2.3.3 further discusses pyrolysis-gas chromatography/mass spectrometry (py-GC/MS), a method of studying the chemistry of nonvolatile solids.

2.3.1 Railway Tie Wood

Wooden railway ties are made of rough-cut, creosote-treated hardwood, 8” × 12” (20 × 30 cm) in cross section and 6’-8’ (1.8-2.4 m) long. Creosote has antibacterial and antifungal properties, and prolongs tie lifetime; typically, railway ties are 10-15% creosote, by weight, though that can vary by tie and creosote content can decrease over time [87]; nonetheless, the wood may have rotted before disposal, and creosote would not affect oxidation. Therefore, the chemistry of a creosote-treated, wooden railway tie depends on creosote, wood and weathering.

Creosote, a brown, viscous liquid, is derived from the middle oil (boiling point: 220°-375°C) of coal tar distillation [88]. Creosote is composed of several hundred chemicals, over 75% of which are polycyclic aromatic hydrocarbons (anthracene,
napthalene and phenanthrene derivatives) [89]. There are many creosote-treatment processes; for instance, the Bethel process first uses a vacuum to draw moisture and air out of wood, and then immerses ties in creosote at high pressures. Alternatively, creosote may simply be painted onto wood [90].

Wood is both chemically and structurally complex — most of a living tree is formed of the hollow walls of dead cells (the xylem). Wood cell walls persist after cellular death, providing mechanical support and transport functions — wood is therefore slightly permeable [91]. Cell walls are made of several layers, each of which is composed of different amounts of lignin, cellulose and hemicellulose [92]. These polymers make up 96-99 wt% of the wood; their length, and to an extent their composition, depends on tree species and growing conditions. The remainder of the wood is made of small cellular components (known as the extractives) and metal ions (the ash) [93]. Overall, wood has an elemental composition of 50% C; 6 % H; 44 % O, and trace amounts of many metals.

Cellulose makes up 40-50% of wood weight [94]. Cellulose is a linear homopolysaccharide formed of 1-4 linkages of β-D-glucopyranose units, with an average degree of polymerization of 10,000. Cellulose polymers bind together via hydrogen bonding, and form microfibrils — long fibres with sections of both crystalline and amorphous cellulose. Wood structure is made of these microfibrils, bound together with hemicellulose and lignin.

Hemicellulose makes up 25-35% of wood. Hemicellulose is a weakly branching heteropolysaccharide, formed from several sugars including D-glucose, D-mannose, D-xylose and L-arabinose, as well as the uronic acids of several sugars. “Hemicellulose” in fact describes several distinct polymers, named for their sugar monomers (e.g.
2.3. THE CHEMISTRY OF RAILWAY TIES AND ASPHALT

galactoglucosamannan, formed of galactose, glucose and mannose).

Lignin makes up 18-35% of wood. Lignin is a highly branched phenolic polymer, formed from p-coumaryl, coniferyl and sinapyl alcohol units; they are incorporated into lignin as phenylpropanoids (p-hydroxyphenyl, guaiacyl and syringyl, respectively). Lignin composition depends on species. Softwood tree lignin has abundant guaiacyl, whereas hardwood lignin has abundant guaiacyl and syringyl. The two types of lignin are known as guaiacyl and guaiacyl-syringyl lignin, respectively.

Wood is a biologically active, carbonaceous material; wood self-heats through biological, chemical and physical processes. Wooden railway ties will likely self-heat in a similar manner. Wood may rot despite being treated with creosote [95]. Wood also oxidizes, as shown by the depletion of gaseous oxygen during wood product storage [96] or the increase in wood oxygen content after extended weathering [97]. As creosote is a coal derivative, it may also oxidize. As wood contains significant amounts of cellulose and hemicellulose, hydorlysis may also occur. And, if stored in a moist environment, water may condense into stored wood. As discussed in section 2.1.1, all of these reactions generate heat at low temperatures.

However, the rate of oxidative heating may be affected by weathering. Railway ties have an in-service lifetime of 35-40 years [98], and the wood may have undergone significant weathering. As weathering increases wood oxygen content (e.g. by increasing the carbonyl content of lignin [99]), railway tie wood may oxidize at a slower rate than “fresh” wood.
2.3.2 Roofing Asphalt Shingles

Roofing asphalt shingles are produced from organic or polymer fibres, asphalt and grit, with asphalt making up the largest fraction [100]. Asphalt, a black, colloidal suspension, is either produced from the residuum of petroleum fractionation, or harvested from natural sources [101]. Asphalt chemistry is complex and depends on its source and refinement process [102]. Asphalt may be divided into four fractions based on solubility — carboids, carbenes, asphaltenes and maltenes. Asphaltenes (2-15%) and maltenes (85-98%) make up most of the mass and volume of asphalt. The elemental composition of asphalt is typically 80-85% C; 9-10% H; 2-8% O; 0.5-1% N; and 0.5-8% S.

Asphaltenes are solid at room temperature. Asphaltenes are large molecules — their mass varies within the range 500-2500 u, and is most often 1300-1500 u [103] (note that u is the standard molecular mass unit — 1 u = 1 g/mol). Asphaltenes are more unsaturated than maltenes — their C:H ratio varies from 0.8-1.0 [101] and they have a larger double bond equivalency [104]. Structurally, they are thought to consist of cyclic cores with aliphatic bridges; these bridges may link several small cores (“archipelago” structure) or stem from a large, central core (“island” structure).

In contrast, maltenes are dark and oily. Maltenes are slightly smaller than asphaltenes — their mass varies within the range 500-2000 u, with a peak at 600 u. They are also less saturated (C:H 0.6-0.75, lower double bond equivalency [101, 104]) and less polar. Maltenes are sometimes further divided into saturated, resinous and aromatic fractions (SARA analysis) [105].

Asphalt is a petroleum-derived hydrocarbon; it will undergo oxidative and physical self-heating. Oxidation, which may occur in use, causes asphalt to become brittle;
there are standard methods for studying asphalt oxidation [106]. Oxygen forms carbonyl groups in asphalt [107, 108, 109], and oxidation may increase asphalt aromaticity [108, 109]. Oxygen also attacks thiophenic sulfur in asphalt, and forms sulfoxides or sulfones [105, 110], though it has been suggested that sulfur oxidation only takes place at high temperatures [111]. Similar to wood, water may also condense into stored asphalt. As discussed in Section 2.1.1, both oxidation and condensation generate heat.

Similarly to railway tie wood, asphalt self-heating may be affected by weathering — asphalt roofing shingles have a useful lifetime of 12-20 years [112]. As the shingles will likely have oxidized while in use, oxidative self-heating may proceed at a slower rate.

### 2.3.3 Pyrolysis-Gas Chromatography/Mass Spectrometry

As discussed in the previous sections, self-heating — particularly oxidative self-heating — is material specific, and depends on physical and chemical structure. It has been further noted that the materials of interest in this study may have weathered, either by oxidation or microbial degradation. Coal and wood pellet weathering affects their self-heating behaviour [56, 17]; therefore, weathering may have changed the self-heating properties of the study fuels. However, it is difficult to determine the history of a waste material, and thus to what degree these fuels have weathered. A chemical analysis may help to explain the self-heating behaviour of waste asphalt roofing shingles and creosote-treated wooden railway ties.

Pyrolysis-Gas Chromatography/Mass Spectrometry (py-GC/MS) has proven to
be a valuable technique for studying the chemistry of solid materials, and may therefore reveal the extent of fuel weathering. Pyrolysis refers to the high-temperature degradation of materials by free radical reactions, initiated by thermal bond-breaking. The pyrolysis products — or pyrolyzates — of a given compound depend on the strength of chemical bonds. Thus, pyrolyzates give information about chemical structure. Pyrolyzate analysis, or the identification and quantification of pyrolysis products, has been particularly useful for the study of solid biomass or fossil fuel derivatives [113].

For instance, lignocellulosic materials (e.g. wood) have been studied by pyrolyzate analysis — Galletti and Bocchini provide an excellent review of the subject [114]. In general, lignins produce phenolic or benzoic pyrolyzates, while polysaccharides (cellulose and hemicellulose) produce pyranic and furanic compounds, as well as smaller oxygenated species. Lignin pyrolysis is particularly informative; for instance, different oak species may be identified by their lignin pyrolyzates [115]. Pyrolyzate analysis has also revealed the structure of asphalt and similar materials. Pyrolyzate analysis has identified functional groups in asphalt [116], thiophenic sulfur structures in kerogens [117], and estimated asphaltene aromaticity and average aliphatic bridge length [118].

Pyrolyzate analysis has been combined with thermogravimetry in techniques such as thermogravimetric — mass spectrometry (TG-MS) and thermogravimetric — fourier transform infrared spectrometry (TG-FTIR) [119]. TG-MS and TG-FTIR can infer relationships between pyrolyzates, time, weight change, and temperature; however, they have limited identification abilities. For instance, a pine TG-FTIR pyrolysis study [120] could not identify hydrocarbons that had greater molecular mass.
than phenol \((M = 94 \text{ u})\). Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) cannot observe weight changes, but it can identify large pyrolyzates such as heptacosane \((M = 380 \text{ u})\) [121].

A py-GC/MS system (Figure 2.7) is composed of an analytical pyrolyzer, directly interfaced with a gas chromatograph equipped with a mass spectrometer. The pyrolyzer heats an analytical sample, and the sample releases a mixture of pyrolyzates. This mixture is introduced into the chromatographic column and separated; pyrolyzates are then eluted into the mass spectrometer. Finally, the mass spectrometer identifies and quantifies each separated pyrolyzate [113, 122].

![Figure 2.7: Schematic of pyrolysis-gas chromatography/mass spectrometry system](image)

Three pyrolyzers are commonly used in py-GC-MS — the microfurnace, curie-point or resistive filament pyrolyzers. Of these, the resistive filament provides the most flexible temperature control. Samples are heated in a quartz tube, around
which an electrically-powered platinum wire heater is wound. In all three devices, pyrolyzates are introduced into the chromatographic column with the carrier gas.

As stated above, the gas chromatograph separates the mixture of pyrolyzates. Chromatography is the technique of separating mixtures using a mobile and stationary phase — in gas chromatography, the carrier gas and column, respectively. The column is a tube, which may be packed with a permeable solid solvent, or the interior surface may be coated with a solvent film. If a compound is introduced to the column inlet, and forced towards the column outlet by the carrier gas, it will be retained in the column as the compound migrates between the carrier gas and the solvent. Mixtures become separated as components are retained for different amounts of time [123].

Compounds with different molecular mass and different polarity will have different retention times. Retention times also depend on solvent, solvent film thickness and column temperature. There are many commercially available columns, and columns are further suspended in a circulating air oven, both of which make it possible to effectively separate mixtures of 100 or more species. Common chromatographic practice is to slowly ramp the column temperature, as lighter species will elute without separation if the column temperature is too high, whereas heavier species may be retained for inconveniently long time periods if the column temperature is too low. Note then that a successful py-GC/MS experiment involves specifying pyrolysis and column temperature separately, in order to effectively generate and then separate pyrolyzates.

The final component of a py-GC/MS system is the mass spectrometer, which identifies each separated pyrolyzate. Mass spectrometry is based on how molecules ionize and fragment. Ionized molecules fragment in predictable ways — if furfural
(C₅H₄O₂) were ionized with free electrons, then it would produce different amounts of C₅H₃O₂⁺, C₄H₃O₁⁺, C₃H₃⁺, and CHO⁺. A mass spectra is a bar graph that shows the relative amounts of positive ions produced after ionization-initiated fragmentation, plotted against the mass-to-charge ratio (M/z) of each ion (Figure 2.8). In order to identify an unknown species, mass spectrometers ionize the analyte, sort and count fragmentation product ions by M/z, and produce a mass spectra.

![Figure 2.8: Furfural mass spectrum, showing some major peaks. Adapted from [124]](image)

The ionization process described above is electron ionization (EI). Electrons are produced via thermionic emission, energized to 70 eV and then bombard a cloud of molecules in a chamber held at near vacuum [125]. EI is known as a hard ionization technique, as it frequently causes fragmentation. Soft ionization causes less fragmentation. For instance, in chemical ionization, molecules react with methanium (CH₅⁺); the reaction causes some fragmentation, but but often produces (M − 1) ions [126]:
After fragmentation, product ions are sorted by $M/z$ and then counted. Py-GC/MS often uses time-of-flight (TOF) or quadrupole mass spectrometers. TOF spectrometers sort ions by accelerating them through an electric potential — ions with larger $M/z$ travel a defined path more slowly than lighter ions [127]. Quadrupole mass spectrometers send fragments through an oscillating electric field. The field exclusively allows ions with a defined $M/z$ pass to an ion detector [128]. By manipulating the electric field, the quadrupole scans and counts ions with different $M/z$. Thus, mass spectrometers build mass spectra.

Species — in py-GC/MS, pyrolyzates — may then be identified by their mass spectra. Molecules may be reverse-engineered from mass spectra; however, molecules are more commonly identified by comparing spectra to spectral libraries, such as the NIST database [129]. In both cases, molecular or $(M - 1)$ ion peaks greatly assist with identification. Mass spectrometry is most powerful when identifying pure compounds — if two compounds are co-eluted into the mass spectrometer, then it may not be possible to identify either chemical. Thus, py-GC/MS is a powerful pyrolyzate analysis technique, because it separates pyrolyzate mixtures before identification.

2.4 Chapter Summary

This chapter discussed the fundamental heat generation and heat and mass transfer processes that cause spontaneous combustion, as well as a simplified spontaneous combustion model (i.e. the Frank-Kamenetskii theory.) As this thesis is focused on the spontaneous combustion of creosote-treated railway ties and asphalt roofing
shingles, the chemistry of wood, creosote, and asphalt were also summarized. Py-GC/MS was also reviewed in order to give a background to Chapter 4, which presents a chemical analysis of the above materials. That analysis will show the effect of weathering on asphalt or railway tie spontaneous combustion.

The next chapter presents a Frank-Kamenetskii spontaneous combustion study of railway tie wood and asphalt shingles. Self-heating was measured with isothermal calorimetry, and thermal conductivity was measured with a guarded hot plate. Critical spontaneous combustion conditions were then determined with the Frank-Kamenetskii parameter.
Chapter 3

Calorimetric and Heat Transfer Studies of the Spontaneous Combustion of Two Waste Fuels
Calorimetric and Heat Transfer Studies of the Spontaneous Combustion of Two Waste Fuels

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Abstract

The self-heating and heat transfer characteristics of creosote-treated wooden railway tie dust and roofing asphalt shingle particles, which are considered as low carbon fuels, are investigated. Self-heating was measured with isothermal calorimetry and thermal conductivity was measured using a guarded hot plate. The self-heating of petroleum coke and poplar wood pellets were also measured as reference materials. Self-heating models and heat transfer parameters were then defined assuming constant moisture content. The self-heating of petroleum coke was found to be similar to coal, while both poplar pellets and railway tie dust were found to be more reactive compared to oven test results of similar materials. As both poplar pellets and railway ties both had significant water content, the higher reactivity was attributed to the effect of moisture. Furthermore, critical conditions for spontaneous combustion were evaluated with the Frank-Kamenetskii parameter, assuming an ambient temperature of 40°C. It was found that cubic volumes of railway tie dust and asphalt particles, 1.6 m and 58 m to a side, respectively, would spontaneously combust; however, compaction effects associated with asphalt softening may invalidate the assumptions of the Frank-Kamenetskii spontaneous combustion theory.
3.1 Introduction

Spontaneous combustion depends on the self-heating behavior and heat transfer properties of a material. The spontaneous combustion characteristics of coal [6, 17] and wood products [4, 5, 57] are well understood; however, many materials that have outlived their original useful operational life, will have aged and may present different self-heating and heat transfer properties than when in either their pristine component state or prior to their initial product state. For example, every year Canadian Pacific and Canadian National Railways will collectively discard approximately 800,000 creosote-treated railway ties in western Canada [130], and the Canadian construction industry creates 1.5 million tons of waste asphalt roofing shingles [112]. Discarded rail ties are typically 35 years old, while the age of asphalt shingles varies from 12-20 years [98]. Chipped railway ties or shredded asphalt shingles could be either each or in combination significant sources of fuel for electricity generation, cement production and other industries; however, before these materials can be safely stored in fuel handling systems, spontaneous combustion risks must be addressed.

The isothermal oven test [2] and a basket-heating method [131] are commonly used to study spontaneous combustion. They both rely on the Frank-Kamenetskii parameter, $\delta$, which provides a measure of the spontaneous combustion risks relative to a critical value, $\delta_C$. These tests have serious practical limitations, especially for low carbon fuels such as asphalt shingles and railway ties. In fact, self-heating of carbonaceous fuels is largely oxidative [132] and low temperature self-heating is related to moisture content [41] and to the presence of microorganisms [64], which can cause significant changes in temperature of a pile. These moisture effects are not seen in oven tests, which are conducted in a relatively high temperature environment.
3.2. THEORY

The moisture content of a pile can also affect heat transfer in these tests [45]. As a result, moisture has been claimed to cause fires in fuel stores that were deemed stable using oven tests [23]. Similarly, microbial degradation causes self-heating at low temperatures, and is not accounted for by oven tests. Microbial activity has caused temperature increases, and may cause storage fires [35].

In this paper, the spontaneous combustion risks of discarded railway ties and asphalt shingles were investigated with isothermal calorimetry and thermal conductivity tests. The experiments include the effects of moisture content. Assays were conducted at low temperatures or in sealed ampoules, thereby ensuring that water remained in the system. The Frank-Kamenetskii parameter, \( \delta \), was then calculated from the resulting self-heating [79] and thermal conductivity data [56]. The paper is laid out as follows: the next section reviews the Frank-Kamenetskii parameter, as well as how this may be calculated from calorimetric and heat transfer data. The calorimetric and heat transfer experiments are then described. Finally, the results are analyzed, and the spontaneous combustion risks of the studied fuels are calculated.

\[ \delta = \frac{E/R}{T_A^2} \cdot \frac{r^2 \rho QA}{\lambda} \exp \left[ -\frac{E/R}{T_A} \right] \] (3.1)

A critical value, \( \delta_C \), of the FKP is defined by volume geometry (e.g. short cylinder, cube, etc.) [2]. If \( \delta < \delta_C \), then the volume of material under consideration would undergo a limited temperature increase. If \( \delta > \delta_C \), this volume would undergo runaway
heating and combustion may occur. Using this approach, eqn. 3.1 can be rearranged to obtain the critical size, $r_C$, of a material, which is defined as the size of volume in which spontaneous combustion will occur at a given ambient temperature, $T_A$:

$$r_C = \sqrt{\frac{\delta_C T_A^2}{E/R} \cdot \frac{\lambda}{\rho QA} \exp \left[ \frac{E}{R T_A} \right]}$$  \hspace{1cm} (3.2)

Alternatively, by setting $\delta = \delta_C$ and rearranging, eqn. 3.1 can cast into

$$\ln \left[ \frac{\delta_C T_A^2}{r^2} \right] = \ln \left[ \frac{E/R \rho QA}{\lambda} \right] - \frac{E/R}{T_C}$$  \hspace{1cm} (3.3)

This form enables simple oven tests to be performed that determine the critical temperature at which spontaneous combustion will occur. That is, eqn. 3.1 may be reformulated to $\ln \left[ X T_C^2 \right] = \ln \left[ Y \right] - Z/T_C$, where $X = \delta_C/r^2$, $Y = (E/R)\rho QA/\lambda$ and $Z = E/R$. In an oven test, fuel samples are placed in baskets and then immersed in various constant temperature environments. A critical temperature is defined by the average of the lowest temperature where the fuel combusts, and the highest temperature where the fuel exhibits stable self-heating. The critical oven temperature for spontaneous combustion of at least four differently sized baskets of fuel is thus obtained. Each basket has a specific value of $X$ that is independent of the fuel under consideration. A plot of $\ln \left[ X T_C^2 \right]$ vs $1/T_C$ can be drawn from the oven test data. If the material behaves according to eqn. 3.1, this plot will yield a line with intercept $\ln \left[ Y \right]$ and slope $-Z$.

Eqn. 3.2 can then be used to obtain the critical sizes by substituting these lumped parameters to get
Note that in this approach, material characteristics such as the thermal conductivity ($\lambda$) and the heat of reaction ($Q$) need not be known — oven tests are comparatively simple and convenient, if time-intensive. However, as discussed in the introduction, oven tests do not account for moisture effects, as they are performed at sufficiently high temperatures to cause sample drying; similarly, they cannot account for microbial heating. Therefore, this study does not consider spontaneous combustion risks with oven tests.

Another approach is to obtain the values for the heat of reaction, activation energy and the thermal conductivity of the fuel under consideration, and then solve for critical sizes. The FKP was derived assuming that self-heating obeyed a volumetric, Arrhenius law,

$$q = \rho QA \exp \left[ -\frac{E}{RT} \right]$$  \hspace{1cm} (3.5)

where $q$ is the volumetric heating rate, $\rho$ is bulk density, $Q$ is the heat of reaction, $A$ is the Arrhenius pre-factor and $E/R$ is the activation energy. Such information could be obtained using sealed isothermal calorimetry — sealed systems would have the added benefit of retaining sample moisture content within the calorimetric ampoule. The FKP assumes that the fuel oxidizes homogenously, i.e. that oxygen concentration is constant in space and time; however, oxygen would be consumed in a sealed calorimetric system. Calorimetric data could be extrapolated to determine self-heating at atmospheric oxygen concentrations, if fitted to kinetic models. Self-heating caused by
a single first-order oxidation reaction would generate exponentially decreasing amount of heat, $\dot{q}$ [133]

$$\dot{q} = mkQ \exp \left[ -kt \right]$$  \hspace{1cm} (3.6)

where $m$ is the sample mass, $k$ is the rate of reaction, and $t$ is the time since onset of reaction.

Competing reactions, diffusion effects and higher-order reactions could cause more complicated heating behavior. In that case, an empirical model could be fit to the calorimetry data, such as an exponential plus constant model [4],

$$\dot{q} = mk_1Q_1 \exp \left[ -k_1t \right] + mk_2Q_2$$  \hspace{1cm} (3.7)

Such a model would represent the total heat of all reactions and would enable extrapolations to be considered. Alternatively, if oxidation is sufficiently slow, then heating may behave linearly with time, as shown by performing a Taylor expansion of eqn. 3.5 and taking the leading term

$$\dot{q} \approx mkQ \left( 1 - kt \right)$$  \hspace{1cm} (3.8)

As $k$ and $Q$ are related to the volumetric heating model described by eqn. 3.5, the above calorimetric curves can be used to calculate the FKP (and critical storage sizes) once thermal conductivity has been measured. The FKP also depends on the thermal conductivity of the fuel and the ambient (environmental) volume temperature. Many solid fuels are stored after grinding- in addition to moisture content, the conductivity of a ground fuel depends on porosity, compaction, particle size, shape,
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and hardness [46, 52, 63]. It has been previously discussed that sealed calorimetry retains sample moisture; conductivity experiments could do the same. Therefore, the combination of calorimetric and heat transfer tests allows for FKP-based spontaneous combustion risk assessments, which take into account fuel moisture content. This approach will further show whether or not self-heating or thermal conductivity behavior violates the assumptions of the Frank-Kamenetskii theory, i.e. homogenous thermal conductivity and Arrhenius-like volumetric self-heating. Importantly, any deviation from these assumptions may not be detected by oven tests.

3.3 Experiments

3.3.1 Calorimetric Self-Heating Measurements

The self-heating behavior of four fuels — waste asphalt shingle particles, discarded railway tie dust, poplar wood pellets and petroleum coke — is considered in this paper. Petroleum coke and poplar wood pellets served as reference materials. Wood pellet self-heating is well understood [4], as is coal self-heating [134, 135]. As both coal and pet-coke are carbonaceous materials, they are likely to exhibit similar self-heating; therefore, petroleum coke and wood pellets are good reference materials. Shredded asphalt shingles were obtained from the Lafarge Cement, St. Constant Plant in the Province of Quebec. The shingles were oven-dried at 103°C until the sample weight did not alter by more than 0.5% over three hours. The asphalt was then propeller milled and sieved to minimize particle size variation (0.590 < d < 1.190 mm). A discarded, creosote-treated wooden railway tie, which was at least 20 years old, was obtained. The tie was hammer milled to pass through a 1/8” (3.175 mm) screen, then sieved to the same size fraction as the asphalt particles. Fresh hybrid poplar (populus

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hybrid, variety DM-77) was harvested at the Ferguson Forest Centre near Ottawa, Ontario, and then, within two days of harvest, was chipped, partially dried and then formed into 1/4” (6.35 mm) cylindrical pellets using a commercial wood pellet mill located in our laboratory. Petroleum coke dust (d < 355 μm) was obtained from a ball mill at the Lafarge Bath cement plant. All calorimetric samples were sealed in air-tight, nonporous HDPE storage bottles and refrigerated for a few days until immediately before testing; due to HDPE’s low permeability, moisture migration did not cause significant change in sample moisture content [136]

Self-heating was measured using an 8-channel TA Instruments TAM Air Calorimeter, configured for 20 mL ampoules. The TAM Air is an 8-channel, differential heat flow calorimeter with sub-μW sensitivity and temperature stability to within ±0.02°C. Each of the four fuels were tested in duplicate at 50°, 70° and 90°C, for a total of 24 samples. Samples of 1-3 g were removed from the storage bottle and placed into 20 mL crimp-sealed glass ampoules immediately before testing. Heat flow signals in comparison to a sealed, empty reference ampoule were recorded for 24 hours, though the 50°C experiment was interrupted after 16 hours because of operator error. This interruption did not adversely affect the self-heating analysis.

Subsequently the moisture content of each material was measured according to ASTM E871-82 [137]. The poplar pellet and railway tie dust samples had moisture content of 13.6% and 6.2%, respectively, and the asphalt and coke samples both had negligible moisture content (< 0.5%).
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3.3.2 Thermal Conductivity Measurements

Thermal conductivity was determined using a purpose built single-sided, heat-flow compensated guarded hot plate, which was constructed according to Reid [138]. The device consisted of a 30 cm square aluminum guard plate and cold plate, 10 cm square aluminum heater plate, and 1-3 cm thick sample layer, all of which were embedded in a polyethylene foam insulation block (Figure 3.1). An on/off PID temperature controller and heating pad controlled the guard plate temperature to within $\pm 0.1^\circ C$. The cold plate was cooled with temperature-controlled air, and was also stable to within $\pm 0.1^\circ C$. The heater plate was heated by a heating pad, powered by a 30V DC power supply. An Eko MF-200 heat flux sensor measured heat flows ($\bar{q}$) between the guard and heater, and a calibrated type-K differential thermocouple measured the temperature difference between the guard/heater assembly and cold plate, which was typically between 8°-12°C. The apparatus was validated by measuring the conductivity of agar gel (1 g agar: 100 g H$_2$O), and found to agree with Zhang et al. within 4-8% [139]. This difference was caused by variation in heat flow caused by the on/off control of the guard plate.

The thermal conductivity of railway tie dust and asphalt shingle particles were measured using the aforementioned apparatus. Railway tie dust was obtained from the same tie that was used for the calorimetric tests, by chipping and hammer milling through a 1/8” (3.75 mm) screen, then oven drying the resulting dust. Similarly, the same asphalt shingles that were used in the calorimetric tests were used in heat transfer tests, though using a different particle size. That is, the shingles were oven-dried and then sieved into a “coarse” and “fine” fraction by sieving through a 1/4” (6.35 mm) square mesh, as the shingles exhibited a large particle size variation. The
shingle and railway tie samples were stored in sealed, air-tight nonporous HDPE bottles until testing, which occurred within a few days from when they were stored.

Ideally, these heat transfer experiments would have used identically sized particles as for the calorimetric tests; the particle size of a granular media may affect its thermal conductivity. In fact, as will be shown in the results, the fine asphalt has approximately 10% greater thermal conductivity than the coarse asphalt (Figure 3.3). However, there was insufficient sample to apply the same particle size restrictions. The use of larger particles in conductivity experiments than calorimetric tests ($d < 6.35$ mm and $0.590 < d < 1.190$ mm, respectively) makes our spontaneous combustion predictions more conservative. Gertrude [53] found that both the thermal conductivity, and the rate of change of conductivity, of granular biomass tends to decrease with increased particle size. Further, spontaneous combustion risks increase in more insulative materials. Thus, the fine asphalt is less thermally conductive than the calorimetric sample, and using that value makes this study’s spontaneous combustion
predictions more conservative.

Thermal conductivity samples were loaded into the hot plate by piling material into a cone in the centre of the tester. A scraper was used to level the sample without applying downward force. The cold plate was lowered onto the sample, and the guard and heater plates left on at a designated temperature (50°C or 90°C) for 24 hours to minimize moisture transport and compaction effects. The plate temperatures were then set to make a specific measurement. After the plate temperatures stabilized to 0.1°C, the heater plate power was adjusted to minimize the heat flow sensor signal. Conductivity calculations were based on 10-15 minute averages of sensor signals taken after the heat flow and temperature sensors returned stable values for at least 20 minutes ($\delta T < 0.1^\circ\text{C}$, $-0.05 < \bar{q} < 0.05$ W). Plate temperatures were then reset and the procedure repeated until completing measurements over the range 20°C-90°C or 20°C-50°C; asphalt and railway ties further underwent softening and moisture content tests, respectively, as is described in the next paragraph. After completing temperature and heat flow measurements, the cold plate was removed and the sample thickness was measured at 5 locations — above each corner and the centre of the heater plate.

The conductivity of dry railway tie dust and both coarse and fine asphalt particles were measured over the temperature range 30°C-90°C. As roofing asphalt softens at 55°C [140], the asphalt conductivities were measured twice, once before softening (i.e., conductivity was measured in the range 20°C < T < 50°C), and once after softening at 85°C. Asphalt is hydrophobic, while wood is hydroscopic; therefore, the effect of moisture on the thermal conductivity of railway tie dust was also investigated. Railway tie dust samples were rehydrated to different moisture contents (0, 1, 11, 16, 21, 26 and 42 wt%), and the conductivity of the rehydrated samples was measured at
3.4. RESULTS AND DISCUSSION

55°C. Following each experiment, the moisture content of each sample was measured according to ASTM E871-82 [137].

3.4 Results and Discussion

3.4.1 Calorimetric Results

Calorimetric results are presented in Figure 3.2. These plots display the heat generation, $\dot{q}$, of the 24 fuel samples considered when subjected to one of three constant temperature environments. The primary fuel self-heating reaction at these temperatures is usually oxidation; this was confirmed by the decreasing heating rate with time, and by features of the 90°C poplar pellet reactions. Oxygen was the limiting reagent, and there was a similar mass of oxygen in the 1.8 and 3.1 g sample ampoules, as the pellets were much more dense than air. Thus, the samples generated heat until the oxygen was exhausted, and produced nearly equal amounts of total heat — 92.7 and 96.2 J, respectively. Oxidation is also evidenced by the different rates of oxygen consumption; the 3.1 g sample had greater sample surface area and therefore, more reactive sites. Therefore, the 3.1 g sample generated heat and consumed oxygen more quickly than the 1.8 g sample.

Oxidation was also complex — the calorimetric results show features that could not be caused by first-order oxidation. For instance, oxygen consumption during the 90°C poplar pellet reactions accelerated, as evidenced by inflection points at $18 \cdot 10^3$ s and $30 \cdot 10^3$ s for the 3.1 and 1.8 g samples, respectively. Such acceleration is inconsistent with first-order oxidation. Petroleum coke and railway tie dust self-heating did not accelerate, but their heating was also inconsistent with first-order oxidation. As asphalt self-heating was sufficiently slow as to appear linear, it was
difficult to determine the order of oxidation of asphalt.

![Graph A](image1.png)

![Graph B](image2.png)

![Graph C](image3.png)

![Graph D](image4.png)

Figure 3.2: Self-heating data of calorimetric materials: A, poplar pellets; B, petroleum coke; C, railway tie dust; D, asphalt particles. Inflection points, as discussed in the results and discussion section, are marked in A.

### 3.4.2 Conductivity Results

The thermal conductivity of both the railway tie dust and asphalt particles was found to increase slightly with temperature (Figure 3.3). Furthermore, railway tie dust conductivity was found to strongly increase with moisture content (Figure 3.4).
Since asphalt is hydrophobic, the effect of moisture was not considered. Nonetheless, asphalt underwent a conductivity hysteresis related to softening. Asphalt softens at 55°C, and the conductivity of both the coarse and fine asphalts increased after a 24 h softening period at 85°C, due to compaction and, presumably, decreased inter-granular contact resistances.

### 3.4.3 Spontaneous Combustion Analysis

In order to quantify spontaneous combustion risks with the Frank-Kamenetskii parameter, volumetric Arrhenius self-heating models must be derived from calorimetric data and characteristic thermal conductivities must be chosen. The characteristic thermal conductivity may be chosen by accounting for temperature and moisture content; derivation of heating models requires either kinetic analysis or extrapolation of calorimetric data.

Oxygen depletion can also limit self-heating during fuel storage, and piles are sometimes compacted or covered with an ash-water slurry to decrease oxygen transport and therefore, self-heating. However, these measures have been known to fail — fires in “safely” compacted coal piles have begun after piles were disturbed, or under extremely windy conditions [70]. Further, some storage methods, such as a walking floor bins, continuously disturb stored fuel, which may increase oxygen transport. Thus, the spontaneous combustion predictions made in this paper ignore oxygen depletion. In order to model self-heating without oxygen depletion, Arrhenius self-heating models based on eqn. 3.5 (eqn. 3.9) were developed for each fuel, by extrapolating calorimetric data.
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\[ \lambda_{F,S} = 0.00013T + 0.074 \]
\[ \lambda_{F,L} = 0.00024T + 0.0594 \]
\[ \lambda_{C,S} = 0.00021T + 0.058 \]
\[ \lambda_{C,L} = 0.0002T + 0.053 \]
\[ \lambda_{RT} = 0.00011T + 0.046 \]

Figure 3.3: Thermal conductivity of dry coarse asphalt \((d > 1/4")\), fine asphalt \((d < 1/4")\), and railway tie dust \((d < 1/8")\). Average error for the railway tie dust, fine asphalt and coarse asphalt were 7%, 8%, and 11%, respectively.

\[ \lambda = 0.0012MC + 0.0479 \]
\[ R^2 = 0.951 \]

Figure 3.4: Thermal conductivity of railway tie dust, as a function of moisture content. Tests were performed with \(T_{CP} = 50^\circ C\) and \(T_{HP} = 60^\circ C\), i.e. \(T = 55^\circ C\). Average error was 8%.
3.4. RESULTS AND DISCUSSION

\[ q_m = Q A \exp \left[ -\frac{E/R}{T} \right] \]  \hspace{1cm} (3.9)

Not shown in Figure 3.2 are equilibration periods, which are the periods between sample insertion and thermal equilibrium. Sample ampoules were at room temperature when inserted into the calorimeter, and sample warming was recorded as an endothermic reaction. The exothermic peak in each calorimetric curve indicated when a sample reached thermal equilibrium with the calorimeter. During these equilibration periods self-heating consumed oxygen in the sealed ampoules, especially during the latter portion of the time period when the sample temperature approached the calorimeter temperature. Therefore, the maximum calorimetric signal does not show self-heating at atmospheric oxygen concentrations. A kinetic analysis, as used by Guo [4], could separately determine \( Q, A \) and \( E/R \); however, as discussed in Section 3.4.1, self-heating was too complex to justify a kinetic analysis. It was therefore necessary to extrapolate calorimetric data to within the equilibration period and thus, determine self-heating at atmospheric oxygen concentrations.

The exponential plus constant model (eqn. 3.7) was fit to the poplar pellet, petroleum coke and railway tie dust data, using data 10-30-10^3 s after the sample reached thermal equilibrium with the calorimeter. The linear model (eqn. 3.8) was fit to asphalt heating 40-70-10^3 s after equilibrium was reached, as the calorimetric signals became linear at this time. These fits were extrapolated to the middle of the equilibration period, \( i.e. \) halfway between sample insertion and sample equilibrium, to produce onset heat values that accounted for oxygen consumption during equilibration, as discussed above; these onset heating values were always greater than the maximum calorimetric heat flow signal. Arrhenius heating model parameters were
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derived by fitting eqn. 3.9 to onset heating values through an iterative procedure that maximized $R^2$ (Figure 3.5, Table 3.1, Table 3.2). These Arrhenius models were used to calculate critical sizes in combination with the thermal conductivity measurements.

![Figure 3.5: Arrhenius heating models, developed from onset heating values extrapolated from empirical fits of calorimetric data](image)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>$QA$ (W/g)</th>
<th>$E/R$ (K)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poplar Pellet</td>
<td>$1.2 \cdot 10^{10}$</td>
<td>10790</td>
<td>0.999</td>
</tr>
<tr>
<td>Petroleum Coke</td>
<td>$3.7 \cdot 10^{5}$</td>
<td>7220</td>
<td>0.973</td>
</tr>
<tr>
<td>Railway Tie Dust</td>
<td>$1.1 \cdot 10^{5}$</td>
<td>7200</td>
<td>0.909</td>
</tr>
<tr>
<td>Asphalt Particles</td>
<td>$1.7 \cdot 10^{8}$</td>
<td>12000</td>
<td>0.976</td>
</tr>
</tbody>
</table>

The Frank-Kamenetskii theory considers a self-heating volume to have a constant thermal conductivity, so a representative value was used to calculate critical sizes. Storage temperatures at industrial sites are unlikely to exceed 40°C, and the low reactivity of asphalt suggests it is unlikely to undergo large temperature increases,
Table 3.2: Summary of data used to calculate Frank-Kamenetskii parameter, based on calorimetric and heat transfer parameters. Pellet and coke conductivity taken from [56, 141]

<table>
<thead>
<tr>
<th></th>
<th>Poplar Pellet</th>
<th>Petroleum Coke</th>
<th>Railway Tie</th>
<th>Asphalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E/R$ (K)</td>
<td>10790</td>
<td>7220</td>
<td>7200</td>
<td>12000</td>
</tr>
<tr>
<td>$\sigma_{E/R}$ (K)</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$QA$ (W/g)</td>
<td>$1.2 \cdot 10^{10}$</td>
<td>$3.7 \cdot 10^{5}$</td>
<td>$1.1 \cdot 10^{5}$</td>
<td>$1.7 \cdot 10^{8}$</td>
</tr>
<tr>
<td>$\sigma_{QA}$ (W/g)</td>
<td>$2 \cdot 10^{9}$</td>
<td>$2 \cdot 10^{4}$</td>
<td>$2 \cdot 10^{4}$</td>
<td>$2 \cdot 10^{7}$</td>
</tr>
<tr>
<td>$\lambda$ (W/m·K)</td>
<td>0.154</td>
<td>0.3</td>
<td>0.0517</td>
<td>0.069</td>
</tr>
<tr>
<td>$\rho$ (g/m³)</td>
<td>$3.3 \cdot 10^{5}$</td>
<td>$4.97 \cdot 10^{5}$</td>
<td>$2.51 \cdot 10^{5}$</td>
<td>$4.49 \cdot 10^{5}$</td>
</tr>
<tr>
<td>$MC$ (wt%)</td>
<td>13.6%</td>
<td>&lt; 0.5%</td>
<td>6.2%</td>
<td>&lt; 0.5%</td>
</tr>
</tbody>
</table>

so the conductivity of loose fine asphalt at 40°C (0.0690 W/m·K) was used. The calorimetric railway tie dust sample had a moisture content of 6.3%, so the thermal conductivity of railway tie dust with 6.3% moisture content at 55°C (0.0517 W/m·K) was used. A higher temperature was specified, as railway tie dust would likely undergo a greater temperature increase than the asphalt because of its greater reactivity. Published conductivity data are available for both wood pellets [56] and petroleum coke [141], the values for which (0.154 and 0.300 W/m·K for the pellets and coke, respectively) were used to calculate critical sizes.

The critical sizes of cubes ($\delta_C = 2.57$) of each material were calculated using eqn. 3.2 — $r_C$ is a critical characteristic length, usually the distance from the geometric centre of a self-heating volume to the closest exterior surface; for a sphere ($\delta_C = 0.340$), $r_C$ is a critical radius, and for a cube, $r_C$ is one-half side length. Calculated critical cube side lengths (i.e., $2r_C$) are and presented and compared to data from oven tests available in the literature in Table 3.3. Published data includes oven test plots (eqn. 3.3), or kinetic parameters (i.e. activation energy and rate of reaction) deduced from oven tests or calorimetric studies. Petroleum coke appears to be more
stable than similarly-sized coal particles \( (d = 1.18 \text{ mm}) \) [135], probably because of differences in density or thermal conductivity; the similarity is sufficient to demonstrate that heat transfer and calorimetry experiments produce similar predictions to those obtained using oven tests. However, oven tests indicate significantly larger stable cube sizes for wood chips [5], sawdust [57] and pine pellets [4] than was calculated for either railway tie dust or wood pellets. The spontaneous combustion of wood products varies due to age, compositional and physical differences due to processing, but 75-90% decrease in critical size is a larger change than would be expected. This increased reactivity could be a result of smaller particle sizes, but is probably due to moisture content, as will be discussed below.

Table 3.3: Critical cube side length of various fuels at 40°C. Side lengths of study fuels are compared to the critical side lengths of other materials, as determined by oven tests or calorimetric methods

<table>
<thead>
<tr>
<th>Material</th>
<th>Test Type</th>
<th>Particle Size ( (\text{mm}) )</th>
<th>Moisture Content</th>
<th>Critical Cube Side Length ( (\text{m}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt Particles</td>
<td>Calorimetry/Conductivity</td>
<td>( 0.59 &lt; d &lt; 1.2 )</td>
<td>&lt; 0.5</td>
<td>58</td>
</tr>
<tr>
<td>Poplar Pellets</td>
<td>Calorimetry/Conductivity</td>
<td>6.4</td>
<td>13.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Railway Tie Dust</td>
<td>Calorimetry/Conductivity</td>
<td>( 0.59 &lt; d &lt; 1.2 )</td>
<td>6.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Petroleum Coke</td>
<td>Calorimetry/Conductivity</td>
<td>&lt;0.36</td>
<td>&lt;0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Coke</td>
<td>Oven Tests</td>
<td>Unknown</td>
<td>0 (( T&gt;100^\circ \text{C} ))</td>
<td>25</td>
</tr>
<tr>
<td>Sawdust [57]</td>
<td>Oven Tests</td>
<td>2</td>
<td>0 (( T&gt;100^\circ \text{C} ))</td>
<td>18</td>
</tr>
<tr>
<td>2 mm Wood Chips</td>
<td>Oven Tests</td>
<td>6.4</td>
<td>0 (( T&gt;100^\circ \text{C} ))</td>
<td>9</td>
</tr>
<tr>
<td>Wood Pellets [4]</td>
<td>Calorimetry/Conductivity</td>
<td>6.4</td>
<td>8</td>
<td>0.50</td>
</tr>
<tr>
<td>Wood Pellets [4]</td>
<td>Oven Tests</td>
<td>1.18</td>
<td>0 (( T&gt;100^\circ \text{C} ))</td>
<td>0.95</td>
</tr>
<tr>
<td>Bituminous Coal [135]</td>
<td>Oven Tests</td>
<td>1.18</td>
<td>0 (( T&gt;100^\circ \text{C} ))</td>
<td>0.95</td>
</tr>
</tbody>
</table>
The railway tie dust was smaller than wood chips (d = 2 mm), [5], and particle sizes were not reported for sawdust, [57]. Faster oxidization is expected for finer dust particles since their surface area is large. However, this does not explain the increased reactivity of the poplar pellets; rather, the reactivity is a result of moisture content, due to either hydrolysis [23] or water-activated oxidation [16]. Jones and Puignou [57] and Ferrero *et al.* [5] used oven tests, during which water evaporates from the samples. This has been observed previously when oven test results are compared to calorimetric tests. Guo’s [4] calorimetric study of pellet self-heating showed increased reactivity compared to oven tests when pellets from the same source were used. This is further supported by the results of coal oven tests; petroleum coke had low moisture content, and volumetric heating models for small coal particles (d = 1.18 mm) derived from oven tests show similar kinetics ($E/R = 7500$ K, $Q_A = 2.13 \cdot 10^5$ W/g) [135].

Despite accounting for moisture effects in spontaneous combustion predictions, caution must be given regarding moisture transport: calorimetric experiments enforced constant moisture content, while in a real pile transport effects such as condensation could cause temperature changes that might lead to spontaneous combustion. Convective effects and diffusion can cause moisture transport in fuel stores [66]. Calorimetry and hot plate tests prevent moisture transport, and therefore do not account for consequent effects such as condensation. Condensation has greatest influence on dried materials [41], and so moisture transport must be considered an indicator of increased spontaneous combustion risks in such cases. Moisture transport also leads to changes in moisture content, which affects other fuel self-heating and heat transfer processes that depend on absolute moisture content (*e.g.* water-activated
oxida\n
3.4. RESULTS AND DISCUSSION

These changes can be studied by varying moisture content in calorimetric or heat transfer tests. Therefore, extra care should be taken when studying the spontaneous combustion risks of materials that will undergo moisture transport.

Changing moisture content may also lead to microbial self-heating. As mentioned in the introduction, microbial degradation generates heat, which may lead to increasing temperatures and ignition. However, microbes require moisture to digest biological matter; for instance, microbes cannot digest wood if moisture content is less than 20\% [37]. The study fuels were sufficiently dry (< 15\%) to prevent microbial heating. However, if their moisture content were to increase due to moisture transport, microbial heating could occur.

Further caution must be given regarding asphalt — asphalt self-heating and heat transfer behavior may deviate from the assumptions of the FKP. Self-heating routinely raises internal temperatures to above 65\°C, which is above the softening temperature of asphalt. While asphalt conductivity increased after softening, it also compacted, which would alter the internal structure of the pile. What these structural changes might be have not been explored in this paper. Furthermore, asphalt self-heating may not follow an Arrhenius model. During the 50\°C calorimetric experiment, asphalt underwent a 10 h endothermic reaction, which was probably devolitization. As this reaction was not observed at higher temperatures, it is unclear that the Arrhenius model developed in this study accurately reflects low-temperature asphalt behaviour.
3.5 Conclusions

The combination of calorimetric and heat transfer experiments provide sufficient information to assess spontaneous combustion risks with the Frank-Kamenetskii parameter. Predictions made using calorimetry and heat transfer data account for moisture effects, which are not seen in oven tests. Railway tie dust is reactive and acts as a thermal insulator, whereas asphalt is inert and only slightly more conductive. Railway tie dust therefore has larger spontaneous risks than asphalt, as shown by the critical side length of cubes of each material (1.6 and 58 m, respectively). However, softening effects and endothermic reactions in asphalt may violate the assumptions of the Frank-Kamenetskii parameter. Further caution must be given regarding moisture transport; as discussed, the calorimetric experiment enforced constant moisture content, and transport effects such as condensation could cause temperature changes that would lead to spontaneous ignition.

3.6 Acknowledgements

The authors would like to thank Lafarge, Canada for providing sample materials and funding support, as well as Kenneth Trischuk at NRC and Dr. Nathan Hess at TA Instruments for their assistance with calorimetry. Funding for this research was provided by the Ontario OCE TPS program, Lafarge Cement and Queen’s University for graduate student support.
3.7 Chapter Summary

This chapter presented a spontaneous combustion study of creosote-treated railway tie dust and asphalt roofing shingle particles. Poplar wood pellet and petroleum coke self-heating were also studied. As was discussed, oven tests cause sample drying, which affects spontaneous combustion properties. Therefore, an Arrehnius heating model was developed from calorimetric self-heating measurements, and a characteristic thermal conductivity value was determined with a guarded hot plate. These data were used to calculate the Frank-Kamenetskii parameter and thereby evaluate critical conditions for spontaneous combustion. It was found that railway tie dust is reactive, and presents high spontaneous combustion risks. In contrast, asphalt is unreactive and presents low spontaneous combustion risks. Further details regarding the guarded hot plate and calorimetric experiments are given in Appendices A and B, respectively.

The next chapter presents an analysis of asphalt shingle and railway tie chemistry. Both materials may have been affected by weathering, and may exhibit different spontaneous combustion behaviour as compared to their pristine or initial product states. Therefore, they were studied with py-GC/MS, a method of analysing solid chemistry. Thus, Chapter 4 determines what chemical changes occurred as these fuels weathered.
Chapter 4

The Effects of Weathering on the Pyrolysis of Two Low-Carbon Fuels
The Effects of Weathering on the Pyrolysis of Two Low-Carbon Fuels

G. Leslie, A. Rutter, A. Pollard, and D. Matovic

Queen’s University at Kingston
ON K7L-3N6 CANADA

Abstract

Creosote-treated wooden railway ties and roofing asphalt shingles are discarded in large quantities, and may be significant energy sources; however, they may have rotted or oxidized, and the chemical changes that result from such weathering would affect their behaviour as a fuel or pyrolysis feedstock. Such changes in railway tie wood and roofing asphalt shingles were studied by identifying isothermal 250° and 550°C pyrolysis products with pyrolysis-Gas Chromatography/Mass Spectrometry (py-GC/MS). Poplar wood pyrolyzates were also identified. Rotting or oxidation did not cause sufficient chemical changes in the railway tie wood to affect its pyrolyzates. 250°C wood pyrolyzates also included the products of polysaccharide ring-breaking and lignin pyrolysis, confirming other low-temperature pyrolysis studies. Roofing asphalt pyrolyzates included many carbonyl, hydroxy and ether functionalized cyclic species, as well as sulfur dioxide; these pyrolyzates indicate extensive and preferential oxidation of cyclic carbon and sulfur.
4.1 Introduction

Solid end-of-life materials, wastes and virgin biomass are used as fossil fuel alternatives, as they have lower life-cycle carbon emissions than coal. These fuels are collectively known as low carbon fuels, or LCFs. Their combustion and pyrolysis behaviour depends on their chemical makeup. Many end-of-life LCFs will have undergone significant weathering (i.e. oxidation or microbial digestion), which may have changed their chemistry compared to their initial product state. In particular, large quantities of creosote-treated wooden railway ties and roofing asphalt shingles are discarded every year [98, 112]. Discarded railway ties are typically 35 years old [98], whereas the age of waste shingles ranges from 12 to 20 years [112]. To better use these materials as fuels or pyrolysis feedstocks, the effect of weathering on their chemistry must be explored. Pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) has shown the chemical structure of many fuels, as well as fuel pyrolysis behaviour, by identifying and quantifying pyrolysis products or “pyrolyzates” [122]. Py-GC/MS has been particularly useful for studying wood, [114], and may also show such chemical changes that have occurred in LCFs such as railway tie wood or roofing asphalt shingles.

Wooden railway ties are treated with creosote, and so their chemistry depends on wood and creosote. Wood is primarily composed of three bio-polymers— two polysaccharides, cellulose and hemicellulose, and a phenolic polymer, lignin [92]. All three polymers rot or oxidize — for instance, the carbonyl content of lignin increases during oxidation or microbial digestion [142]. Creosote is a coal tar distillate with antibacterial and antifungal properties, and is predominantly composed of aromatic and polycyclic aromatic hydrocarbons [89]. Creosote does not affect wood chemistry,
except in that it preserves the wood and may prevent chemical changes; however, rotting and oxidation depend on environmental factors, and creosote does not completely halt microbial activity [95]. It is therefore difficult to predict the extent of rot or oxidation that may occur before the disposal of a railway tie. During pyrolysis, wood polysaccharides produce pyranic and furanic compounds, while lignin produces phenolic species; these pyrolyzates show polymer structure [143, 144, 145]. Railway tie pyrolyzates may show to what extent its creosote and wood chemistry have changed due to oxidation or rotting.

Pyrolyzates may also indicate to what extent roofing asphalt shingles have oxidized, particularly their asphalt fraction. Asphalt is produced from the residuum of petroleum fractionation, or harvested from bitumen. Asphalt chemistry is complex, and depends on its source and processing; however, the gross chemical structure of asphalt is well understood. Asphalt is a homogeneous, impermeable, colloidal substance composed of solids (asphaltenes) distributed in an oily matrix (maltenes) [102]. Asphaltenes are large molecules, composed of cyclic cores connected by aliphatic bridges. Maltenes are smaller, and may be divided into saturated, aromatic and resinous fractions. Asphalt may be oxidized during production, and may also oxidize under exposure to light and air; oxidized asphalt contains sulfone, carbonyl and hydroxy functions [105, 107]. During pyrolysis, asphaltenes tend to produce cyclic and linear pyrolyzates (from cyclic or aliphatic structures [118, 146, 147]), whereas maltenes tend to evaporate [147]. Therefore, oxygenated pyrolyzates may be associated with specific asphalt structures, and thereby show the extent and pathway of asphalt oxidation.
In addition to studying asphalt roofing shingle and railway tie weathering, py-GC/MS may give new information regarding low-temperature \( (T < 300^\circ C) \) wood pyrolysis. As discussed above, wood is composed of cellulose, hemicellulose and lignin, each of which pyrolyze differently. Wood pyrolysis therefore produces a complex mixture of different species, many of which are commercially valuable as fuels or raw materials [148]. Wood pyrolysis is therefore a subject of interest, and poplar pyrolysis has been particularly well-studied [143, 148, 149, 150]. However, the mechanism of wood pyrolysis — specifically, of the cellulose fraction — is disputed. Diebold [151] proposed that cellulose pyrolysis proceeded by competing dehydration, chain cleavage, vapourization and char-formation reactions (Figure 4.1). According to that model, low-temperature cellulose pyrolysis produces char, water, a small amount of carbon dioxide and a smaller amount of oxygenated, gaseous hydrocarbons. However, Gu et al. [152] observed that 250-350\(^\circ C\) poplar pyrolysis produced more carbon dioxide than water, which is inconsistent with Diebold’s model. Gao et al. [120] observed similar CO\(_2\) emissions during low-temperature pine pyrolysis. In response to these findings, Gu et al. proposed that cellulose and hemicellulose pyrolysis proceeded by depolymerization and pyranose ring-breaking; products of these reactions may further degrade to oxygenated hydrocarbons or repolymerize into char (Figure 4.2).

Low-temperature pyrolysis has been studied with hyphenated thermogravimetric techniques, particularly thermogravimetric-mass spectrometry (TG-MS) and thermogravimetric-fourier transform infrared spectroscopy (TG-FTIR). These techniques can only identify permanent gases or small hydrocarbons, as they do not separate pyrolyzates [153]; for instance, the largest pine pyrolyzate identified in Gao et al.’s TG-FTIR study was phenol \((M = 94 \text{ u})\) [120]. Py-GC/MS is capable of identifying
much larger pyrolyzates, by separating pyrolyzates in the gas chromatograph. Py-GC/MS has been used to study high-temperature pyrolysis (T > 350°C); however, as pyrolysis has a slow rate of reaction at low temperatures, it has been difficult to study low-temperature pyrolysis with py-GC/MS [143]. Increasing sample mass or pyrolysis time may sufficiently increase the rate of eluted gases to identify pyrolyzates; such pyrolyzates may confirm, or disconfirm, Gu et al.’s proposed pyrolysis mechanism.

Therefore, in this study, the 250°C and 550°C pyrolysis products of poplar wood, discarded creosote-treated wooden railway ties and discarded roofing asphalt shingles were identified with py-GC/MS. As 550°C poplar pyrolysis is well-understood, poplar pyrolysis was studied as a reference reaction, and identified species assisted in the
analysis of railway tie and roofing asphalt pyrolyzates. Railway tie and roofing asphalt 250°C and 550°C pyrolyzates were identified and analyzed to determine the effects of before-disposal weathering. Railway tie and poplar 250°C pyrolysis products were further examined for consistency with Diebold’s and Gu et al.’s pyrolysis mechanisms.

4.2 Experimental Approach

4.2.1 Materials

A discarded, creosote-treated wooden railway tie, which was at least 20 years old, was obtained from near Gananoque, Ontario. Poplar (Populus hybrid) was harvested from a greenhouse near Cornwall, Ontario. Waste asphalt shingles were provided by the Lafarge, Canada St. Constant cement plant in Quebec. Since these samples, with the exception of poplar, were harvested from waste processes, it was difficult to determine their history or species. Asphalt and railway tie samples were oven-dried at 104°C and then milled or cut to pass through a 1190 μm sieve, whereas the poplar sample was oven dried and ground to pass through a 250 μm sieve.

Proximate and ultimate analysis of the asphalt and railway tie dust samples (Table 4.1) were performed according to ASTM E1755, ASTM D5291 and ASTM E3177, by Keystone Materials Testing. The ultimate analysis of poplar was available in the literature, and was taken from Gu et al. [152].

4.2.2 py-GC/MS analysis

Pyrolysis was performed with a CDS 5000 pyroprobe, directly interfaced to a gas chromatograph/mass spectrometer (HP 5890 Series II GC/HP 5972 MS) with a CDS 1500 on-column interface. Helium was used as the carrier gas, at a constant flow
4.2. EXPERIMENTAL APPROACH

Table 4.1: Proximate and ultimate analysis of materials, given on a dry basis by weight percent

<table>
<thead>
<tr>
<th></th>
<th>Railway Tie</th>
<th>Asphalt</th>
<th>Poplar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>1.2</td>
<td>42.4</td>
<td>4.1</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>86.6</td>
<td>53.5</td>
<td>83.6</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>12.2</td>
<td>4.1</td>
<td>12.3</td>
</tr>
<tr>
<td>C</td>
<td>50.50</td>
<td>31.64</td>
<td>45.50</td>
</tr>
<tr>
<td>S</td>
<td>0.07</td>
<td>1.43</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>5.94</td>
<td>3.55</td>
<td>6.26</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>0.17</td>
<td>1.04</td>
</tr>
<tr>
<td>O</td>
<td>42.25</td>
<td>20.81</td>
<td>47.20</td>
</tr>
</tbody>
</table>

rate of 1.2 ml/min. The mass spectrometer ran in electron ionization mode at 70 eV, and detected ions with a mass-to-charge ratio between 50 and 500 u/e. Compounds were identified by their retention times and by comparing their mass spectra to the NIST/EPA/NIH mass spectral library with the NIST mass spectral search program (version 1.6, 1997).

Accurately weighed 10-20 mg samples of each study material were pyrolyzed in glass tubes at 550°C for 10 s. Both ends of each sample tube were packed with quartz wool to prevent sample movement during pyrolysis. Pyrolyzates were eluted through a fused silica Agilent HP-5MS column (phenyl-methylpolysiloxane film, 30 m length × 0.25 mm ID × 0.25 μm film). During separation, the column temperature was held at 50°C for 2 minutes, then ramped to 300°C at 10°C/min, and held at 300°C for 5 minutes.

15-20 mg samples of the three study materials were similarly pyrolyzed at 250°C for 40 s. The 250°C pyrolyzates were eluted through a fused silica Supelco VOCOL™ column (60 m length × 0.32 mm ID × 1.8 μm film). During separation, the column temperature was held at 50°C for 2 minutes, then ramped to 200°C at 10°C/min, and
held at $200^\circ$C for 10 minutes.

### 4.3 Presentation and Discussion of Results

Pyrolysis produced over 100 chromatographic peaks (Figures 4.3 and 4.4). Over 75 pyrolyzates were identified, including furans, paraffins, olefins, and many saturated and aromatic cyclic species (Tables 4.2 and 4.3); however, as several peaks showed poor signal-to-noise ratios and some analytes co-eluted, the software could only partially identify several compounds. It is also interesting to note that the pyrolysis of 15-20 mg samples for 40 s at $250^\circ$C produced detectable concentrations of several compounds — as discussed above, previous py-GC/MS studies use pyrolysis temperatures of $350^\circ$C or higher.

#### 4.3.1 Poplar Wood and Low-Temperature Pyrolysis

As discussed in the introduction section, poplar pyrolysis is well studied; therefore, $550^\circ$C poplar pyrolysis products were identified and compared to extant pyrolysis literature. These pyrolyzates were consistent with published results [143, 148, 149, 150, 152, 154, 155]. In particular, characteristic lignin (i.e. guaiacol, syringol), cellulose (furfural) and hemicellulose (methylfuran) pyrolyzates were identified. Some poplar pyrolyzates (indole and heptacosane) are associated with leafy matter [121], which possibly means that some leaves or bark were mixed into the ground poplar sample. Nonetheless, the molecular masses and retention times of asphalt and railway tie pyrolyzates were compared to the molecular mass and retention times of known poplar pyrolyzates; this cross-comparison made identifications more certain.
4.3. PRESENTATION AND DISCUSSION OF RESULTS

Figure 4.3: Total ion chromatograms of railway tie (A), poplar (B) and asphalt (C) 550°C pyrolysis. Numbered peaks identified in Table 4.2
Figure 4.4: Total ion chromatograms of railway tie (A), poplar (B) and asphalt (C) 250°C pyrolysis. Numbered peaks identified in Table 4.3
### 4.3. PRESENTATION AND DISCUSSION OF RESULTS

Table 4.2: Identified compounds in 550°C pyrolysis chromatograms

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Mass</th>
<th>Railway Tie</th>
<th>Poplar</th>
<th>Asphalt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td># Ret. Time</td>
<td># Ret. Time</td>
<td># Ret. Time</td>
</tr>
<tr>
<td>Furan</td>
<td>68</td>
<td>1.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylfuran</td>
<td>82</td>
<td>2.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m/z=60 (^1)</td>
<td>60</td>
<td>2.18</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>92</td>
<td>3.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propionic acid</td>
<td>74</td>
<td>3.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furfural or 2,5-Dimethylfuran</td>
<td>96</td>
<td>4.49</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>1,4 Dimethylpyrazole</td>
<td>96</td>
<td></td>
<td></td>
<td>4.55</td>
</tr>
<tr>
<td>Styrene</td>
<td>104</td>
<td>5.41</td>
<td>5.50</td>
<td></td>
</tr>
<tr>
<td>Trimethylfuran(^2)</td>
<td>110</td>
<td></td>
<td></td>
<td>5.74</td>
</tr>
<tr>
<td>Cyclohexanone or 2-Methylcyclopentane</td>
<td>98</td>
<td>5.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Furanmethanol</td>
<td>98</td>
<td>6.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethylfuran</td>
<td>110</td>
<td>6.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>94</td>
<td>7.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,4-dihydro-2-methoxypyran</td>
<td>114</td>
<td>7.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl(tert-butyl)amine</td>
<td>129</td>
<td>7.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corylon</td>
<td>112</td>
<td>7.69</td>
<td></td>
<td>7.68</td>
</tr>
<tr>
<td>Methylphenol(^2)</td>
<td>108</td>
<td>8.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylphenol(^2)</td>
<td>108</td>
<td>8.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,4-Trimethyl-2-cyclopenten-1-one</td>
<td>124</td>
<td>8.68</td>
<td></td>
<td>3 8.68</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>124</td>
<td>8.69</td>
<td></td>
<td>8.69</td>
</tr>
<tr>
<td>O-Decylhydroxylamine</td>
<td>173</td>
<td>8.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylbenzofuran</td>
<td>132</td>
<td>8.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylethylalcohol</td>
<td>122</td>
<td>9.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4 Alkylbenzene(^3)</td>
<td>134</td>
<td>9.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-(2-Propynyloxy)-2-pentanol</td>
<td>142</td>
<td>10.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methoxy-4-methylphenol</td>
<td>138</td>
<td>10.27</td>
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### 4.3. PRESENTATION AND DISCUSSION OF RESULTS

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<th>Poplar #</th>
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<th>Asphalt #</th>
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<td>Palmitic acid</td>
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<td>Heptacosane or Octacosane</td>
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<td></td>
<td>26</td>
<td>26.88</td>
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250°C poplar pyrolyzates were similarly compared to 250°C railway tie and asphalt pyrolysis products, and to pyrolyzates predicted by Gu et al.’s and Diebold’s pyrolysis mechanisms. According to Deibold, cellulose depolymerizes to “active cellulose”, which then degrades to char, permanent gases, and oxygenated hydrocarbons (Figure 4.1) [151]. In contrast, Gu et al. proposed that cellulose depolymerizes

<sup>1</sup>This spectra showed only one m/z=60 peak. Acetic acid, methylformate or hydroxyacetaldehyde could produce this spectra, as the spectrometer detected ions with m/z in 50-500

<sup>2</sup>Isomers of these species produce similar mass spectra

<sup>3</sup>Dimethyl-ethyl-benzene, diethylbenzene, and tetramethylbenzene produce similar mass spectra

<sup>4</sup>Alkane/alkene pairs are produced by the pyrolysis of asphaltene, however, these spectra could not specify length
### Table 4.3: Identified compounds in 250°C pyrolysis chromatograms

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Mass</th>
<th>Railway Tie</th>
<th>Poplar</th>
<th>Asphalt</th>
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<td></td>
<td></td>
<td># Ret. Time</td>
<td># Ret. Time</td>
<td># Ret. Time</td>
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<tr>
<td>Sulfur Dioxide m/z=60</td>
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<td>5.20</td>
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<td>8.48</td>
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<td>Dimethylpentanal</td>
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<td>Benzyl alcohol or Methylphenol</td>
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<td>2-Methylfurandione</td>
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<td>Napthalene</td>
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to anhydrosugars; cellulose and anhydrosugars may further undergo pyranose ring-breaking or repolymerize into char (Figure 4.2) [152]. Both mechanisms predict that, at 250°C, cellulose pyrolysis produces water and carbon dioxide; however, the mass spectrometer used in this study could not identify these gases due to their small mass (M = 18 u and 44 u, respectively). Nonetheless, the mass spectrometer could identify compounds with M > 64 u. Diebold’s model predicts that only trace amounts of these larger compounds (on order \(\mu g/g\)) would be produced at 250°C. Poplar and railway tie pyrolysis produced detectable concentrations of dimethyl furan, furanone, and furandione. The production of such species in detectable quantities at 250°C is more consistent with Gu et al.’s model than Diebold’s. Lignin pyrolyzates (e.g. phenol and methylphenol) were also detected; lignin pyrolysis begins at low temperatures (200°C) [120].
4.3. PRESENTATION AND DISCUSSION OF RESULTS

4.3.2 Railway Tie Wood

Railway tie wood pyrolyzates, particularly those that originated from lignin pyrolysis, were examined for signs of wood oxidation or microbial degradation. Both processes cause characteristic chemical changes in lignin, notably the addition of carbonyl, carboxyl and hydroxy groups [142], and the removal of methoxy groups and destruction of syringyl [156]. Weathering also consumes wood polysaccharides, but does not leave characteristic polysaccharide markers. Identified railway tie wood pyrolyzates did not show a demonstrable increase in oxygen functions, or a decrease in syringyl content; in fact, the pyrolyzates were typical of oak pyrolysis [115].

Lignin pyrolysis produces many benzoic and phenolic species; only two such railway tie pyrolyzates (trimethoxybenzene and dimethylbenzaldehyde) are atypical of wood pyrolysis. Dimethylbenzaldehyde is a possible result of rotting, as it contains a carbonyl group; trimethoxybezene indicates the opposite. The railway tie wood also had a low oxygen-to-carbon ratio (0.84), which is typical of hardwoods [157]. Further, as shown by relative peak areas (Figure 4.5), the railway tie wood lignin had abundant syringyl — the railway tie wood released proportionally more syringol and syringol derivatives, than guaiacol and guaiacol derivatives. Thus, the railway tie lignin lacks the characteristic chemical changes discussed above, and it is unlikely that the tie underwent extensive oxidation or microbial degradation. The railway tie retained some creosote, as evidenced by the napthalene and anthracene pyrolyzates. Creosote probably protected the railway tie from significant rotting, though other ties may be more degraded.
Figure 4.5: Normalized peak areas of representative compounds identified in 550°C railway tie dust and poplar chromatograms

4.3.3 Asphalt

Roofing asphalt produced fewer pyrolyzates than either the railway tie or poplar samples. Sufficient pyrolyzates were eluted to partially or completely identify 36 species. Some of the identified products were similar to asphaltene [118, 158] and natural asphalt [147] pyrolyzates; however, pyrolysis also produced many oxygenated species, which is atypical of asphaltene or asphalt pyrolysis. As the asphalt had high oxygen content (20.8%), these compounds are products of asphalt oxidation. It is interesting to note that some asphalt pyrolyzates were functionalized with ether groups (e.g. 2-methoxy-4-methylphenol); previous studies have found carbonyl or hydroxy groups following oxidation, but not ethers.
4.4. CONCLUSIONS

In addition to showing that the asphalt was heavily oxidized, asphalt pyrolyzates show that oxidation favoured sulfur or cyclic carbon structures. Previous asphalt pyrolysis studies have detected organosulfurs, particularly thiophenic species [116, 117]. Their absence in these results is striking. Thiophene would have been detected if produced at low concentrations (<500 μg/g), as was shown by doping samples with a thiophene standard; therefore, organosulfurs could only have been produced at low concentrations. Only one sulfur compound — sulfur dioxide — was produced in detectable concentrations. It is likely that whatever sulfur was present in the asphalt was oxidized during either production or weathering — sulfur in asphalt oxidizes to form sulfoxides or sulfones [110, 111]. These structures could have degraded into sulfur dioxide during pyrolysis. Other pyrolyzates indicated that oxidation favoured cyclic carbon. Asphalt molecules generally take the form of polycyclic cores linked by aliphatic bridges; during pyrolysis, aliphatic bridges undergo beta-scissioning and form alkane/alkene pairs, whereas polycyclic cores degrade into smaller cyclic compounds [158]. Pyrolysis produced unoxidized alkane/alkene pairs, whereas the majority of detected cyclic products were oxidized.

4.4 Conclusions

High-temperature (550°C) poplar pyrolysis products were consistent with existing pyrolysis literature, and served as a good references when identifying of other pyrolysis products. Low-temperature pyrolysis was made to produce compounds in detectable concentrations by increasing sample mass and pyrolysis time, as compared to other wood pyrolysis studies. Low-temperature (250°C) wood pyrolyzates included products of Gu et al.’s proposed depolymerization/pyranic ring-breaking pyrolysis
mechanism, and were not predicted by Diebold’s char-formation model; thus, the low-temperature pyrolysis products were more consistent with Gu et al.’s proposed mechanism.

The ultimate analysis and pyrolysis products of the railway tie wood showed few signs of bacterial degradation or oxidation, indicating that this particular tie did not undergo extensive weathering. While different railway ties may undergo different amounts of weathering, this research shows that discarded railway ties may act similarly to hardwood when used as fuel or pyrolysis feedstock.

In contrast, the roofing asphalt had high oxygen content, and produced many oxygenated species during high- and low-temperature pyrolysis; the asphalt was extensively oxidized, either during production or in use. Oxidation appeared to favour cyclic and sulfuric compounds, as indicated by the number of oxygenated cyclic species, the production of sulfur dioxide during low-temperature pyrolysis, and the absence of other sulfurous compounds. Interestingly, ether functions were detected, which are atypical products of asphalt oxidation. Roofing asphalt pyrolyzates were otherwise typical of asphaltenes and asphalt pyrolysis.

4.5 Acknowledgements

The authors would like to thank Lafarge, Canada for providing sample materials and financial support. Funding for this research was provided by the Ontario OCE TPS program, Lafarge Canada, and Queen’s University for graduate student support.
4.6 Chapter Summary

This chapter examined the chemistry of creosote-treated railway tie wood, asphalt roofing shingles and poplar wood, in order to determine the effects of weathering on fuel chemistry. To that end, fuel samples were pyrolyzed and identified with py-GC/MS. The railway tie wood was not affected by weathering, whereas asphalt was extensively oxidized. Pyrolysis products also gave information regarding pyrolysis mechanisms, though that information is not the focus of this thesis.

Chapter 3 determined the reactivity and spontaneous combustion behaviour of railway tie wood and asphalt. Samples for both that study and this analysis were taken from the same source. Chapter 5 summarizes and compares the results of both studies in order to determine how weathering changes spontaneous combustion behaviour.
Chapter 5

Summary and Conclusions

5.1 Conclusions

This thesis focused on determining LCF spontaneous combustion risks, and analysing LCF chemistry in order to explain those risks. Experiments were carried out to measure LCF self-heating and thermal conductivity, and a pyrolysis study was performed in order to determine the extent of LCF weathering. The following conclusions can be drawn from this study.

5.1.1 LCF Spontaneous Combustion Risks

Chapter 3 presents a self-heating and heat transfer study of poplar pellets, petroleum coke, railway tie wood dust and roofing asphalt shingle particles. Self-heating was measured using isothermal differential calorimetry. The self-heating of each fuel was primarily oxidative, and consistent with a volumetric Arrhenius heating model. Poplar pellet and railway tie dust self-heating was greater than is reported in the literature, possibly because of moisture effects. In contrast, petroleum coke self-heating was similar to coal self-heating, and asphalt self-heating was negligible.
The heat-transfer behaviour — specifically, the thermal conductivity — of railway tie wood dust and roofing asphalt shingle particles were measured by a single-sided, heat-flow compensated, guarded hot plate. Conductivity was measured at various temperatures and, in the case of the railway tie wood dust, at various moisture contents. The dry asphalt particles had greater thermal conductivity than the railway tie wood dust. Conductivity also increased with temperature and moisture content. A conductivity hysteresis was further observed in asphalt, as asphalt softens at 55°C.

These self-heating and thermal conductivity measurements were used to evaluate spontaneous combustion risks with the Frank-Kamenetskii parameter. Calculations showed that the railway tie wood dust was much more likely to spontaneously combust than the asphalt — a cube of the asphalt, 55 m to a side, would be stable at 40°C, whereas a 2 m cube of the railway tie dust would spontaneously combust at the same temperature.

5.1.2 Chemical Investigation

Chapter 4 presents a py-GC/MS study of creosote-treated railway tie wood, poplar wood, and roofing asphalt shingles. The study examined railway tie wood and asphalt pyrolyzates for signs of weathering. Poplar wood was examined as a reference material, as poplar wood pyrolysis is well understood. Asphalt pyrolysis produced many oxygenated species, because the asphalt underwent extensive oxidative weathering or was oxidized during production. In contrast, the railway tie wood pyrolyzates were typical of creosote-treated wood, indicating that the tie did not weather extensively.

It is interesting to compare the self-heating behaviour of the railway tie wood and asphalt to their degree of weathering. As discussed above, railway tie dust self-heating
was greater than that reported for wood self-heating, whereas asphalt self-heating was negligible. As self-heating was primarily oxidative, weathering probably decreased asphalt self-heating. However, asphalt is also impermeable, and oxidation could also have been slow due to reduced access to active sites.

5.2 Reccomendations

Lafarge, Canada intends to store LCFs in two walking floor bins on-site at their Bath cement plant. These bins are larger then the maximum safe size of the woody fuels studied in this thesis — a 4.1 m$^3$ cube of railway tie dust would self-ignite at 40$^\circ$C, whereas the bins have a volume of 450 m$^3$. In contrast, the asphalt fuel is sufficiently stable to not ignite within the Lafarge bins, and may in fact act as a dilutent. Lafarge should therefore express caution storing railway tie wood or similar fuels, as they may spontaneously combust after as little as two days of static storage.

However, as discussed in the previous section, the railway tie wood was relatively pristine, and the asphalt extremely oxidized. Thus, a volume of less-weathered asphalt may have lower self-ignition thresholds than were identified in this study. Lafarge should therefore express more caution when storing ‘fresh’ fuels than when storing ‘weathered’ fuels.

5.3 Future Work

Pyrolysis experiments demonstrated that the asphalt was extensively oxidized, whereas the railway tie wood was well-preserved. LCFs are to be harvested from waste streams — it is likely that differently weathered fuels will be included in the same storage bin.
The extent and range of LCF weathering, and its effects on LCF spontaneous combustion, should be investigated.

The calorimetry/heat transfer method presented in Chapter 3 may be the method of choice for such an investigation, as the method retains sample moisture and therefore accounts for effects such as water-activated oxidation. Isothermal oven tests are performed at high temperatures, and therefore cause sample drying. A course of calorimetry/heat transfer experiments is also considerably faster than a course of oven tests, and requires much smaller samples. Thus, calorimetric/heat transfer experiments are more convenient, and may be more accurate, than oven tests.

However, isothermal oven tests are well understood, and calorimetric self-heating experiments are relatively novel and much less common. Further, while the method assumes constant moisture content, real fuel stores will exchange water with the storage environment, and internal temperature gradients can cause changes in fuel moisture content within the same fuel store. While such moisture effects are not easily studied without numerical methods, they can significantly affect spontaneous combustion. Thus, calorimetric results should be treated with a degree of caution until the method is verified. A verification study might compare calorimetric and oven test measurements of an homogeneous, chemically consistent material such as protein powder, and further compare these results to the behaviour of large-scale storage tests.
Bibliography


[53] A. Gertrude, *Thermal properties of selected materials for thermal insulation available in uganda*. Master’s, Makerere University, Kampala, Uganda, 2011.


Appendix A

Guarded Hot Plate Design and Construction

This Appendix describes the design, construction validation and use of the single-sided, heat flow compensated guarded hot plate used in Chapter 3. Section A.1 describes the design and construction of the apparatus; Section A.2 describes the experimental procedure; and Section A.3 provides a discussion of the experimental error associated with the apparatus and procedure, as well as validation tests.

A.1 Design and Construction

A guarded hot plate generates a known, one-dimensional heat flux through sample layers, such that, within a specific metered area, the samples act as slabs of infinite width, bound by isothermal planes of different temperature [59]. To achieve this, a guarded hot plate makes use of a heater plate, an annular guard around that heater plate, and one or more cold plates, as described in Section 2.1.2 (Figure 2.3). As the guard plate minimizes stray radial heat flows from the heater plate, and the width of the device minimizes lateral heat flows in the sample layer, heat flux between the heater and cold plates is effectively one-dimensional. This region between the heater plate and cold plate is known as the metered area, as mentioned above. As the
heat flux in the metered area is therefore known, and the temperature gradient is
determined by the temperature difference between the heater and cold plates as well
as sample thickness, thermal conductivity may be calculated by

$$\lambda = \frac{\tilde{q} L}{T_{HP} - T_{CP}}$$  \hspace{1cm} (A.1)$$

where $\lambda$ is thermal conductivity, $\tilde{q}$ is heat flux, $T_{HP}$ is the temperature of the guard
and heater assembly, and $T_{CP}$ is the temperature of the cold plate.

This arrangement may be achieved using single-sided or double-sided hot plates.
The operation of a single-sided guarded hot plate is simpler than that of a double-
sided hot plate, especially when measuring the conductivity of granular materials.
Set-up involves establishing a level sample layer of uniform thickness; establishing
two layers of uniform thickness is more difficult. Control of a double-sided guarded
hot plate is also more complex, as one must control the temperature of two cold
plates. For these reasons, a single-sided, heat-flow compensated guarded hot plate
was constructed (Figure A.1).

![Figure A.1: Schematic of the as-built, single-sided heat-flow compensated guarded
hot plate](image)

A single-sided, heat-flow compensated guarded hot plate tests the conductivity
of a single sample layer (hence, “single-sided”). Such a plate therefore has only two
A.1. DESIGN AND CONSTRUCTION

Figure A.2: Schematic of single-sided, heat-flow compensated guarded hot plate

The geometry of the guard also changes; the guard plate wraps around and below the heater plate (Figure A.2). A heat-flow compensated guard plate further incorporates a heat flow sensor between the guard and heater plates. This sensor has two purposes: first, when heat flow between the guard and heater plates is minimized, the plates approach an isothermal condition. Second, the remaining stray heat flows between the guard and heater may be measured [138].

A.1.1 Dimension and Material Design

As discussed above, a guarded hot plate enforces a one-dimensional temperature gradient in a wide, flat sample, and measures the heat flux required to establish that gradient. Thermal conductivity may then be calculated by eqn. A.1. Eqn. A.1 is valid if $\tilde{q}$ and $T_{HP} - T_{CP}$ are measured at steady-state, there are negligible lateral heat flows within the sample layer, and minimal stray heat flows between the guard and heater plates. The width and thickness of the sample, and the width of the guard and heater plates, minimize lateral heat flows. The width of the guarded hot plate was therefore determined by target sample thickness; target sample thickness was in turn determined by LCF grain size.

LCFs are granular materials, and the effects of voids and contact resistances must be considered. Granular materials act as homogeneous insulators during steady-state
heat transfer [63]; however, the characteristic dimensions of a heat transfer experiment must be larger than the sample particle size. Donk and Tollner [159] measured the thermal conductivity of wood chips (average size: $27 \times 8.2 \times 3.9$ mm). They observed no conductivity differences or void effects in 3-4 cm thick sample layers. Their chips were significantly larger than the largest tested LCF (coarse asphalt, average size: $19.8 \times 13.0 \times 2.4$ mm). 3 cm is therefore a sufficient thickness for measuring LCF thermal conductivity; therefore, the apparatus was designed to accommodate a 3 cm sample layer.

The width of the guard and heater plates were chosen after choosing sample thickness, in order to minimize lateral heat flows. Such heat flows are effectively minimized when the sample and guard plate are ten times wider than the sample thickness, and when the guard plate width is at least twice that of the heater plate [60]. Therefore, the guard plate width was fixed at 30 cm, and the heater plate width was fixed at 10 cm.

Temperature variations in the plates should also be minimized, to ensure that the plates are isothermal. To accomplish this, the guard, heater and cold plates were machined from aluminum. The Biot number provides a measure of temperature variations in a conductive object [160]. The Biot number is given by

$$Bi = \frac{h \cdot L_S}{\lambda_S}$$

(A.2)

where $h$ is the surface heat transfer coefficient, $L_S$ is a characteristic length of the object (for a plate, half width), and $\lambda_S$ is thermal conductivity. Temperature variations would be expected for $Bi > 0.1$. If the object is surrounded by insulation, as is the case for the heater or guard plates in contact with the sample layer, $h$ depends
on the thermal conductivity of the insulation

\[ h = \frac{\bar{q}}{\Delta T} = \frac{\lambda}{\Delta T} \frac{dT}{dx} = \frac{\lambda}{L} \]  

(A.3)

Therefore, the Biot number for the guard, heater or cold plates is given by

\[ Bi_P = \frac{L_S \cdot \lambda}{L \cdot \lambda_S} \]  

(A.4)

LCF thermal conductivity ranges from 0.01-0.5 \( \frac{W}{m \cdot K} \), whereas the thermal conductivity of aluminum is 205 \( \frac{W}{m \cdot K} \). The guard plate Biot number is thus of order \( 10^{-2} - 10^{-3} \); therefore, the guard, heater and cold plates did not present surface temperature variations.

### A.1.2 Guard and Heater Assembly

The guard and heater assembly formed the bottom plate of the test unit. It was assembled from an aluminum guard plate, heat flux sensor, aluminum spacer, and aluminum heater plate (Figure A.3). Component surfaces were bridged with thermal paste (Thermalcote I, AAVID Thermalloy) to minimize contact resistances and provide mechanical binding.

As shown in Figure A.4, there was a 0.3 mm difference in height between the heater and guard plate surfaces. There was also a horizontal gap of 6 mm between the guard plate and test heater surfaces. This gap was covered with aluminum tape during experiments.
Figure A.3: Guard and heater assembly.

Guard Plate

The guard plate (Figure A.5) was machined from aluminum. The plate was 300 mm square, with a square pocket $113 \times 113 \times 6$ mm deep, milled in the centre. Two access holes were drilled into the plate: one 10.4 mm in diameter, and one 3.2 mm in diameter. A $3.2 \times 25.4 \times 2$ mm channel was milled along the guard surface from the 3.2 mm hole to secure the guard control thermocouple.
The guard plate was held above the insulation block using wooden spacers. It was heated from below by a 305 × 305 mm heat sheet, controlled by an Omega CN9000A on/off PID temperature controller. The guard control thermocouple, an uncalibrated cold-junction type K, was inserted into the guard thermocouple channel and covered in aluminum tape. Uncalibrated cold-junction type K are accurate to ±1°C. During operation, the guard plate temperature was stable to ±0.1°C.

**Heat Flux Sensor**

The heat flux sensor (EKO Instruments, MF-200: 50 × 50 × 0.7 mm) was placed directly onto the guard plate. The heat flux sensor provided two functions. First, it measured stray heat flows between the guard and heater plates. Second, when the average signal was at or close to zero, it indicated that temperature differences between the guard and heater plates were minimized. The heat flux sensor has a

---

**Figure A.5: Guard plate schematic**
voltage-proportional output \( (0.00532 \, \text{mV/Wm}^{-2}) \), which was measured by a Keithley 2010 multimeter. The sensor was guaranteed to a temperature dependency of less than .05 \( \% \). A maximum calibration error of 3.4\% resulted over the 22\(^\circ\) to 90\(^\circ\)C temperature range of the experiment.

**Heater Plate**

The heater plate was machined from aluminum. The plate was 100 × 100 × 2.5 mm, with a 1 × 3.2 mm thermocouple channel milled from side to center (Figure A.6). The heater plate was heated from below with a 76.2 × 76.2 × 0.2 mm heat sheet, \( R = 287 \, \Omega \). The heat sheet was powered by either a DC power supply or variac, depending on required power.

![Heater plate schematic](image)

Figure A.6: Heater plate schematic

**A.1.3 Cold Plate and Gas Heater**

The cold plate was cooled using temperature-controlled air; air from a compressor was raised to a controlled temperature using the gas heater, and then circulated through an interior manifold in the cold plate. Air cooling ensured a constant rate of heat
removal from the cold plate. However, the cold plate temperature was not exactly known as a result. A test thermocouple (cold-junction type K, uncalibrated) was taped to the top surface of the cold plate during operation, and indicated temperature stability to ±0.1°C.

**Cold Plate**

The cold plate was machined from aluminum, with an internal reverse-flow manifold. A reverse flow manifold ensured a more isothermal plate than a forward-flow manifold (Figure A.7). The plate was 300 mm square, ±1 mm. An interior manifold was used because interior manifolds provide more contact with the thermal fluid than exterior manifolds. Reverse-flow manifolds (Figure A.7) further exhibit excellent evenness of flow [138], which ensures equal heat loss throughout the cold plate area.

![Figure A.7: Forward Z manifold (left) and reverse manifold (right)](image)

Figure A.7: Forward Z manifold (left) and reverse manifold (right)
The cold plate was machined by milling channels into 3 plates, to form a bottom, top and exit plate. The plates were 6.35 mm thick, and channels were 6.35 mm wide. 15 channels were milled into the bottom and top plates (Figure A.8), 4 mm deep into the bottom plate and 2 mm deep into the top plate. A channel, 2 mm deep, was milled into the top of the cold plate, and holes were drilled through to 7 channels. A 4 mm deep channel was milled into the exit bar, and 1/4”-20 threads were drilled and tapped in the top sides of the top and exit plates. 1/4 steel tube was threaded and fit to these holes to form the entry and exit ports. The three plates were then welded together, forming a manifold of 8 forward-flow and 7 return-flow channels, with an entry, return and exit bar (Figure A.9).

Figure A.8: Internal manifold: left, bottom plate; right, top plate; and top, exit plate
Gas Heater and Air Supply

The gas heater was made from a 3 ft steel tube, fitted with compression fittings to attach Teflon gas lines (Figure A.10). The tube was wrapped with a 3 ft heater cord, powered with an OMEGA CN9000A on/off PID temperature controller. Gas temperature was measured with an in-line thermocouple (cold-junction type K, uncalibrated). The heater assembly was insulated using rock wool. A building air compressor supplied air for the gas heater and cold plate manifold. Flow was controlled using a pressure regulator, rotameter and needle valve. Hot air flowed from the heater to the cold plate through an insulated Teflon gas line.
A.1.4 Differential Thermocouple

A differential thermocouple was used to accurately measure the temperature difference between the heater plate and the cold plate ($\Delta T = T_{HP} - T_{CP}$ in eqn. A.1) as differential (i.e. two-junction) thermocouples measure temperature differences more accurately than cold-junction thermocouples. Calibrated thermocouples are accurate to 0.1$^\circ$C [161]. Since two cold junction thermocouples are required to measure a temperature difference, such a measured difference would have minimum uncertainty of ±0.2$^\circ$C.

The differential thermocouple was made from spot-welded, 0.25 mm type K thermocouple wire (chromel-alumel-chromel). The thermocouple was calibrated over the temperature range 20-85$^\circ$C, using two stirred isothermal baths, as will be discussed in Section A.3. The thermocouple generated a voltage-proportional output for temperature differences of 0-15$^\circ$C,
\[ \Delta T = 24.3 \times V_{DTC} \]  

(A.5)

where \( V_{DTC} \) is the thermocouple voltage in mV, and \( \Delta T \) is the temperature difference in °C. Thermocouple output was measured using a Kiethley 2010 multimeter. During experiments, the hot junction of the thermocouple was taped into the bottom of the heater plate channel, and the cold junction was taped to the bottom center of the cold plate. The thermocouple wires were in contact with the hot or cold plates for a length of at least 10 cm, to minimize thermocouple temperature variations related to heat flow.

A.1.5 Insulation Block

The insulation block (Figure A.11) improved the stability and control of the guarded hot plate, and provided mechanical support to the LCF fuel samples. The block was built using six 1” (25.4 mm) layers of polystyrene foam. A square well was cut into the top four layers to accommodate the guard plate assembly, sample layer and guard plate. Several channels were also cut into the insulation block for wire access.

A.2 Procedure

The experimental procedure had three phases: setup, testing, and breakdown. During setup, sensors were checked, the sample was loaded and levelled, thermocouples were placed and taped, and gas lines were attached. During testing, plate temperatures were set, stray heat flows were minimized, and data were recorded. During breakdown, sample layer thickness was measured, some sample was reserved for moisture tests, and the apparatus was cleaned.
A.2. PROCEDURE

A.2.1 Setup

Before each experiment, the resistances of the heaters, thermocouples, and the heat flux sensor were measured. The guard and heater assembly was then inspected for damage and cleanliness.

The LCF sample was then loaded into the apparatus. First, the sample was well mixed in its storage container to minimize size segregation. Sample was then poured into the center of the guard assembly to form a conical mound, 15-20 cm in height. A level was then used to establish an even layer above the guard and heater assembly, 15 mm thick for “fine” samples \((d < 1/4’’\) or 30 mm thick for “coarse” samples \((d > 1/4’’\). The level applied only horizontal forces to the sample, \(i.e.\) the sample was spread and not compressed. If there was excess sample, it was removed from sample corners. If there was insufficient sample, more was sprinkled onto the layer from a height no greater than than 20 cm, and the sample was again made level.

The monitoring thermocouple was then taped to the upper center of the cold
A.2. PROCEDURE

plate, and the cold junction of the differential thermocouple was taped to the bottom center. The cold plate was then placed onto the sample. The gas line from the gas heater was attached to the entry port of the cold plate manifold. Finally, a 3” layer of rock wool insulation was then placed over the cold plate.

The compressed air supply was then turned on. Gas pressure at the regulator was set to no more then 10 psi, and a flow rate of 30 lpm was established using the needle valve and rotameter. The temperature controllers were turned on and set. The apparatus was then left idle for at least 6 hr to allow for compaction under the cold plate.

A.2.2 Testing

Samples were tested over the range 30°C-90°C, in 5°C-10°C increments. Tests consisted of a number of repeated steps:

1. The apparatus reached temperature stability. Plate temperatures were measured by three separate thermocouples. The system was considered stable once temperatures remained constant to 0.1°C over a 30 minute period.

2. The average heat flow was minimized. The test heater was powered independently of the guard plate, and heat flow between the guard and heater plates varied depending on the activity of the guard heater. The test heater power was adjusted in 10 minute intervals, until the average heat flow was between -0.05 and 0.05 W, which corresponded to ±0.1 mV heat flux sensor signal.

3. Temperatures and stray heat flows were measured. The heat flow sensor voltage was recorded every 15 seconds for 10 minutes. The differential thermocouple signal, guard plate temperature and test temperature were recorded.
4. If a conductivity measurement at a different temperature was required, new test
temperatures were input into the controllers, and the procedure was repeated.
If the experiment was complete, the breakdown procedure was performed.

A.2.3 Breakdown

The temperature controllers, gas supply and heater power supply were turned off. The
top layer of insulation was removed, and the cold plate was allowed to cool to
45°-50°C. The gas line was then detached from the cold plate. The cold plate was
lifted from the sample, and the differential thermocouple detached from the cold plate.
Sample thickness was then measured using a depth gauge. A total of five thickness
measurements were taken over each corner and the center of the heater plate. 20 mL
of the sample was reserved and sealed into a vial for drying tests. The tester was
then thoroughly cleaned by removing the remaining sample, wiping down surfaces,
replacing tape if necessary, etc.

A.3 Error Estimation and Validation

There were seven possible sources for error in this experiment, four systemic and three
random. Possible sources of systemic errors included lateral heat flows, convective
transfer, contact resistances and temperature effects. Random errors occurred during
the measurement of stray heat flows, sample thickness and temperature difference.
This section discusses each potential source of error, and how they were either ac-
counted for or mitigated. Validation tests performed on water-agar gel showed that
systemic errors were insignificant compared to measurement error.
A.3.1 Systemic Errors in Guarded Hot Plate Measurements

Lateral heat flows would have caused LCF thermal conductivity to be underestimated. The guard and heater plate width was chosen in order to minimize lateral heat flows, as discussed in Section A.1. However, temperature differences between the guard and heater plates could have caused similar lateral heat flows. Minimizing heat flows between the guard and heater plates minimized these temperature differences.

Contact resistances occurred in the mechanical contacts between the sample and plate surfaces. As discussed in Chapter 2, contact resistances result from voids between contact surfaces; these voids cause surface-to-surface temperature discontinuities. Contact resistances would have caused an underestimation of thermal conductivity. They were not significant for LCFs, as LCFs are granular fuels. In a granular or particulate bulk, contact resistances occur between every particle, and so become a component of thermal conductivity. LCFs are also relatively soft, which reduces intergranular and grain-plate contact resistances.

As discussed in the literature review, natural convective flows may occur in permeable media due to temperature gradients. If such flows occurred during a guarded hot plate experiment, they would have caused an overestimation of thermal conductivity. The filtration Rayleigh number describes the onset of such flows [162],

\[ Ra_f = \frac{\kappa g \beta (\rho c) L \Delta T}{\nu \lambda} \]  

where \( \kappa \) is sample permeability, \( \beta \) is sample volumetric thermal expansion coefficient, \( \rho \) is fluid density, \( c_p \) is fluid heat capacity, \( L \) is sample thickness, \( \Delta T \) is the temperature difference, \( \nu \) is fluid kinematic viscosity and \( \lambda \) is sample thermal conductivity. For reasonable estimates of the permeability of low carbon fuels \( (10^{-9} < \kappa < 10^{-7} \text{m}^2) \),
Convective flows cause significant heat transfer if \( Ra_f > 26 \) \([163]\); therefore, they did not affect these experiments.

Large temperature gradients can also cause property changes. Thermal conductivity increases with temperature; an ideal conductivity experiment would test an isothermal sample. However, conductivity measurements are impossible without heat flows, which cause temperature gradients. Guarded hot plates measure average thermal conductivity, at the temperature given by

\[
T_\lambda = T_{HP} - \frac{\Delta T}{2}
\]  

(A.7)

where \( T_{HP} \) is the temperature measured by the guard control thermocouple. This average approximates the ‘true’ thermal conductivity, if \( \Delta T \) is not too large. A target \( \Delta T \) of 10°C is commonly used as a compromise between measurement averaging and reducing random errors in measurement. Initial LCF conductivity measurements showed that \( \Delta T \approx 10^\circ \text{C} \) was appropriate — the measured LCF conductivity temperature dependence (i.e. \( \frac{d\lambda}{dT} \)) was of order \( 10^{-4} \frac{\text{W}}{\text{m} \cdot \text{K}^2} \). Conductivity differences caused by temperature gradients were therefore of order \( 10^{-3} \frac{\text{W}}{\text{m} \cdot \text{K}^2} \), an order of magnitude smaller than measured LCF conductivity.

The type K thermocouple used to measure \( T_{HP} \) had a calibration error of \( \pm 1^\circ \text{C} \). However, this was an error in accuracy, not precision, as it resulted from metallurgical differences in the thermocouple alloys. This caused a 1-3% error in \( T_\lambda \), which did not affect thermal conductivity measurements.
A.3.2 Random Errors in Guarded Hot Plate Measurements

Random errors occurred during the measurement of the quantities used to calculate thermal conductivity; namely, heat flux, sample depth and temperature difference.

Error in heat flux measurements resulted from the on/off temperature controller used to power the guard heater. While the temperature of the plate remained constant to ±0.1°C, pulsing the guard heater produced a 6-7% variation in the stray heat flows between the heater and guard plates. The variability and average heat flow signal were calculated from the recorded heat flux sensor signal (Figure A.12). The average heat flux sensor signal was used to correct the heat flux term in eqn. A.1,

\[
\tilde{q} = \frac{\bar{q}_P + \bar{q}_S}{a}
\]  

(A.8)

where \( \tilde{q} \) is the heat flux through the sample, \( \bar{q}_P \) is the power of the heater plate, \( a \) is the area of the heater plate, and \( \bar{q}_S \) is the stray heat flow measured by the heat flux sensor. The error in \( \bar{q}_S \) was propagated to the thermal conductivity calculation as an error in \( \tilde{q} \).

During the breakdown procedure, sample thickness was measured using callipers. The true thickness of the sample was difficult to measure, as the materials were soft and thickness measurements disturbed samples. To compensate, a total of five thickness measurements were made during each breakdown, and average values and standard deviations were taken as estimates of true values and errors. The error in thickness was 1-3% of the measured value.

Random errors in temperature difference were probably caused by contact effects between the differential thermocouple and the voltmeter. The thermocouple was calibrated by measuring the temperature difference between two stirred, isothermal
baths, and output ($V_{DTC}$) was measured using the same Keithley 2010 multimeter used during thermal conductivity experiments. Six calibration sweeps were performed, measuring temperature differences of 0°-15°C at various bath temperatures, in the range 20°-85°C. A random error of 0.016 mV was evident, particularly when the thermocouple was attached and detached from the voltmeter.

A systemic error was also noted during thermocouple calibration. When the baths were set to the same temperature, $V_{DTC} = -0.029 \pm 0.012$ mV. The thermocouple should return a zero voltage signal when the two junctions are isothermal, and the thermocouple generated no voltage ($V_{DTC} = 0$) when both junctions were in contact with an isothermal aluminum block. This 'zero voltage' was probably a result of temperature differences in the isothermal baths, perhaps caused by miscalibrated bath sensors. The calibration curve (Figure A.13) was corrected for this effect. The error in the calibration ($T = (24.3 \pm 0.1) V_{DTC}$) and contact effects caused a measurement
A.3. ERROR ESTIMATION AND VALIDATION

The error in heat flux measurement, \( \sigma_q \), sample thickness, \( \sigma_L \), and temperature difference, \( \sigma_{\Delta T} \) were known, so thermal conductivity errors were found by propagation,

\[
\sigma_\lambda = \sqrt{\sigma_q^2 \left( \frac{L}{\Delta T} \right)^2 + \sigma_{\Delta T}^2 \left( \frac{\bar{q}L}{\Delta T^2} \right)^2 + \sigma_L^2 \left( \frac{\bar{q}}{\Delta T} \right)^2}
\]  
(A.9)

A.3.3 Validation with Agar Gel

The thermal conductivity of a 1 wt\% agar-water gel was measured to test error estimates and ensure that systemic errors did not cause mis-measurements. Highly purified agar is cheap and available, and the thermal conductivity of agar-water gels have similar thermal conductivities as LCFs (\( \lambda_{Gel} = 0.5 \ \text{W/mK} \), \( \lambda_{LCF} = 0.05-0.2 \ \text{W/mK} \)) [139]. Gel conductivity was measured according to Section A.2, but the apparatus was modified to contain the gel. A plastic sheet was placed onto the guard to contain the gel.
mixture while it set. Contact resistances between the plastic sheet, hot plate and gel layer resulted in a 0.5°C temperature discontinuity between the guard plate and bottom surface of the agar gel, which was accounted for during thermal conductivity measurements.

17.6 g of agar flakes (Koyo) were dissolved into 1750 g of filtered water (<10 ppm dissolved solids) on a hot plate with magnetic stirrer. The resulting 1 wt% agar-water mixture temperature was maintained at 95°C and stirred for 45 minutes, at which time flakes were no longer visible. The mixture was then poured onto the plastic sheet in the guarded hot plate and allowed to cool and set. The results of the test (Figure A.14) show that the systemic errors were not significant in measuring the conductivity of the gel.

![Figure A.14: Thermal conductivity of agar gels, as reported in literature [139] and as measured by the guarded hot plate](image-url)
Appendix B

Calorimeter Details and Procedure

This appendix gives a short description of the TAM Air Calorimeter, as well as details regarding the experimental procedure and analysis that are not reported in Chapter 3. TAM Air specifications and operating parameters were taken from the TAM Air Manual [164].

B.1 TAM Air Calorimeter

The TAM air is an 8-channel, isothermal heat flow calorimeter, with a temperature range of 5-90°C. All 8 channels are mounted on a single calorimeter block or heat-sink, housed in a circulating air thermostat. The air itself is heated by a solid state heat pump, and further insulated from the calorimeter environment. Thus, the calorimetric block is thermally isolated by both solid insulation and an air gap, and is stable to within ±0.02°C during operation. Each calorimetric channel is constructed in a twin, sample-reference configuration (Figure B.1).

During measurement, the sample and reference materials are in 20-mL glass or plastic ampoules. Solids, liquids or slurries may be studied. The sample of interest is held in the sample ampoule, whereas the reference may contain an inert material
Heat generation is measured by the heat flow principle: heat created by any physical or chemical reaction in the sample ampoule will flow into the calorimetric block. The flows in each calorimetric channel are measured by a pair of Seebeck sensors, one for the sample and one for the reference. Strictly speaking, Seebeck sensors or thermopiles are heat flux sensors; they produce a voltage signal proportional to the temperature difference between two faces of a wafer. They may be used as heat flow sensors if calibrated. The differential comparison of sample and reference heat flows minimizes error and baseline drift, which are discussed in the next section.

B.1.1 Error

Performance specifications of the 8-channel TAM Air are shown in Table B.1. The TAM Air suffers from short-term noise, baseline deviations and baseline drift. Note
that there is a 3-channel version of the TAM Air calorimeter, with 125 mL ampoules. The 3-channel TAM Air has different performance specifications; the data in Table B.1 are specific to the 8-channel version.

<table>
<thead>
<tr>
<th></th>
<th>μW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection Limit</td>
<td>4</td>
</tr>
<tr>
<td>Noise</td>
<td>±2.5</td>
</tr>
<tr>
<td>Precision</td>
<td>±10</td>
</tr>
<tr>
<td>Baseline Drift (12 h)</td>
<td>±20</td>
</tr>
<tr>
<td>Error</td>
<td>±14</td>
</tr>
</tbody>
</table>

Table B.1: TAM Air performance specifications

The terms in Table B.1 are defined as follows:

- **Detectability**: The minimum detectable heat flow
- **Noise**: The peak-to-peak variation in a steady heat flow over a 60 s time period
- **Precision**: The standard deviation in the baseline heat flow of ten repeated loadings of an empty 20 mL glass ampoule, *i.e.* the deviation in an exactly repeated experiment
- **Baseline Drift**: The maximum change in baseline over a 12 h period
- **Error**: The error after 12 hours of operation, as determined from precision and drift

Noise occurs due to thermal and electric noise in the Seebeck sensors, but also due to temperature variations in the calorimeter environment. As these noise affects both the sample and reference ampoules, the differential configuration minimizes the impact of random noise. Similarly, precision is measure of random error, and is probably influenced by contact differences between the ampoule and the Seebeck sensor.
Baseline drift occurs because of unequal thermal contacts between the Seebeck sensor and calorimeter, thermal and electrical noise in the Seebeck sensor, and temperature fluctuations in the calorimetric block [165].

This results in a maximum error of \( \pm 14 \, \mu \text{W} \) over a 12 hour calorimetric experiment (note that error increases over time, as a result of drift; a 6 hour experiment has a maximum error of \( \pm 11 \, \mu \text{W} \)). This error was most significant in the low-temperature (50°C) experiment, where heat generation ranged from 30-60 \( \mu \text{W} \). Higher-temperature calorimetric experiments had heat flows in the 75-1000 \( \mu \text{W} \) range.

In order to minimize the impact of random errors, each fuel was tested in duplicate. Further, only the data from the first \( 30 \times 10^3 \, \text{s} \) (8 h) of each experiment was analyzed.

B.2 Procedure

This section describes the calorimetric procedure in some more detail, as well as how the data was analyzed. Calorimetric experiments are conveniently simple - a chemical reaction may be studied by sealing reagents in an ampoule, and then inserting the ampoule into the calorimeter. Chapter 3 therefore describes the procedure reasonably well; however, sample handling details were neglected. 50 g of each fuel were shipped to TA Instruments in New Castle, Delaware, in sealed high-density polyethylene (HDPE) bottles. The bottles were kept sealed and refrigerated during testing, and further shipped in a cooler with ice packs.

B.2.1 Onset Heating Values

An example data set, produced by a calorimetric experiment, is shown in Figure B.2. The sample, initially at room temperature, is inserted at time \( t=0 \), after which it
absorbs heat until it reaches thermal equilibrium with the calorimeter, at \( t \approx 3500 \) s. However, oxygen will be consumed during this equilibration period.

Sufficient oxygen remains in the ampoule to produce a measurable self-heating signal. As discussed in Chapter 3, these data were inappropriate for a kinetic analysis. Therefore, these data were fit to heating models; these models were themselves extrapolated to provide a measure of heat generation at atmospheric oxygen concentrations. These onset heating values therefore provide an estimate of self-heating at ambient fuel storage conditions.

Figure B.2: Sample calorimetric curve. These data were fit to an exponential plus constant heating model (eqn. 3.7), and extrapolated to the mid-point of the equilibrium period.

However, the time to which the calorimetric data should be extrapolated is unclear. Maximum self-heating is measured at thermal equilibrium, but as discussed above, this value underestimates self-heating at ambient conditions due to oxygen depletion. Extrapolating the model to sample insertion \((t = 0)\) would over-estimate
self-heating — a fuel sample would not consume significant amounts of oxygen between 20-50°C, and thus samples underwent some warming before consuming oxygen. Therefore, models were extrapolated to the mid-point of the equilibration period, i.e. halfway between sample insertion and sample equilibrium, as a reasonable self-heating estimate.

This uncertainty in the correct time to evaluate the onset heating value is the largest source of error in the Arrhenius models shown in Figure 3.5. This error was quantified by extrapolating the heating model to different points within the equilibration period (Figure B.3), which gave a range of potential onset heating values. These values were separately used to determine Arrhenius heating models; i.e., three separate Arrhenius models were fit to the data sets corresponding to \(q_{1/4}\), \(q_{1/2}\) and \(q_{3/4}\). The standard deviation of the three activation energies and \(QA\) factors so evaluated are reported in Table 3.2.
Figure B.3: Error in onset heating value. $t_i$ and $t_e$ are sample insertion and equilibrium, respectively, $t_{1/2}$ is the mid-point of the equilibration period, and $t_{1/4}$ and $t_{3/4}$ are other possible times to evaluate the self-heating model.