

Imperial College London

**Self-heating ignition of natural reactive
porous media**

A thesis submitted in partial fulfilment of the
requirements for the degree of

Doctor of Philosophy

in

Mechanical Engineering

by

Francesco Restuccia

2017

Supervised by Dr Guillermo Rein

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Declaration of Originality

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Francesco Restuccia

2017

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a mio nonno,
Domenico Franco

ABSTRACT

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Self-heating is the tendency of certain porous solid fuels to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures. Self-heating can cause accidental ignition of reactive porous media leading to wildfires, ecosystem damage, property damage, loss of industrial facilities and even loss of life. Traditional self-heating ignition literature studies have been dominated by coal. However, there are many other materials prone to self-heating ignition like biomass and other natural occurring materials. Using oven basket experiments coupled with the Frank-Kamenetskii theory of ignition, this thesis aims at quantifying self-heating ignition risk and properties, and quantifying the chemical kinetics and thermal properties of natural fuels such as shale, carbon-rich soils such as peatlands, and biochars produced from wheat, rice husks, and softwood upscaling the results to real systems. This method requires extensive laboratory time, but gives the most accurate self-heating results. The thesis focuses on the effect of three main physical parameters: carbon content, inorganic content, and particle size of the fuel. I show that shale rock can self-heat in normal ambient conditions. Using soil biomass samples with inorganic content between 3% and 86% of dry weight, I quantify the effect of inorganic content on self-heating ignition, and show that self-heating can initiate wildfires in some soil types and conditions. I quantify the reactivity of softwood biochar produced as a function of the pyrolysis reactor temperature. I show that the reactivity of softwood is not a monotonic function of pyrolysis reactor temperature. I present an experimental comparison of wheat, rice husk, and softwood biomass and biochar, quantifying the differences between different feedstock sources and what effect this has on the biochar's relative fire risk. Finally, I quantify the effect of particle size diameter on self-heating ignition for wheat, showing that the critical temperature for self-heating ignition decreases with particle size.

ACKNOWLEDGEMENTS

I would like to begin by thanking my supervisor, Dr Guillermo Rein, for his continuous encouragement, enthusiasm and support through the duration of my research project. Thank you for giving me the opportunity of joining your research group back in 2014, it has been an incredible growing experience both on the personal and professional side. It has been an amazing experience having you as a supervisor.

This project would not have been possible without the financial support of the Engineering and Physical Sciences Research Council (EPSRC, UK) which funded the thesis through an International Doctoral Training Partnership (DTP) Studentship (grant EP/L504786/1), and their support is gratefully acknowledged.

A big thank you to all the members of Hazelab during my time here, Xinyan, Egle, Izabella, Nils, Yuqi, Franz, Virginia, Nieves, Santoso, Matt, Eirik, and Han. Thank you for your support, help, advice, and for making our group a big family. Thanks to my undergraduate placement student Nicolas for his assistance and valuable input in the lab and Tarik Saif for his help in procuring the shale rocks. I would like to thank Ondřej Mašek and Rory Hadden (University of Edinburgh) for their contribution to the biochar chapters, especially Ondřej for producing and providing the biomass and biochar samples from the UK Biochar Research Centre at the University of Edinburgh, and Rory for providing the guarded heat flow meter I used to measure thermal conductivity of all the samples.

A special thank you to my second family: Marie, Antoine, and Laurentiu. Thank you to Johannes and Simon for making Gabor my home for the last two years.

Finally, and most importantly, thanks to my family: my parents, my grandparents, my sister Sara and brothers Davide and Domenico, for your constant support, encouragement, patience, and for always being there for me.

Francesco Restuccia

London, UK

August 2017

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NOMENCLATURE

A	area (m ²)
D	diameter (m)
L	length or thickness (m)
V	volume (m ³)
m	mass (kg)
E	activation energy (kJ/mol)
f	mass action law (-)
k	thermal conductivity (W/m.K)
Q	heat of reaction per fuel mass (W/m ³)
R	universal gas constant (J/mol.K)
t	time (s)
T	temperature (K or °C)
T_r	temperature of pyrolysis reactor (K or °C)

Greeks

α	thermal diffusivity (m ² /s)
δ	Frank-Kamenetskii parameter (-)
ρ	density (kg/m ³)

Superscripts

a	fuel concentration exponent
b	oxidizer concentration exponent

Subscripts

a	ambient
c	critical
p	peat
s	sand
min	minimum

Abbreviations

1/2/3D	one/two/three-dimensional
C	carbon
H	hydrogen
N	nitrogen
S	sulfur
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DAF	dry ash free
EN	european standard
IC	inorganic content
MC	moisture content
MLR	mass loss rate
TGA	thermogravimetric analysis

Preface

This thesis has an introduction chapter presenting the theory of self-heating, experimental techniques, current literature and experimental methodology used for all the chapters. All subsequent chapters are integrated documents suitable for journal publication. The material is presented as follows:

Chapter 2 presents the first experimental quantification of the self-heating behavior of shale rock, and the effect of shale rock particle diameter on its reactivity properties. The chapter is based on:

F. Restuccia, N. Ptak, G. Rein (2017) *Self-heating behavior and ignition of shale rock*, **Combustion and flame** 176:213-219.

Chapter 3 presents an experimental quantification of ignition criteria based on inorganic content, size and ambient conditions for carbon-rich soils and demonstrates for the first time that wildfires can start by spontaneous exothermic reaction of soil for ambient conditions and soil types found in nature. The chapter is based on:

F. Restuccia, X. Huang, G. Rein (2017) *Self-ignition of natural fuels: Can wildfires of carbon-rich soil start by self-heating?*, **Fire Safety Journal** 91C:828-834.

Chapter 4 investigates self-heating behaviour as a function of pyrolysis reactor temperatures of softwood biomass and quantifies the different reactivities based on biochar production temperature, showing that the reactivity of the softwood is not a monotonic function of pyrolysis reactor temperature. The chapter is based on:

F. Restuccia, O. Mašek, R. M. Hadden, G. Rein (2017) *Quantifying reactivity of biochar as a function of the pyrolysis reactor temperature using self-heating ignition properties*, **Bioresource Technology**, (to be submitted).

Chapter 5 investigates the propensity to self-heat for different torrefied biomass, studying the different self-heating ignition behaviours of softwood pellets, rice husks and wheat straw pellets and their respective biochar produced at temperatures of 450 °C, 550 °C and 700 °C. The chapter is based on:

F. Restuccia, O. Mašek, R. M. Hadden, G. Rein (2017) *Self-heating and ignition behaviour of torrefied biomass and biochar from softwood pellets, wheat pellets and rice husks*, **Bioresource Technology**, (to be submitted).

Chapter 6 investigates the effect of particle size in biomass self-heating ignition, quantifying the difference in self-heating behaviour of wheat biomass ranging 4 particle sizes distributions from dust to pellet size. The chapter is based on:

F. Restuccia, N. Fernandez-Anez, G. Rein (2017) *Experimental measurement of particle size effect on self-heating ignition of biomass pellets*, **Proceedings of the Combustion Institute 2018** (submitted).

Other Publications

The following scholarly output has also been produced as a result of this research:

Conference communications

- F. Restuccia, X. Huang, G. Rein, *Self-ignition of natural fuels: can wildfires of carbon-rich soil start by self-heating?*, **International Association for Fire Safety Science Symposium 2017 (IAFSS17)**, Lund, Sweden, 11-18 June, 2017.
- F. Restuccia, X. Huang, G. Rein, *Wildfires caused by self-heating ignition of carbon-rich soil*, **European Geosciences Union (EGU) General Assembly 2017**, Vienna, Austria, 23-28 April, 2017.
- F. Restuccia, O. Mašek, R. M. Hadden, G. Rein, *Self-heating and ignition behaviour of torrefied biomass and biochar*, **International Bioenergy Conference 2017**, Manchester, UK, 22-23 March, 2017.
- F. Restuccia, N. Ptak, G. Rein, *Experimental study of shale rock self-heating*, **European Geosciences Union (EGU) General Assembly 2016**, Vienna, Austria, 17-22 April, 2016.

Publications produced not part of thesis

The following publications were co-authored during the course of this PhD on combustion and fire related topics, but are not part of this thesis.

Journal Publications

- G. Rein, X. Huang, F. Restuccia, T. McArdle (2017), *Detection of landmines in peat soils by controlled smouldering combustion: Experimental proof of concept of O-Revealer*, **Experimental Thermal and Fluid Science**, 88C:632-638.
- X. Huang, F. Restuccia, M. Gramola, G. Rein (2016), *Experimental study of the formation and collapse of an overhang in the lateral spread of smouldering peat fires*, **Combustion and Flame**, 168:393-402.
- I. Vermesi, F. Restuccia, C. Walker-Ravena, G. Rein (2016), *Carbon monoxide*

diffusion through porous walls: evidence found in incidents and experimental studies, **Frontiers in Built Environment** , (under review).

Conference communications

- X. Huang, F. Restuccia, M. Gramola, G. Rein, *Experimental study on the surface spread of smouldering peat fires*, **5th International Fire Behavior and Fuels Conference**, Portland, USA, 11-14 April, 2016.
- F. Restuccia, G. Rein, X. Huang, T. McArdle, *O-Revealer: novel technology for demining of peatlands by the use of smouldering combustion*, **IOP Current Research in Combustion**, Loughborough University, UK, 9 September, 2015.
- I. Vermesi, F. Restuccia, C. Walker-Ravena, G. Rein *Carbon monoxide diffusion through walls: a critical review of literature and incidents*, **Suppression, Detection and Signaling Research and Applications Symposium (SupDET 2015)**, Orlando, Florida, 3-6 March 2015.

Chapter 1

Introduction

1.1 Motivation and Objectives

Fire safety is a major issue in the world, with a need to protect both citizens and the environment from the effects of fires. Fire is a complex phenomenon, linking chemistry, thermodynamics and heat transfer. How fires ignite is a fundamental problem. Many natural materials can ignite, both by external ignition sources and self-heating ignition. The ignition of reactive porous media, such as biomass and soils, is a major issue. Self-heating ignition is an issue that is of importance for natural fuels, especially with regards to transport and storage. Self-heating is the tendency of certain porous solid fuels to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures. This process starts by slow exothermic oxidation at ambient temperature, but the reaction alone is insufficient to raise the material temperature. The temperature rise is determined by the imbalance between the rate of heat generation and the rate of heat losses [1]. Fire initiated by self-heating ignition is a known hazard for many natural materials, but there is very limited studies quantifying self-heating ignition tendencies and associated chemical kinetic and thermal properties for materials including shale, soil, softwood, rice husk, and wheat biomass and associated biochar products from the same materials. This thesis focuses on the self-heating tendencies of these materials.

Wildfires are a fundamental fire science problem. Forest fires, soil fires, coal fires, shale fires are all examples of fires that can be initiated by self-heating ignition and are a known natural hazard. Once ignited, these materials often burn in the form of smouldering combustion, which can burn for months and release large amounts of greenhouse gases [2–4]. Shale wildfires have been reported all over the world, from Scotland to Alaska, UK, India and Russia [5–8]. Similarly carbon rich soils are unfortunately a common event in certain areas of the world, especially south-east Asia [4]. Similarly for

coal, many wildfires have been reported in the literature all over the world [9–14]. The ignition of these fires can be from an external ignition source, or self-heating ignition.

Wildfires are not the only field of studies where the propensity of natural materials to self-ignite is of interest. Another area is the energy sector. In the current times, different options are being studied to modify the traditional fossil fuel driven energy market. This has been spurred by a desire to reduce carbon emissions, increase sustainability and energy security. The burning of fossil fuels emit carbon-compound gases which are pollutants and increase the global greenhouse effect. For example, one of the main gases emitted by these fuels is carbon dioxide, which is responsible for 80% of the increase in radiative forcing over the past decade, increasing the greenhouse effect [15]. The need to decrease carbon emissions has brought on the development of many international protocols and regulations aiming to decrease climate change effects worldwide. The 1998 Kyoto protocol was the beginning of a new worldwide strategy to reduce emissions and increase energy efficiency. The European Union member states are working towards the target that by the year 2020 greenhouse gas emissions should be reduced by 20 percent, renewable energy should represent 20 % of the European final energy consumption, and energy efficiency should increase by 20 % [16]. In this scenario, the role of biomass as an alternative energy source becomes crucial to try and achieve these targets. The use of biomass, organic matter used for energy production that could replace fossil fuels, has already started to take place in the UK. For example, Drax power plant, which supplies 4 GW of power and 7 % of UK electricity needs, reconverted 3 of its 6 electricity generation units in 2013 so that it now produces 68 % of its power from biomass instead of coal [17]. But one of the fuel characteristics of biomass that is particularly important for safety and fire prevention is the self-ignition tendency of the materials. There are various factors that can affect the ignition tendency of biomass, such as particle size, moisture content, pyrolysis processes that can lead to different physical and chemical properties, to name a few.

Coal self-heating has received extensive attention in the past 5 decades, and abundant work exists in literature on the study of coal self-heating ignition both experimentally and computationally quantifying the effects of coal particle size, different origin of coal, moisture effect and geometrical effects. The experimental work was mainly carried out using hot plate and oven basket experiments, which will be described in more detail section 1.2, and modelling work based on the kinetics, heat transfer and mass transfer conditions of the laboratory-scale experiments [18–28]. Results for coal have shown the importance of particle size in coal ignition, with finer particles leading to coal more prone

to self-heating ignition. Moisture levels can affect the heat transfer via evaporation, condensation and by changing the thermal diffusivity of the coal. Finally, coal originating from different sources was shown to have a wide range of effective activation energies, from 50 kJ/mol all the way up to 120 kJ/mol.

This thesis focuses on self-heating ignition of certain reactive media which has received much less attention in current literature, namely shale rock, carbon-rich soils, biomasses and biochars. The objectives of this thesis are to quantify self-heating ignition risk and properties, and quantify the chemical kinetics and thermal properties of natural fuels such as shale, natural carbon rich soils such as peatlands, and biochars produced from wheat, rice husks, and softwood. I focus on the effects of three main physical properties: carbon content and inorganic content, particle size of the reactive media, and origin of the reactive natural fuel. The resulting manuscript aims at filling these fundamental knowledge gaps present in the literature. More specifically, the thesis focuses on quantifying self-heating ignition properties of reactive porous media for (i) coarse and fine sized shale rock, (ii) carbon rich soils with inorganic content ranging from 3% to 86%, covering the range of organic soils found in natural ecosystems, (iii) torrefied softwood biomass and biochar produced at 7 different pyrolysis reactor temperatures, (iv) biochar produced from softwood, wheat and rice husk produced at varying pyrolysis reactor temperatures and for (v) four different particle sized wheat biomass samples.

1.2 Theory of self-heating

Any natural material can decompose or be oxidized by air in an exothermic reaction. These exothermic reactions cause the internal temperature of the material to increase. The rate at which that heat is dissipated to the environment versus the rate at which it is generated determines if the material will reach self-heating ignition conditions or not. This problem corresponds to the transient heat conduction equation, shown in Eq. 1.1

$$\nabla^2 T + \frac{QF(t)e^{-\frac{E}{RT}}}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (1.1)$$

where T is the temperature of the fuel sample, E is the activation energy of the reaction, k is the conductivity of the fuel, R is the universal gas constant, Q is the heat of reaction per fuel mass, α is the thermal diffusivity of the fuel, t is time and $F(t)$ is the mass action law based on concentration of fuel and oxygen at any given time. There is no need to specify the dependency on concentration but an often invoked representation of this law is $[\text{fuel}]^a [\text{O}_2]^b$, [1].

In the literature, there are three main models that can be used in analysing oxidation and self-heating reactions present in this heat transfer problem [29]. The first model is the Semenov model, which describes spontaneously-heating systems by assuming uniform temperature distributions, neglecting consumption of the reactant material and assuming that the chemical reaction follows a one-step Arrhenius temperature dependence. The second model is the Frank-Kamenetskii model, which builds on the Semenov model but incorporates heat conduction through the solid material due to the chemical heat release of the material, therefore does not assume uniform temperature profiles. The third available model is known as the Thomas model and it builds upon the Frank-Kamenetskii model by additionally considering the convective heat loss effects from the surface. All three models assume a single step global reaction, constant thermal properties of the material, no reactant consumption and no restriction of oxidizer availability [1,30]. Therefore they only apply to materials for which a global one-step kinetic model provides a reasonable approximation to the actual chemical scheme of the material. The current state of the art in modelling of self-heating ignition is still limited to small scales or to the modelling of a specific experimental setup [26–28]. A large scale 3D model with governing equations imposing conservation of mass species and energy both in the condensed and gas phases has yet not been developed in the state of the art as it is still too computationally expensive.

The most appropriate model for experimental work in the literature to investigate self-ignition properties of materials is the Frank-Kamenetskii theory of ignition criticality [1, 31, 32]. The reason for this is that a basket heating experimental technique was developed based on this theory which allows the determination of critical ambient temperatures for a given sample size for ignition. The theory can be used to extrapolate data from experimental measurements to predict the expected behaviour of very large stockpile sizes of that same material. The data and the analysis serve to quantify the risks in realistic conditions if the mechanism of heat generation is unchanged when extrapolating the results to larger sizes [1, 32]. These models are very effective to predict critical temperature and critical size for ignition, but are not as effective when used to assess the time to ignition, as the models assume steady-state conditions and therefore make the time to ignition harder to quantify. The disadvantage of using Frank-Kamenetskii theory coupled with basket experiments is that it is a very time-intensive method and requires a lot of material, as many experiments have to be carried out. However, Frank-Kamenetskii theory coupled with the oven basket methodology has been shown to give the most robust results for scaling results of laboratory-scale experiments to larger size [1, 32]. Despite it

requiring a large time and resource investment, this method was used for the analysis of all the experimental work on self-heating presented in this thesis to obtain robust results that can be utilised to study the widest range of length scales.

To carry out the analysis of experimental results, the Frank-Kamenetskii theory of ignition assumes that the material being studied is reactive and 1D, and that the heat release is from a 1-step exothermic reaction which contains numerous chemical and biological elemental reactions as described earlier. For organic materials such as biomass there are two main sources of heat generation that make up this global 1-step reaction, a chemical process at higher temperatures and a biological process at lower temperatures [33]. The biological process can range from temperatures under 20 °C to up to 70 °C and is usually caused by growths of psychrophilic, mesophilic and thermophilic micro-organisms [34]. The biological process will have a contributing effect at lower temperatures in raising the biomass temperature. However already from 40 °C carbon oxidation will start contributing to the heat generation and as the temperature increases it becomes the dominating heat generation process [34]. This global reaction is also assumed to have a high activation energy so that a steady-state solution exists [1, 32].

To solve the transient heat conduction equation, Frank-Kamenetskii theory defines a dimensionless parameter δ (Eq. (1.2)),

$$\delta = \frac{QEfL^2}{kRT_a^2} e^{-\frac{E}{RT_a}} \quad (1.2)$$

where E is the activation energy of the 1-step global oxidation reaction, k is the effective thermal conductivity of the sample, R the universal gas constant, T_a is the ambient temperature, L is the characteristic length of the sample (for a cube basket the side length, and for an infinite slab the thickness), Q is the heat of reaction per fuel mass, and f is the value of the mass action law which relates the concentration of fuel and oxygen at the initial time to reaction rates, and is based on initial concentrations of fuel and oxygen [32]. Expressing the reaction rate as the Arrhenius law for dependence on temperature, the transient heat conduction equation is solved and the following dependence of critical sample size and ambient temperature is obtained, Eq. (1.3).

$$\ln \left(\frac{\delta_c T_{a,c}^2}{L^2} \right) = \ln \left(\frac{QEf}{Rk} \right) - \frac{E}{RT_{a,c}} \quad (1.3)$$

where δ_c is the critical value of the dimensionless parameter in Eq. (1.2) for which ignition occurs, which is a function of the geometrical shape of fuel; and $T_{a,c}$ is the critical (minimum) ambient temperature for which self-ignition occurs. This parameter can be considered analogous to the critical Damköhler number.

A solution to Eq. (1.3) satisfying the boundary condition at the surface $T = T_a$ only exists when the condition $\delta \leq \delta_c$ is satisfied. δ_c is a function of geometry which has been precisely calculated and can be found in the literature [31,32,35]. The experimental work carried out in this thesis utilises cubic baskets, which have a critical value $\delta_c = 2.52$ [32]. Eq 1.3 can be used to create what is known as a Frank-Kamenetskii plot to determine the kinetic parameters of the self-heating sample being studied. An example is given in Fig. 1.1, taken from Thomas et al [36], where the theory is used to determine the kinetic and thermal parameters of wood fibre insulation board.

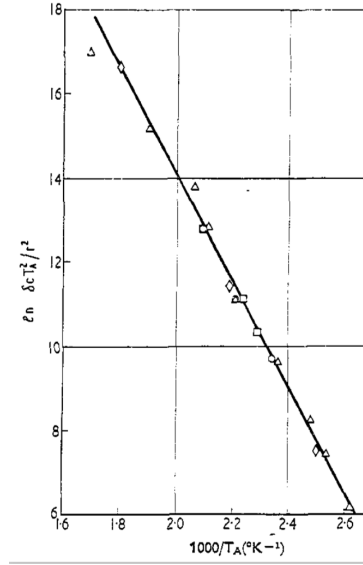


Figure 1.1: A Frank-Kamenetskii plot [36]. The slope of this plot can be used to determine kinetic and thermal parameters for self-heating of wood fibre insulation board.

The steady-state theory presented allows us to determine if runaway conditions will happen, and at what critical size and temperature they will happen at. However, they do not allow an estimation of how long ignition will take if the system is one where thermal runaway will occur. This is of particular interest when studying materials that are in storage, maybe for a limited amount of time, where storage time might be lower than the amount of time it would take for that material to reach runaway conditions. There are several numerical methods developed to try and obtain solutions to the nonlinear heat conduction equation to solve for time to ignition for several geometries, namely [37–39]. An approach to determining this time to ignition was proposed by Bowes, relating the ignition delay time t_i to the characteristic length L as in Eq (1.4, where m is the a constant and can be determined from experimental results) [31]

$$\ln t_i = m \ln L \quad (1.4)$$

A standard method is used for the assessment of ignition delay time, found in BS EN 15188:2007. However there are very large errors associated with predicting time to ignition from self-heating. In large scale piles of a material, during self-heating the centre and surface temperature of materials will not be the same, and parts of the material will be at different temperatures giving very different reaction rate in different parts of the material and therefore changing the delay time depending on size and gradient in temperature within the material. Furthermore, time to ignition is very sensitive to some of the initial chemical reactions at the early time scales, which might be different reactions to those that determine the temperature and size criticality condition and are used to represent the single exothermic reaction in the arrhenius equation [32]. As shown earlier these reactions might have negligible effect on the critical temperature determination, but they can have very important effects on the time to ignition. Determining precise ignition delay times is very challenging both theoretically and numerically.

1.3 Experimental techniques

To study self-heating ignition experimentally, there are several methodologies that are used to determine the thermal and chemical properties for understanding bulk-scale self-heating behaviour. They include thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), hot plate tests, oven basket tests and a modified version of oven basket tests known as the crossing point method. Strengths and weaknesses of each method are explained below [35].

TGA, DTA, and DSC are all techniques that are used for studying the thermal variables required for self-heating ignition. However, these techniques have many limitations. All of these techniques use milligram samples, exposing them to heating conditions such that a sample is effectively all at a uniform temperature, thus ignoring effects of thermal variation across a sample. Because of the small mass of sample used, the accuracy of measurement is quite limited. Furthermore, each individual method has several limitations: TGA does not measure heat, so can only be used to find the activation energy and pre-exponential factor, but not the heat of reaction. That can be determined by coupling TGA with DTA or DSC. However, DTA requires a reference material to be used with identical heat capacity to the material being tested which is quite difficult to find for most solids. DSC is a calorimetric technique that is not optimised for accuracy, and so results from this can only provide a rough guidance, as the values found are not extremely precise. Furthermore, these methods are highly sensitive to the assumptions of

reaction chemistry, and assuming single-step global reactions of the Arrhenius form can lead to extrapolations of the results that are not very realistic. These measurement techniques are very useful for the purpose of estimation, but not as highly accurate sources of data [32, 35].

Another methodology used to study self-heating is the hot plate test. This technique uses uniform layers of the tested material placed on a hot plate of uniform temperature. This methodology requires hot plate diameters which are between at least 7 and 10 times greater than the thickness of the layer of material being tested. Furthermore, the high temperatures required to conduct these experiments sometimes cause depletion of the original fuel, which needs to be accounted for in the analysis of the results. The advantage of this methodology is that it is relatively quick to carry out the experimental measurements, and the results obtained can be very useful when requiring only small scaling. This methodology is most often used when studying the effect of self-heating ignition on dust layers [35]. The typical experiments using this setup follow standard EN 50281-2-1, and a diagram of the setup is given in Fig 1.2.

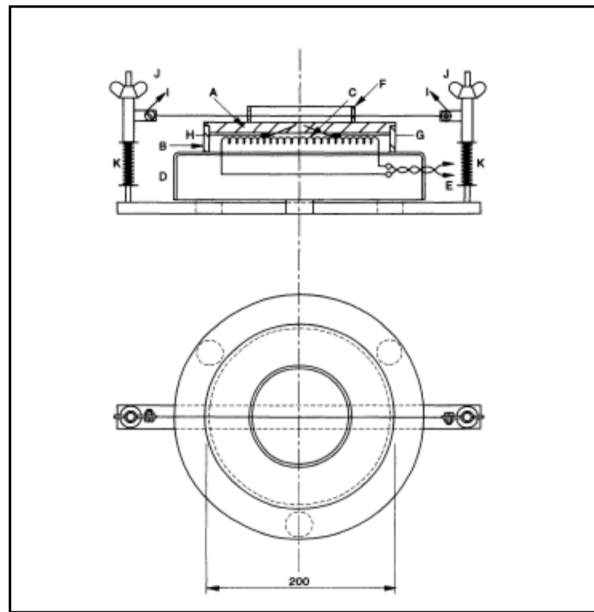


Figure 1.2: Typical Hot plate that are used for self-heating ignition studies from EN 50281-2-1. [40].

The most commonly used methodology to study self-heating behaviour at laboratory size and use results to predict the material's large scale behaviour to self-heating is known as the oven basket methodology, which was developed by the Fire Research Station and refined by Philip Bowes [35]. This method packs the sample being tested in wire gauze baskets of different dimensions, and places them in a temperature controlled

oven equipped with a fan to keep the temperatures uniform and provide a high convective heat transfer coefficient. The samples are placed in the oven at a prescribed oven temperature, and the temperature rise at the core of the sample is measured over time. Depending on the oven temperature, the sample will either heat past the oven temperature by a modest temperature and plateau, or have a sharp temperature increase due to thermal runaway and then ignite. In the first case, the experiment is repeated at a higher temperature with a fresh sample. In the second case, the experiment is repeated at a lower temperature. This procedure is carried out until the critical oven temperature is determined within a prescribed error range, usually within 5 °C. This is done for baskets of 3 differing sizes for each sample, determining the critical temperature for each basket size. The results from these experiments are coupled with what is known as the Frank-Kamenetskii ignition theory to extract thermal and kinetic parameters of the sample being tested. The disadvantages of using this method are that it is very time-intensive and requires a lot of material, as many experiments have to be carried out. The main advantages of this method are that it is not as sensitive to the reaction chemistry nor the experimental setup as the methods previously described. Furthermore, the results from the basket methodology have been shown to be less affected by temperature-dependent thermal properties and constants than all other methods. All of these characteristics of the oven methodology allow its results to be scaled to larger sizes than any other methodology described [31, 32, 35]. An example of ignition versus no-ignition for an ambient temperature difference of 5 °C is seen in Fig. 1.3, where Bowes experimentally measured sawdust sample self-heating ignition and showed self-heating with no ignition (left) and self-heating with transition to thermal runaway and ignition (right). The sample in the same sized basket ignites at 145 °C but not 140 °C, therefore defining the critical ignition temperature between 140 and 145 °C [31]. The oven methodology experimental setup is seen in Fig 1.4, taken from literature [41].

A second oven methodology exists, the crossing point method, and works by equipping a sample with two thermocouples, one at the centre and one on the surface, then placing the sample in a pre-heated oven. This is done at various pre-heated oven temperatures. The advantages over the traditional oven method is that only one specimen size is required, and less experiments are needed so it is a faster method and requires less material. However the main disadvantages of this methodology are that the analysis of results has a much weaker theoretical foundation as it cannot adopt the Frank-Kamenetskii theory of ignition, it requires very precise measurements of temperature at the centre of the sample so thermocouple placement must be exact, and the thermocouples must have a

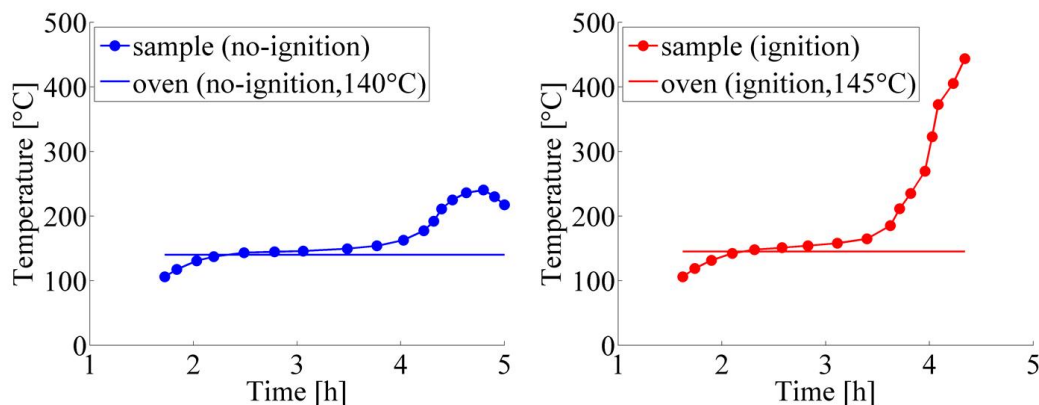


Figure 1.3: Ignition versus no-ignition for sawdust samples [31]. The difference in behaviour for ignition and no-ignition is clearly seen by the sharp temperature increase, and is used to determine the critical ignition temperature for one basket size.

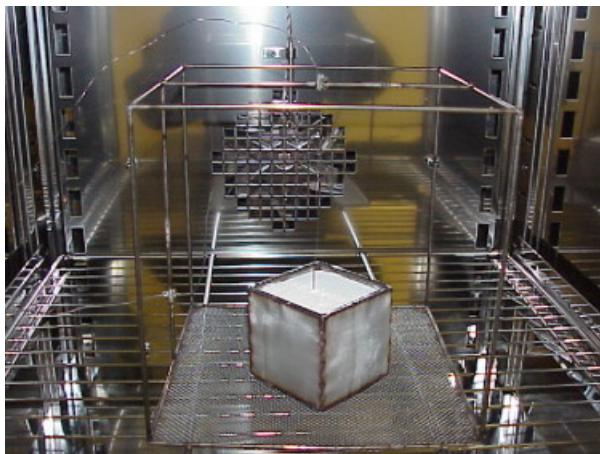


Figure 1.4: Setup for the oven methodology to determine self-heating ignition (from [41])

very small uncertainty range as measurement must be very accurate, requires knowledge of the thermal conductivity of the material being tested, and requires the chemical reactions to be very well described by a 1-step global reaction, as the results are much less tolerant to changes in reaction mechanism than the traditional oven method [32, 35].

This thesis on self-heating ignition utilises the oven basket methodology for all experiments because it has been shown to give the most accurate and most fundamental results as well as allows the extraction of kinetics for scaling results of laboratory-scale experiments to larger size. However it is most often not used because it is the method which requires the largest amount of samples and the longest amount of experimental time. As the thesis progressed, small improvements were made to both the experimental setup and the analysis methods, and these are seen from Chapters 2-6. The total number and cumulative oven run time of experiments required over the duration of this thesis is

287 oven basket experiments requiring 1705 hours of oven run time.

1.4 Experimental methodology

The laboratory setup to determine the minimum critical ambient temperature for self-heating $T_{a,c}$ that leads to self-ignition was constructed following a similar procedure to the British Standards EN 15188:2007. Fig. 1.5 shows the overall experimental setup, with the different baskets used. This setup was chosen to allow the use of Frank-Kamenetskii theory for data analysis. The reactive media was packed into cubic shaped wire mesh baskets of different sizes to study the size effect. I chose a cube shape for the baskets as it is the easiest shape with which to increase geometry size in a rectangular oven without making the larger samples approach the oven walls. The baskets were made of 0.5 mm diameter wire mesh with volumes of 131, 442, 1049, 3540 cm³. These baskets ensure a range of sizes to allow for the measurement of the largest possible temperature range at the laboratory scale given the dimensions of the isothermal oven. As the basket size increases there are lower critical ignition temperatures as the ratio of heat losses to the environment to heat generated by chemical reactions decreases [35]. Each basket filled with reactive sample was placed in the middle of a thermostatically controlled laboratory oven (with forced air circulation to prevent temperature stratification and provide good oxygen supply). The oven was initially preheated to a given uniform ambient temperature T_a to ensure the sample was exposed to the same environmental temperature for the entire duration of the experiment. In order to limit the influence of the forced flow changing cooling conditions at the surface of the baskets, a large mesh cage was placed around the sample, made of fine stainless steel mesh of 0.5 mm thickness. The temperature inside the sample was monitored using two thermocouples placed at the centre of the sample 0.5 cm apart. Based on the standard, only one thermocouple is needed, so the second one provides redundancy in case of failure of a thermocouple, and can be used for diagnosis of eventual equipment error. Oven temperature was also measured by a thermocouple placed several centimetres away from the basket, inside the mesh cage, in the vertical middle plane of the oven, and corresponds to the ambient temperature the sample is exposed to for convective cooling at the surfaces.

The minimum critical ambient temperature ($T_{a,c}$) is defined as the temperature for which thermal runaway leads to ignition and is determined using the procedure defined by Bowes and presented in Section 1.3. If the reactive sample failed to reach ignition the experiment was repeated with a fresh sample at a higher temperature. If the soil reached

ignition, then the experiment was repeated with a fresh sample at a lower temperature. The experiments were carried out until $T_{a,c}$ for ignition was located within ± 2.5 °C for each sample size. Multiple experiments were carried out for each specific sample.

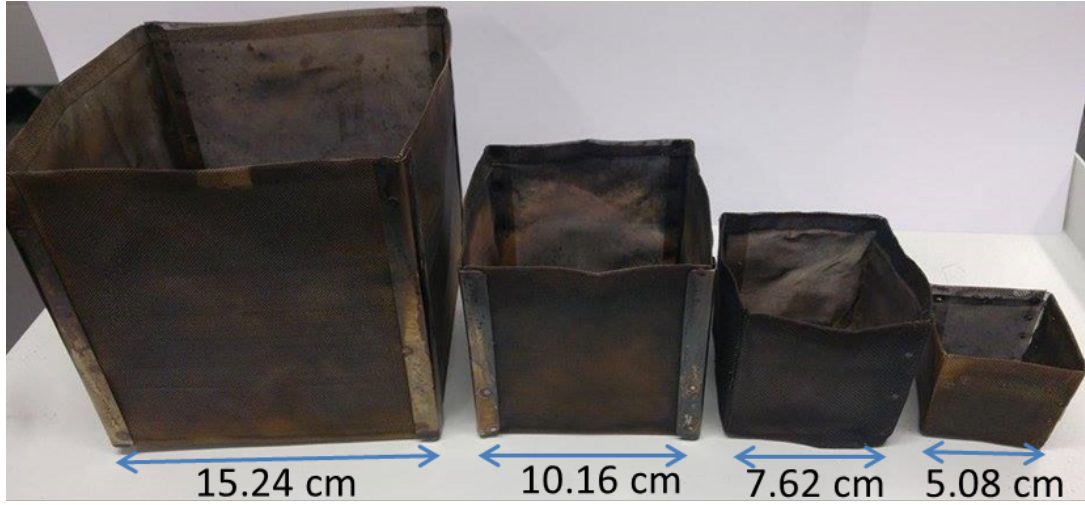


Figure 1.5: Experimental setup for studying self-heating of a sample placed at the centre of the thermostatically controlled oven with thermocouples for measuring the ambient and soil temperatures (left) and meshed test baskets (right).

In the next 5 chapters, I will present experimental results of self-heating ignition for various reactive porous media using this experimental methodology, modified as needed to best study each individual material, and the theory and experimental methodologies presented in section 1.2.

Chapter 2

Self-heating behaviour and ignition of shale rock

Summary¹

The combustion of shale, a porous sedimentary rock, has been reported at times in outcrop deposits and mining piles. However, the initiating event of most of these fires is unknown. It could be that, under the right conditions, shale rock undergoes spontaneous exothermic reactions in the presence of oxygen. This chapter studies experimentally and for the first time the self-heating behaviour of shale rock. Because shale has high inert content, novel diagnostics such as mass loss measurements and visual observation of charring are introduced to detect self-heating ignition in respect to other self-heating materials with lower inert content. Using field samples collected from the outcrop at Kimmeridge Bay (UK) and the Frank-Kamenetskii theory of ignition, I determine the effective kinetic parameters for two particle-size distributions of shale. These parameters are then used to upscale the results to geological deposits and mining piles of different thicknesses. I show that for fine particles, with diameter below 2 mm, spontaneous ignition is possible for deposits of thickness between 10.7 m and 607 m at ambient temperatures between -20 °C and 44 °C. For the same ambient temperature range, the critical thickness is in excess of 30 km for deposits made of coarse particles with diameter below 17 mm. The results indicate that shale rock is reactive, with reactivity highly dependent on particle diameter, and that self-ignition is possible for small particles in outcrops, piles, or geological deposits accidentally exposed to oxygen.

1. This chapter is based on “F. Restuccia, N. Ptak, G. Rein (2017) *Self-heating behavior and ignition of shale rock*, **Combustion and flame** 176:213-219.”

2.1 Introduction

Unconventional oil, as opposed to conventional oil extracted from reservoirs where petroleum can flow naturally, is trapped inside tight porous media that requires enhanced recovering processes like hydraulic fracturing to release oil and gas [42]. Unconventional oil may be trapped in rocks, sands or coal; the most common examples being oil sands, coalbed methane, shale gas and shale oil [42]. Shale oil and shale gas both originate from the same source rock, shale, as shown in Fig. 2.1. Shale is a general term used to describe a large array of clay rich sedimentary rocks. It is fine grained and is estimated to represent 50% of all the sedimentary rocks deposited on Earth [43]. The thickness of shale rock deposits varies widely with location around the world, but it ranges from 1 m to 600 m [44].

Sedimentary rocks containing significant amount of organic matter are reactive porous media. This includes coal, oil sand, and shale. Reactive porous media are materials where small free spaces (pores) are embedded in the solid together with a presence of a carbon-rich component [43], as shown in the sketch on the lower right of Fig. 2.1. This allows the rock to be permeable to a variety of fluids such as air, water, or oil, and greatly increases its surface area making the organic particles reactive because it allows oxidation to take place if O_2 is supplied [43]. Such reactive porous rocks might undergo self-heating. Self-heating is the tendency of certain materials to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures [1]. This process starts by slow oxidation at ambient temperature, but the reaction alone is insufficient to raise the material temperature. The temperature rise is determined by the balance between the rate of heat generation and the rate of heat losses [45]. Fire initiated by self-heating ignition is a well-known problem for many types of porous reactive media [31]. Of the reactive porous sedimentary rocks shown in Fig. 2.1, extensive studies on self-heating ignition behaviour have been conducted for coal, both experimentally and computationally [13,14,31,46–50]. Some work is present in the literature on the thermal degradation of shale and kerogens (in environments without oxygen) [51,52]. However, very little work has been done in understanding the behaviour of shale rock exposed to an oxidizing environment which might undergo self-heating. Early work was carried out on shale rock ignition in 1982, when the US Mining bureau reported initial measurements of the self-heating of shale dust [53]. The report acknowledges that self-heating of shale rock is of importance, and states that in-depth investigation is needed. No studies have been reported in literature since.

There are two systems of interest when studying shale self-heating, because of the presence of oxygen: The first is piles of shale accumulated on the surface during excavations, also known as heaps. These are very common from coal mining, both historically and currently. The second is geological formations, especially outcrops.

The ignition of heaps is common. For example, the landfill in Texas in 2000 [54].

The excavated shale rock was piled loosely to one side of the landfill, and the hot summer brought the environmental critical conditions for self-heating and ignition, causing the shale to burn for more than 12 months [54]. Another common shale fire is witnessed in spoil heaps, or bings as they are known in Scotland [55]. Spoil heaps were formed in the period when coal mining boomed in the UK, from the late 18th century to the mid 20th century. These heaps are piles consisting of shales, siltstones, and coal fines that were separated from usable coal as well as rocks that were removed during mining operations, and there are as many as 560 of such heaps in Scotland alone [55]. Because of their porous nature, and high carbon content, these heaps are susceptible to self-heating ignition. Heap shale fires have been witnessed for years, even recently, and in 2008 the Bogside fire in a 34 m tall heap was documented through an experimental campaign [55].

Combustion of shale outcrop formations has been observed in the past, with the most recent case being the Windfall Mountain in Alaska in 2012 [5]. A geological formation of shale ignited and burned for more than 24 months. The site was analyzed by the US National Park Service to determine the cause of the fire, and initial conclusions point towards self-heating as the most likely ignition event [5]. Other shale rock fires have been observed in several regions in California [7], over the course of many years, and the cause of fire was not found but self-heating was not ruled out either.

Other shale fires can be found all over the world, with outcrop or formation fires reported over the last centuries in India, Russia, the UK, Australia, the USA and Greenland [6,56]. However, even with so many shale fires pointing to self-heating as the possible ignition event, self-heating of shale has never been thoroughly investigated until now.

For the first time in literature, this chapter experimentally studies the self-heating behaviour of shale rock. The technique used for the self-heating study is known as oven-basket experiments [57]. This chapter contributes to understanding and predicting the initiation of shale fires and related geological combustion processes [6] by finding the effective kinetics and thermal properties of shale.

2.2 Self-heating ignition theory

Frank-Kamenetskii theory is usually employed in the literature to investigate spontaneous ignition [1,32]. The theory allows for the calculation of ignition conditions from reactive properties like the activation energy and other physical parameters of the material such as the conductivity and the heat of reaction by finding the critical ambient temperature for a given sample size. Total heat production from reactions inside a material sample is proportional to its volume, but heat loss is proportional to its area. This means that as the size of the sample becomes larger, because volume increases with size faster than area, then the critical ambient temperature required for ignition decreases. The theory can therefore be used to predict spontaneous ignition for larger sizes at lower temperatures, provided that the mechanism of heat production is unchanged [1,32]. The

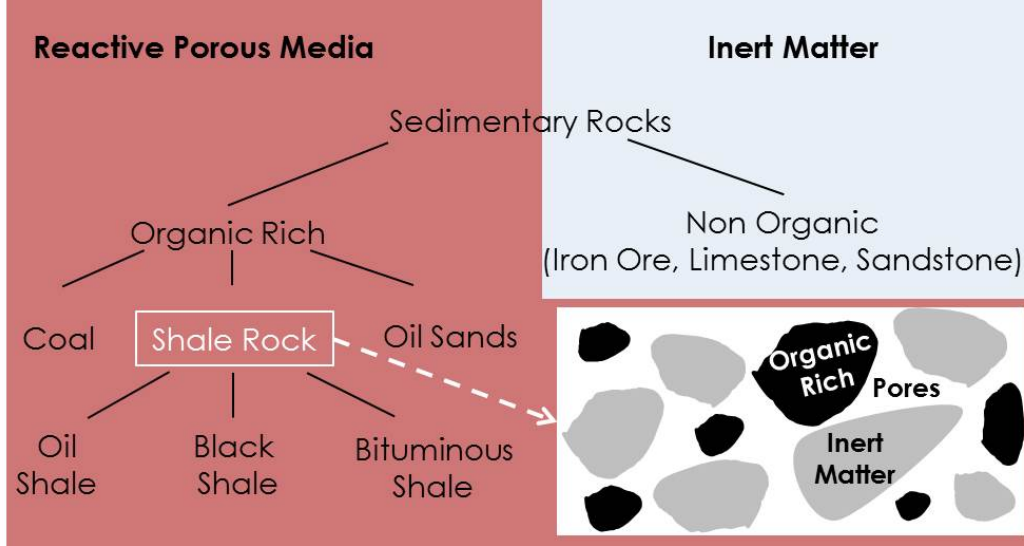


Figure 2.1: Sedimentary rocks arranged according to their reactivity and geology. A sample sedimentary rock is sketched on the lower right showing the presence of inert matter, organic rich material, and pore space within the porous rock.

heat transfer problem in this study corresponds to the transient heat conduction equation, as explained in Ch 1, section 1.2.

In this experimental work I use cubic baskets, so $\delta_c = 2.52$ [32], and for geological formations and heaps I assume slab geometry which has $\delta_c = 0.878$ [32]. By plotting the experimental data of $\ln\left(\frac{\delta_c T_{a,c}^2}{L^2}\right)$ against $\frac{1}{T_{a,c}}$ (Eq. 1.3), I obtain a correlation. If the correlation is a straight line, this validates the Frank-Kamenetskii theory. The slope of the straight line corresponds to $-\frac{E}{R}$, while the y-intercept is $\frac{QEf}{Rk}$.

2.3 Experimental method

A large shale formation is present in southern England in the Weald Basin near Southampton [58]. The shale for these experiments was collected with the aid of Tarik Saif, Nicolas Ptak and Antoine Lamarche from the outcrops of this formation on the coastal cliffs of Kimmeridge Bay, shown in Fig. 2.2, in large blocks to ensure the homogeneity of the samples.

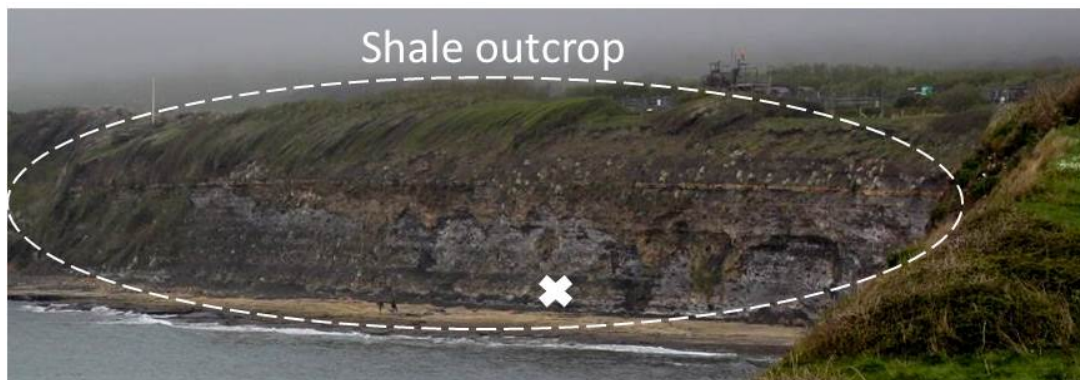


Figure 2.2: Cliff at Kimmeridge Bay where shale outcrop formations are visible. The samples were collected from this coastal site, marked with a cross. Photo taken on 25/4/2015.

The time delay between field collection of all samples and the last experiment conducted was 7 months. This was the shortest possible delay I could manage to complete the series of 37 experiments. I do not expect this delay to have effects on the results because shale samples are chemically stable (fossil matter was extracted from the free surface of the formation, and hence already weathered). The shale blocks were all collected from the same area to ensure homogeneity in the rock contents. To ensure further control and minimize loss of water or oxidation, once crushed, the samples were stored in sealed containers.

Elemental analysis was carried out on the samples, measuring the carbon, hydrogen, nitrogen and sulphur contents, and the results are provided in Table 2.1. The crushed samples have a density of $1200 \pm 10 \text{ kg/m}^3$. The low carbon content of 13% makes shale a weakly reactive porous media compared to other porous fuels like coal which have much higher carbon contents.

Proximate analysis of the shale was carried out and is shown in Table 2.2 as % of total sample weight. It shows low moisture content, and high ash content.

Thermogravimetric analysis (TGA) of the shale samples was conducted in air with a heating rate of 5 K/min, and is shown in Fig. 2.3. The error cloud corresponds to 10.9% of the mass measurement based on the worst case found in TGA mass measurements by Grønli et al. [59]. The first peak seen in the mass loss rate (MLR) corresponds to drying. The mass loss resulting in that temperature range matches the measured moisture content from the proximate analysis (Table 2.1). There are two other peaks in MLR, at 500 °C and 730 °C. By comparing this TG curve with typical data for coal, I see that the reactivity of shale develops in the same temperature range as coal, with the location of these two MLR peaks at similar temperatures to those of bituminous coal [60]. The large amount of residue mass left at the end of the test shows the high inert content of shale, in agreement with Table 1. The total mass loss from the TGA was found to be 18.6%, which is close to the sum of the moisture (Table 2.2), C, H and S (Table 2.1).

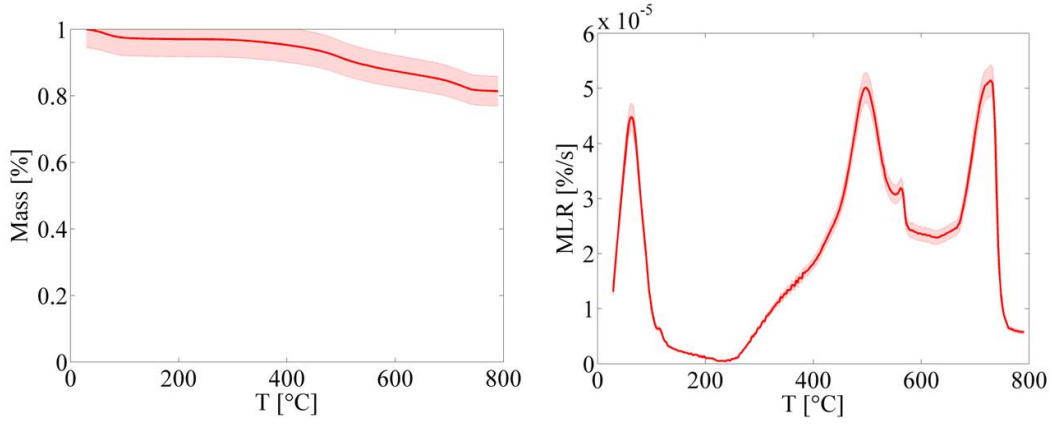


Figure 2.3: Thermogravimetric analysis in air of the shale sample, with a heating rate of 5 K/min. Plots of mass [%] as a function of temperature with error bars (left) and mass loss rate (MLR) as a function of temperature with error bars (right).

Size distribution of particles is important because the reactivity of the material is proportional to the average surface area to volume ratio of the media, A/V , with a decreasing particle size increasing the reactivity. This has been shown for reactive porous media such as coal [18,61].

When designing the experimental programme, it is important to control for the particle size of the samples as much as possible [18]. However, it is also important to retain as much as possible the field origin of the samples which are extracted from a real formation of porous rock as opposed to being monosize samples produced in the lab. I struck a balance between these two competing scientific aims by crushing the samples in a controlled manner and creating two repeatable sets of shale rocks (fine vs. coarse particle). Coarse particles have a diameter smaller than 17 mm. Fine particles have a diameter smaller than 2 mm. These two sets can test the hypothesis of the particle size effect and also retain much of their natural geological state. The coarse and fine sizes were prepared following fixed weight distributions of particles sizes. The resulting distributions are shown in Table 2.3.

The laboratory setup to determine the minimum ambient temperature for self-heating $T_{a,c}$ that leads to ignition was constructed following the procedure shown in Ch 1, section 1.4. The baskets were made of 0.5 mm diameter wire mesh with volumes of 131, 442.5, 1048.8, 3539.6 cm³ to ensure a wide range of sizes to obtain experimental data for a large temperature range. The baskets used are shown in Fig. 2.4, with each cube's length labelled.

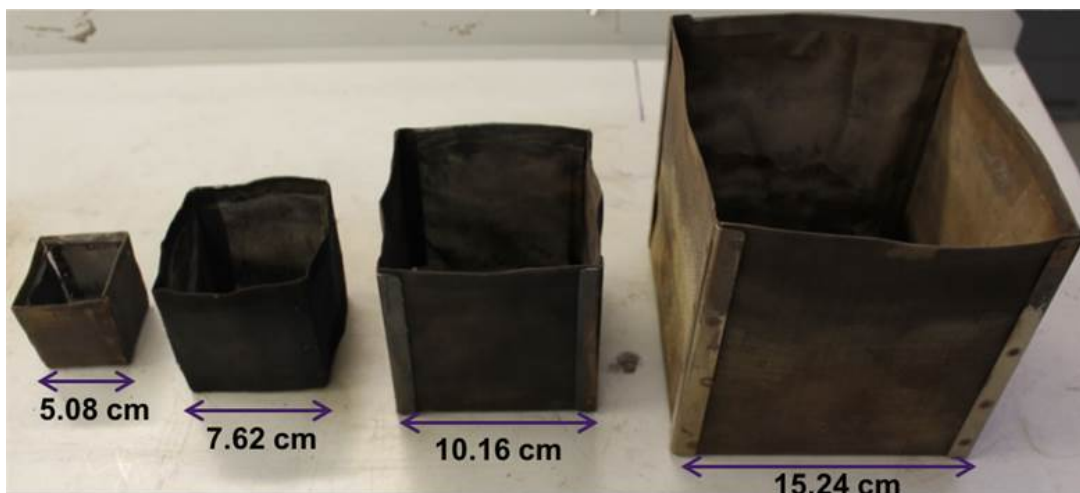


Figure 2.4: The four cubic shaped baskets used for experiments, with side lengths labelled.

Each basket filled with shale was placed in the middle of a thermostatically controlled laboratory oven with forced air circulation to prevent temperature stratification. The oven was initially preheated to a given uniform temperature. In order to prevent the forced flow affecting the results, a mesh cage was placed inside the oven. The temperature inside the sample was monitored using two thermocouples placed at middle depth in the center of the sample 0.5 cm apart. Oven temperature was also measured by a thermocouple placed several centimetres away from the basket, inside the mesh cage, in the vertical mid plane of the oven. Fig. 2.5 shows a sample shale rock collected for the experiments.

Supercritical temperature is defined as the temperature for which heat produced by the reactions exceeds the heat dissipated to the environment, causing a thermal runaway to ignition. If the shale failed to reach supercritical temperature the experiment was repeated with a fresh sample at 10 °C higher temperature. If the shale reached supercritical temperature and ignited, then the experiment was repeated with a fresh sample at 10 °C lower temperature. The repeats were carried out until the minimum ambient temperature $T_{a,c}$ for ignition was located with a maximum error of ± 5 °C. A summary of the experiments carried out, for each basket size and the two particle size distributions, is given in Table 2.4. A detailed summary of all experimental results is presented in Appendices 2.A and 2.B.

Reactivity of shale can be readily identified because once the baskets are placed in the oven the core reaches a temperature higher than that of the oven. Once the local reactions terminate (burnout) the heat dissipates away from the sample bringing the temperature of that location back to the oven temperature. Fig. 2.6 shows the temperature evolution at the core of the sample, where the core temperature at the center of a 131 cm³ basket for fine particle samples is compared to the oven reference temperature throughout the duration of an experiment for both an ignition and a no-

ignition case. The no-ignition experiment is carried out with an oven temperature of 196 °C, while the ignition experiment is carried out with an oven temperature of 244 °C. Both temperature curves present very similar characteristics, with the core of the shale sample reaching higher temperatures and in shorter time for the ignition case. In all the experiments, the center of the sample is allowed to cool down to the oven temperature.

Table 2.1: Basic composition of the shale rock samples collected from Kimmeridge bay.

Element	C	H	N	S
Weight %	13.01	1.67	<0.3	2.22

Table 2.2: Proximate analysis of the shale rock samples collected from Kimmeridge bay.

	Moisture content	Volatile matter	Ash	Fixed carbon
Weight %	2.5	16.5	80.4	0.6

Table 2.3: Distribution of particle diameter D for the two sample sizes used in the experiments for this study. The distributions are expressed as a percentage of the total shale mass of each experiment.

Particle diameter range	$2 \text{ mm} < D < 17 \text{ mm}$	$1 \text{ mm} < D < 2 \text{ mm}$	$D < 1 \text{ mm}$
Coarse particles	57%	20%	23%
Fine particles	0%	40%	60%



Figure 2.5: Sample of shale rock (before crushing) from Kimmeridge Bay used for the experiments.

Table 2.4: Distribution of particle diameter D for the two sample sizes used in the experiments for this study. The distributions are expressed as a percentage of the total shale mass of each experiment.

Basket length	5.08 cm	7.62 cm	10.16 cm	15.24 cm
Coarse particles, # experiments	6	5	5	3
Fine particles, # experiments	8	4	4	2

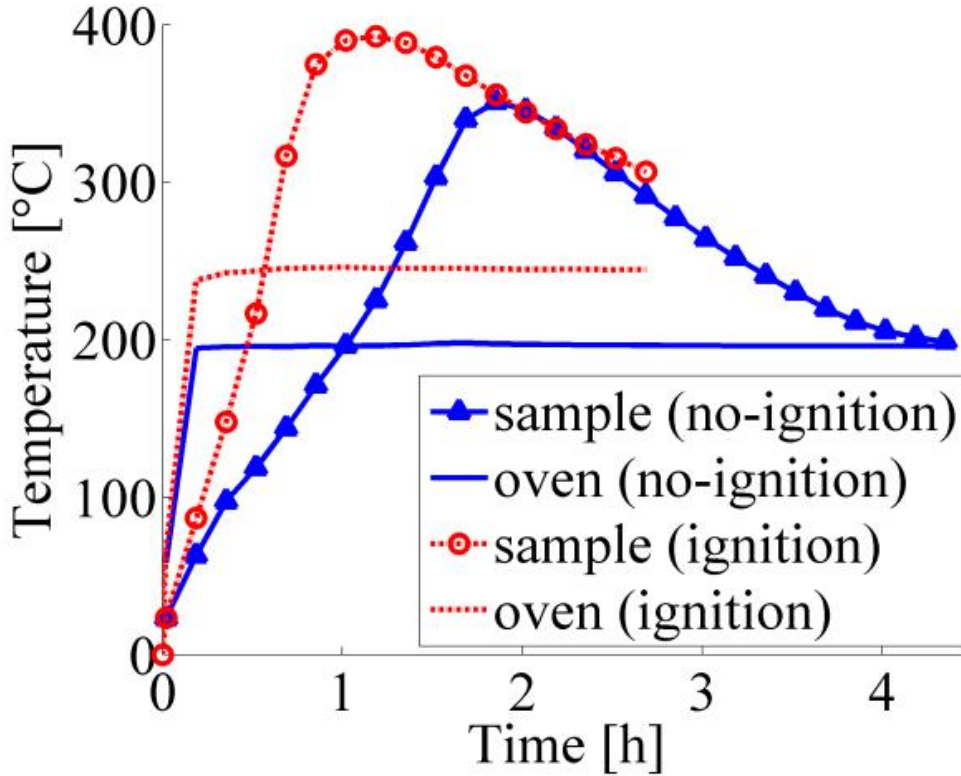


Figure 2.6: Temperature measurements at the centre of the basket and the oven for ignition and no-ignition 131 cm³ sample experiments. The thermal behaviour of both experiments presents similar overall characteristics, with the ignition experiment reaching a higher maximum temperature.

2.4 Results and discussion

When analyzing results for very reactive media, usually the sharp temperature increase after a critical temperature can be used to identify ignition and criticality [1,31,32, 57]. An example of such analysis is shown in Fig. 2.7, where cases of self-heating ignition, and no-ignition, of a different reactive porous media (much more reactive than shale), hardwood sawdust, are taken from literature [31]. In the first case there was no-ignition, while in the second case the sample ignited and the sharp temperature increase is evident.

However, as shown in Fig. 2.6, the shale rock temperature profile is more similar for both the no-ignition and ignition cases. This is due to the low carbon content of the rock, and its very high inert content acting as a heat storage (heat capacity). For shale, the temperature rise is not valid as the only means for identifying ignition. Therefore, two novel diagnostics were introduced to the self-heating ignition criteria: the mass lost (measured after each oven experiment), and the presence of char in the sample. The change in the mass of the shale sample after the experiment exhibited a distinct change in slope for the experiments where ignition took place. This can be seen for the 131 cm³ fine particle size basket experiments on the left of Fig. 2.8. The best linear fits for the experimental mass loss data of no-ignition and ignition cases are plotted as a function of the oven temperature. The change in slope corresponds to the presence of char in the sample after the experiments (right of Fig. 2.8). This triple criteria for ignition provides confidence on the identification of critical conditions, even for low-reactive shale.

Analysis of experiments shows the presence of three regions: one where no critical thermal runaway happens and there is no ignition; a transition zone where we are at the critical thermal run-away limit for ignition and therefore have some ignition cases and some no-ignition cases; and a zone for which ignition happens for all the experiments. In the ignition zone char is observed in all of the samples after the experiments. The slopes of the mass loss curves depend on the particle size distribution, and on the basket size. The marked change in slope is observed in all sizes and particle distributions studied.

Using the critical ignition temperatures found in the experiments for the four different basket sizes, I plot the data of $\ln\left(\frac{\delta_c T_{a,c}^2}{L^2}\right)$ vs $\frac{1}{T_{a,c}}$, and calculate the best linear fit to produce Fig. 2.9. This shows the typical Frank-Kamenetskii plot for both coarse and fine particle sizes. The linear fits have R-squared values of 0.999 for the coarse particles, and R-squared of 0.984 for the fine particles. The slope is confirmed as strongly linear and the data validates the assumption that the Frank-Kamenetskii theory and Arrhenius reactions assumptions apply.

The impact of particle size is large. I can obtain the effective activation energy from the slope of the two lines in Fig. 2.9, where E_c and E_f are the coarse particle and fine particle effective activation energies, and the thermal parameters from the y-axis intercept, as shown in Table 2.5 [32]. The values are calculated based on the best linear fits from Fig. 2.9 with the effective activation energy being half for fine particles compared to that of the coarse particles. The error bounds are calculated using the fits that would give the highest and the lowest possible effective activation energies from the experimental data, so they are the worst-case scenario. The kinetic parameters and effect of particle size obtained in this chapter can be used as parameters for more advanced models of shale self-heating ignition.

Table 2.5: Effective activation energy E and the y-axis intercept of Fig. 2.9 calculated from Eq. (1.3) for both coarse and fine shale particles.

Particle size	E (−error, +error)[kJ/mol]	$\ln\left(\frac{QE_f}{Rk}\right)$ (−error, +error)
Coarse	179.36 (−38.82,+68.18)	60.18 (−8.69,+15.22)
Fine	88.78 (−6.87,+19.44)	41.71 (−1.69,+4.74)

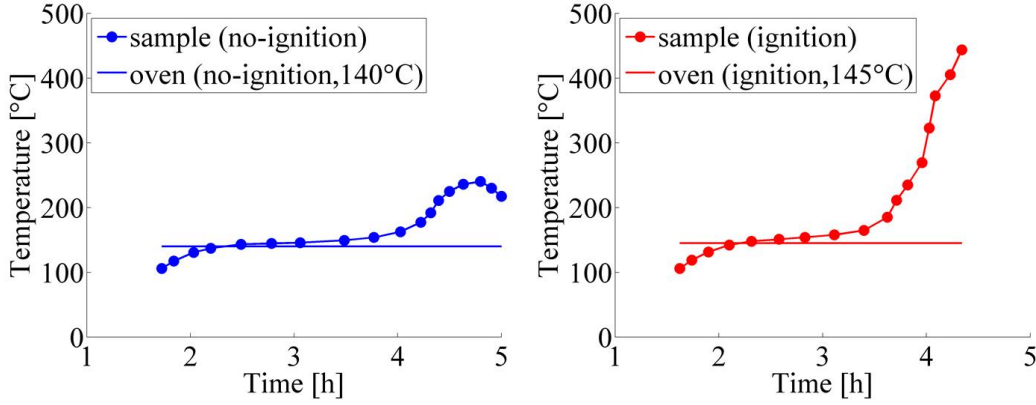


Figure 2.7: Ignition versus no-ignition for sawdust samples [31]. The difference in behaviour for ignition and no-ignition is clearly seen by the sharp temperature increase.

2.5 Upscaling results to the field domain

The activation energies found are used in the Frank-Kamenetskii theory to upscale to geological sizes. A shale formation is usually very wide, up to thousands of kilometers long, but is between 1 m and 600 m thick [44]. Similarly, a heap is typically much wider than thick. They can therefore be modeled as an infinite slab, and determine a critical geological deposit for various temperatures by using Eq. (1.3) with the critical dimensionless parameter $\delta_c = 0.878$ [32]. This approach was used for both sets of particle size distributions for a temperature range between 20 °C and 44 °C, which includes possible ranges of ambient temperature in the natural environment (day and night, winter and summer). It is important to note that this assumes that oxygen is present in the shale for the reactions to occur. Such oxygen supply could be provided at out-crop formations exposed to the atmosphere, as well as by ground perforations providing an accidental route for oxygen ingress from the atmosphere. The upscaled results can be seen in Fig. 2.10. The error bar is purposefully large, as the fits that would give highest and lowest possible effective reactivity are calculated for the error bars of Table 2.5. These represent the worst-case scenario.

Results show that the shale rock geological deposit (or mining pile thickness) required for ignition vary dramatically with shale particle size. For the fine particles, with size distribution below 2 mm, at 22 °C ignition is possible for a thickness of 35 m. For the coarse particles, which include particles up to 1.7 cm diameter, for the same temperature,

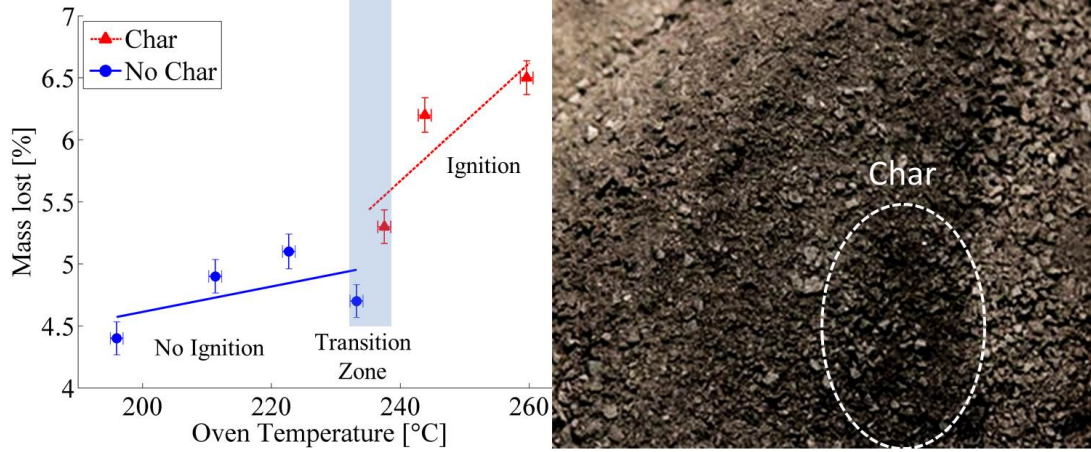


Figure 2.8: Ignition criteria for 131 cm³ fine particle shale basket experiments is shown on the left. Mass lost is plotted as a function of oven temperature. Linear best fits are plotted for the no-ignition and ignition cases. Experiments which showed char presence (shown on right) are indicated by red squares. The no-ignition, transition and ignition zones are determined on the left from these two criteria (mass loss slope and char).

a thickness of 358 km is required for ignition. Spontaneous ignition is possible for rock deposits of thickness between 10.7 m and 607 m for the fine particles. These are all shale thickness sizes that can be found in natural geological deposits present throughout the world which are up to 600 m in thickness [44]. For the coarse particles in the same temperature range, the required thickness is between 30 km and 100,000 km, which are all sizes much greater than the natural geological deposits on Earth.

There are some limitations to consider when upscaling the laboratory results to the field domain. The effect of moisture has not been taken into account but water can affect the heat transfer via evaporation, condensation and by changing the thermal diffusivity [32]. The effect of pressure on self-heating ignition has not been studied although shale can be found at higher pressures than atmospheric pressure, it is known that in general pressure has an effect on ignition and that the effects are dependent on the global reaction order and thus vary depending on the fuel and chemistry [62]. Any natural shale formation would have differing carbon contents and different particle size distributions to those present in this study. The effect of these cannot be quantified at the present moment, but this study is the first time self-heating and ignition conditions for shale are studied and should enable future in-depth studies.

2.6 Conclusions

Shale fires are a common problem in both shale rock outcrop formations and mining heaps throughout the world. The ignition process, which could be due to self-heating of reactive porous shale rock, has not been studied in-depth until now. This study investigates experimentally and for the first time the self-heating and ignition conditions for

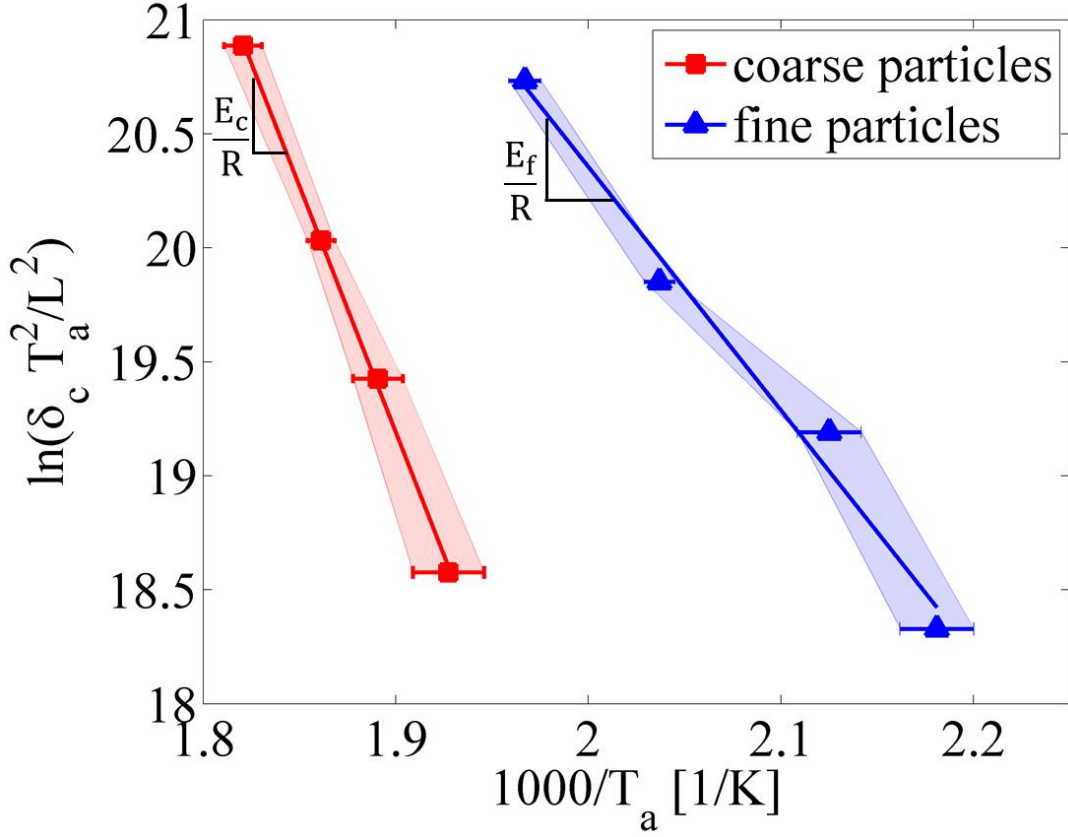


Figure 2.9: Frank-Kamenetskii plot for shale rock of two different size distribution (coarse and fine particles). Experimental errors are indicated by shaded regions, and linear best fits are plotted through the data points. The slopes of both lines represent the E/R .

shale rock at various ambient temperatures and for different particle diameter sizes. Traditional experimental diagnostics for identification of self-heating ignition were enhanced by the addition of two novel diagnostics valuable for samples of high inert content such as in shale. This chapter contributes to understanding and predicting the onset of shale formation fires, which have been observed in nature. The Frank-Kamenetskii theory of ignition criticality shows that Arrhenius reactions apply, as the effective energy is found to be a constant for the temperature range and particle size distributions studied. Self-ignition conditions depend on shale particle size and ambient temperature. It was shown that particle size has a large effect on reactivity, with fine particles being more reactive than coarse particles and presenting a smaller effective activation energy of 88.79 kJ/mol compared to 179.36 kJ/mol, differing by almost a factor of two. Lab-scale results were upscaled to slab formation thicknesses to model real geological shale formations and find critical thicknesses for self-heating and ignition for a range of ambient temperature conditions. For fine particle size it was shown that a small formation thickness is required for spontaneous ignition at ambient temperature. In nature, this can be in outcrop formations exposed to the environment as well as ground perforations providing an accidental

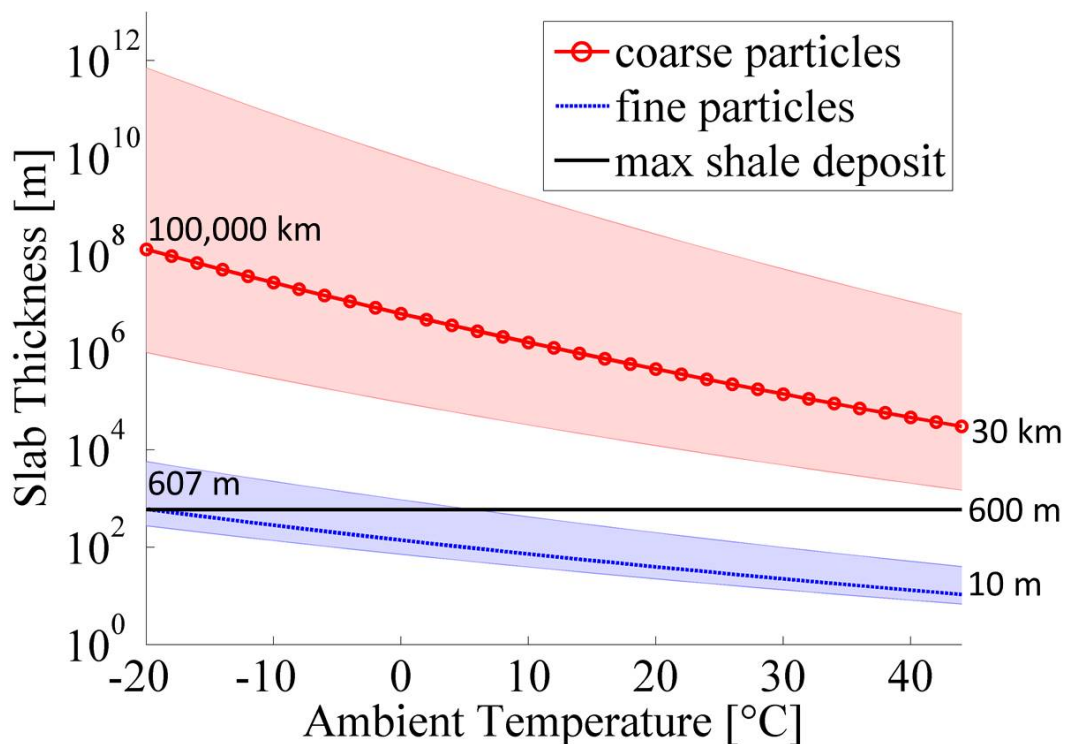


Figure 2.10: 1D upscaled results of shale formation thickness required for self-heating and ignition for a temperature range between -20 °C and 44 °C for both coarse and fine particle size distributions. Error bars are represented by the shaded regions and show the worst-case scenario in terms of lab-scale errors.

route for oxygen ingress from the environment. The upscaling results highlight a very large reactivity change of shale rock with changes in particle size distributions. This chapter provides the first experimental study of the self-heating and ignition conditions for shale rocks.

Appendices

2.A Experimental data from coarse particle shale rock self-heating ignition cubic basket experiments

Table 2.6: This table contains a complete set of experimental data from coarse particles shale rock self-heating ignition cubic basket experiments. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and shale sample temperatures. The data reported includes the dates of experiments, volume of shale basket being tested, oven ambient temperature, fuel mass of shale, bulk density of the shale, residue mass after the experiment, percentage of residue in respect to initial mass, and if the sample ignited or not.

Date experiment was carried out	07/05/15	29/06/15	30/06/15	06/07/15	06/07/15	13/07/15	14/07/15	15/07/15	15/07/15
Volume of basket being tested (mL)	131	131	131	131	131	131	442	442	442
Oven reference temperature (°C)	315.0	302.9	285.0	279.2	273.3	254.4	238.2	252.2	262.3
Fuel mass (g)	160.6	158.8	151.4	156.5	158.6	160.1	524.2	532.2	529.4
Bulk density of fuel (kg/m ³)	1225	1211	1155	1194	1210	1221	1185	1203	1197
Residue mass (g)	147.8	146.2	141.4	147.0	150.1	152.3	501.2	509.7	504.4
Residue mass (%)	92.0	92.1	93.4	93.9	94.6	95.1	95.6	95.8	95.3
Ignition (Yes/No)	Y	Y	Y	Y	N	N	N	N	Y

Date experiment was carried out	27/07/15	21/07/15	22/07/15	19/08/15	24/07/15	27/08/15	20/08/15	28/08/15	02/09/15
Volume of basket being tested (mL)	442	1049	1049	1049	1049	1049	3540	3540	3540
Oven reference temperature (°C)	266.3	244.9	252.3	264.0	266.5	259.5	259.8	250.8	240.9
Fuel mass (g)	531.7	1264.4	1262.8	1259.2	1262.1	1259.0	4279.6	4279.7	4278.8
Bulk density of fuel (kg/m ³)	1202	1206	1204	1201	1203	1200	1209	1209	1209
Residue mass (g)	503.5	1207.3	1202.4	1196.2	1193.1	1190.9	4064.1	3955.4	4067.0
Residue mass (%)	94.7	95.5	95.2	95.0	94.5	94.6	95.0	92.4	95.1
Ignition (Yes/No)	Y	N	N	Y	Y	Y	Y	Y	N

2.B Experimental data from fine particle shale rock self-heating ignition cubic basket experiments

Table 2.7: This table contains a complete set of experimental data from fine particle shale rock self-heating ignition cubic basket experiments. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and shale sample temperatures. The data reported includes the dates of experiments, volume of shale basket being tested, oven ambient temperature, fuel mass of shale, bulk density of the shale, residue mass after the experiment, percentage of residue in respect to initial mass, and if the sample ignited or not.

Date experiment was carried out	24/11/15	24/11/15	24/11/15	10/07/15	10/07/15	17/08/15	13/07/15	01/07/15	20/07/15
Volume of basket being tested (mL)	131	131	131	131	131	131	131	131	442
Oven reference temperature (°C)	177.1	196.0	211.3	222.7	233.2	237.5	243.8	259.6	234.2
Fuel mass (g)	156.7	156.6	155.9	151.1	158.3	157.4	153.2	156.8	530.8
Bulk density of fuel (kg/m ³)	1195	1195	1189	1153	1208	1201	1169	1196	1200
Residue mass (g)	151.4	149.7	148.2	143.4	150.9	149.0	143.7	146.6	502.6
Residue mass (%)	96.6	95.6	95.1	94.9	95.3	94.7	93.8	93.5	94.7
Ignition (Yes/No)	N	N	N	N	N	Y	Y	Y	Y

Date experiment was carried out	20/07/15	21/07/15	31/08/15	31/07/15	11/08/15	24/08/15	18/08/15	23/09/15	02/10/15
Volume of basket being tested (mL)	442	442	442	1049	1049	1049	1049	3540	3540
Oven reference temperature (°C)	216.0	225.2	219.8	219.1	205.8	201.2	193.9	181.5	189.5
Fuel mass (g)	530.3	531.1	531.3	1259.0	1258.8	1259.6	1259.0	4279.0	4279.0
Bulk density of fuel (kg/m ³)	1199	1200	1201	1200	1200	1201	1200	1209	1209
Residue mass (g)	506.2	504.2	503.7	1199.4	1199.9	1202.7	1205.6	4076.3	4068
Residue mass (%)	95.5	94.9	94.8	95.3	95.3	95.5	95.8	95.3	95.1
Ignition (Yes/No)	N	Y	Y	Y	Y	Y	N	N	Y

Chapter 3

Self-ignition of natural fuels: Can wildfires of carbon-rich soil start by self-heating?

Summary¹

Carbon-rich soils, like histosols or gelisols, cover more than 3% of the Earth's land surface, and store roughly three times more carbon than the Earth's forests. Carbon-rich soils are reactive porous materials, prone to smouldering combustion if the inert and moisture contents are low enough. An example of soil combustion happens in peatlands, where smouldering wildfires are common in both boreal and tropical regions. This chapter focuses on understanding soil ignition by self-heating, which is due to spontaneous exothermic reactions in the presence of oxygen under certain thermal conditions. I investigate the effect of soil inorganic content by creating under controlled conditions soil samples with inorganic content (IC) ranging from 3% to 86% of dry weight: I use sand as a surrogate of inorganic matter and peat as a surrogate of organic matter. This range is very wide and covers all IC values of known carbon-rich soils on Earth. The experimental results show that self-heating ignition in different soil types is possible, even with the 86% inorganic content, but the tendency to ignite decreases quickly with increasing IC. A clear increase in ambient temperature required for ignition as the IC increases is reported. Combining results from 39 thermostatically-controlled oven experiments, totalling 401 h of heating time, with the Frank-Kamenetskii theory of ignition, the lumped chemical kinetic and thermal parameters are determined. I then use these parameters to upscale the laboratory experiments to soil layers of different thicknesses for a range of ambient temperatures ranging from 0 °C to 40 °C. The analysis predicts the critical soil layer thicknesses in nature for self-ignition at various possible environmental temperatures. For example, at 40 °C a soil layer of 3% inorganic content can be ignited through self-heating if it is thicker than 8.8 m, but at 86% IC the layer has to be 1.8 km thick, which is impossible to find in nature. I estimate that the critical IC for an ambient temperature of 40 °C and soil thickness of 50 m is 68%. Because those are extreme values

1. This chapter is based on “F. Restuccia, X. Huang, G. Rein (2017) *Self-ignition of natural fuels: Can wildfires of carbon-rich soil start by self-heating?*, **Fire Safety Journal** 91C:828-834.”

of temperature and thickness, no self-heating ignition of soil can be expected above the 68% threshold of inorganic content. This is the first in-depth experimental quantification of soil self-heating and shows that it is indeed possible that wildfires are initiated by self-heating in some soil types and conditions.

3.1 Introduction

Carbon-rich soils are porous reactive natural fuels found in nature, like histosols and gelisols [63]. Examples of carbon-rich soil systems are natural peatlands [64]. Peatlands store most of the terrestrial ecosystem's carbon, roughly three times more carbon than the Earth's forests. Peatlands cover about 3% of the Earth's land surface, and are primarily found in tropical and boreal regions, but store about 25% of the Earth's soil carbon [4]. Peat is an accumulation of decayed vegetation formed in anaerobic conditions [65]. As an organic porous media, carbon-rich soil is prone to smouldering ignition and combustion [1, 66]. Smouldering wildland fires in soil systems, ranging from low to high inorganic contents, are a known natural hazard. Once ignited, carbon-rich soils burn the ancient carbon for months often causing the largest fires on Earth [4]. For example, in 1997 peat fires led to an extreme haze event in Southeast Asia, and released greenhouse-gas equivalent to 13-40% of the global man-made emissions [2, 3]. The effect of wildfires in carbon-rich soils like peatlands can be dramatic, as seen in Fig. 3.1 where a smouldering soil fire burnt for weeks in Las Tablas de Daimiel National park, Spain, in 2009. Global warming can dry the soils and increase soil combustion, creating a positive feedback to the climate system [64, 65].



Figure 3.1: Smouldering wildfire of a carbon-rich soil system in Las Tablas de Daimiel National park [67].

Carbon-rich soil fires can be initiated by an external source, e.g. lightning, flaming

wildfire, and firebrand, or by self-heating due to its propensity to smouldering. Self-heating is the tendency of certain porous solid fuels to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures [1, 31]. This process starts by slow exothermic oxidation at ambient temperature, but the reaction alone is insufficient to raise the material temperature. The temperature rise is determined by the imbalance between the rate of heat generation and the rate of heat losses [1]. Fire initiated by self-heating ignition is a well-known hazard for many natural materials such as coal, biomass [47, 68], and shale as shown in Ch 2. Similarly, the self-heating ignition hazard for carbon-rich soils which are a typical natural biomass should not be overlooked but have not been studied in depth to date.

In the literature, there are only a handful of studies on the forced ignition of soil [69–72]. Frandsen [69, 70] showed that there are two limiting factors, moisture content (MC) and inorganic content (IC)² of soil (i.e. minerals), for the smouldering by an external heating source (forced ignition). Both natural soils and modified soils (i.e. mixing peat with sand) with a wide range of MC and IC were studied. Fig. 3.2 replots these experimental results of ignition and non-ignition limits as well as the recent numerical predictions from [71]. When the soil's IC and MC are such that it is on the left side of the critical conditions, then soil can ignite with an external heat source. If it is on the right, it does not ignite with an external heat source. Moreover, MC is found to be an important factor to determine the soil conditions for ignition, and the value of critical MC is compensated by the value of IC. As the value of MC increases, critical IC for forced ignition decreases. Recently, Hadden et al. [72] and Huang et al. [73] further investigated the influence of oxygen concentration on the forced ignition of soil. However, to the best of my knowledge, so far there is no research on the self-ignition of carbon-rich soil, posing a fundamental knowledge gap.

In this experimental work, I study the self-heating ignition behaviour of modified soil samples with varying IC which covers all IC values of known carbon-rich soils on Earth using bench scale experiments, and aim to determine the limiting IC. The experimental results are then used to predict the ignition behaviour of natural carbon-rich soil systems and its dependence on ambient temperature, IC and soil layer thickness.

3.2 Self-heating ignition theory

As explained in Ch 1, section 1.2, the Frank-Kamenetskii theory of ignition criticality has been used extensively in the literature to investigate self-ignition characteristics of materials [1, 32]. For a given sample size, heat generation from exothermic reactions is

2. Moisture content (MC) is defined in dry basis as the mass of water divided by the mass of a dry soil sample, expressed as %. Inorganic content (IC) is defined in dry basis as the mass of soil inorganic matter (inert matter, like for example minerals) divided by the mass of a completely dry soil sample, expressed as %.

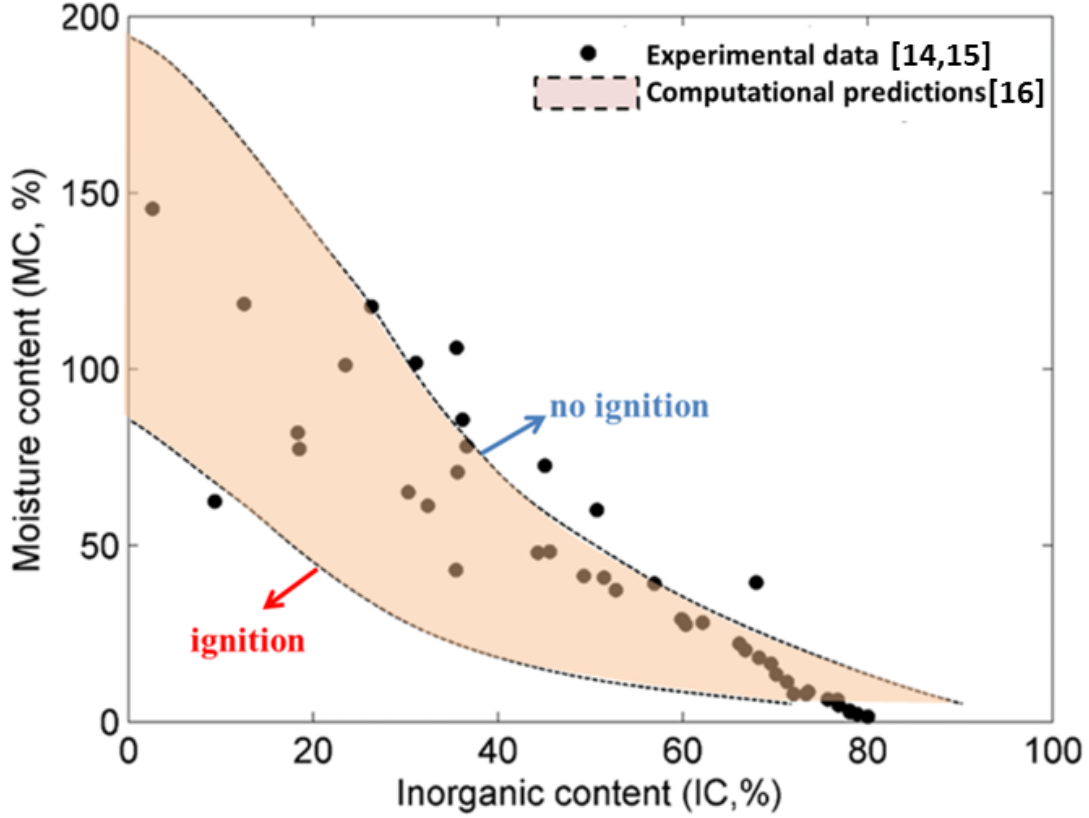


Figure 3.2: Critical moisture and inorganic content for the forced ignition of peat where experimental data is from [69,70] and computational predictions are from [71]. If soil has lower IC or MC than the shaded area, it will ignite with forced ignition. If it is higher than the IC or MC of the shaded area, it will not ignite.

proportional to the volume of the sample, but volumetric heat loss is proportional to the surface area of the sample: as the size of the sample increases, the critical ambient temperature required for self-ignition decreases. In the experimental work I used cubic baskets, so $\delta_c = 2.52$ [32], and for natural soil formations I assume slab geometry which has $\delta_c = 0.878$ [32].

When carrying out bench scale experiments with environmental temperatures greater than 100 °C the effect of moisture cannot be accounted for as the thermostatically controlled ovens used for measurements are at temperatures greater than the boiling point of water. Moisture effects are not studied in this work. The effect of moisture content on self-heating ignition of reactive porous media has been shown to be complex [74]. At low MC an increase in moisture content increases the reactivity of the material. At higher MC values the reactivity of the material decreases dramatically with moisture content [74]. The effect of moisture content has been studied extensively for coal, where moisture content affects the type of radical sites formed in the porous material. At low MC, moisture hinders formation of stabilized radicals where it is tightly bound within the rock, which leads to faster oxidation of the coal and therefore to a material more

prone to self-heating up to approximately 50% MC [75]. At higher MC any non-tightly bound moisture, so excess moisture, takes up extra heat and slows down the release of heat from oxidation [75].

3.3 Experimental methods

The carbon-rich organic soil used as a surrogate in the experiments is a commercial variety, Shamrock Irish Moss peat, provided by Bord na Mona Horticulture Ltd. It was chosen for the experiments because of its low IC ($\leq 3\%$) [76]. Elemental analysis of the organic matter was carried out and yielded 54% C, 39% O, 5% H, 1.2% N and traces of S. Moreover, compared to naturally sourced peat, its advantages include the availability in large quantities, constant composition, homogeneous properties, and the fact that this peat has been used in many previous studies [72, 76, 77]. The peat was oven-dried at 80 °C for 48 h [78] (shown in Fig. 3.3). Inert fine grained silica sand was used to mix with peat to vary the soil IC, (shown in Fig. 3.3). Both peat and sand are porous media, and their respective bulk densities are $223 \pm 18 \text{ kg/m}^3$ and $1477 \pm 3 \text{ kg/m}^3$.

Before each test, the sand and peat were well mixed and left for a day to ensure homogeneity. IC is calculated as the mass fraction of sand as in Eq. (3.1).

$$\text{IC} = \frac{m_s}{m_s + m_p} 100\% \quad (3.1)$$

where m_s is the mass of sand which is used as surrogate for IC and m_p is the mass of peat used as surrogate for the organic matter. Because sand has a higher density than peat, the density of the mixed soil increases as the IC increases (Fig. 3.4). The density increases nearly linearly for IC up to 50%. After this, the space taken up by the IC becomes too large for the pores to contain, and the organic content present per unit volume decreases. This can be seen in Fig. 3.4. The laboratory setup to determine the minimum critical ambient temperature for self-heating $T_{a,c}$ that leads to self-ignition was constructed following the procedure presented in Ch 1, section ???. The soil sample was packed into cubic shaped wire mesh baskets of different sizes to study the size effect. I chose a cube shape for the baskets as it is the easiest shape with which to increase geometry size in a rectangular oven without making the larger samples approach the oven walls. The baskets were made of 0.5 mm diameter wire mesh with volumes of 131, 442, 1049, 3540 cm^3 and are shown in Fig. 3.5. These baskets ensure a good range of sizes for the largest possible temperature range given at the laboratory scale, between 130 °C and 200 °C for these soil samples. As the basket size increases there are lower critical ignition temperatures as the ratio of heat losses to the environment to heat generated by chemical reactions decreases [35]. Each basket filled with soil was placed in the middle of a thermostatically controlled laboratory oven with forced air circulation to prevent temperature stratification and provide good oxygen supply. The oven was initially preheated to a given uniform ambient temperature T_a . In order to

limit the influence of the forced flow, a large mesh cage was placed around the sample. The temperature inside the sample was monitored using two thermocouples placed at the centre of the sample 0.5 cm apart. Based on the standard, only one thermocouple is needed, so the second one provides redundancy. Oven temperature was also measured by a thermocouple placed several centimetres away from the basket, inside the mesh cage, in the vertical middle plane of the oven.

A summary of the experiments is presented in Table 3.1. In total, 39 experiments and 401 h of oven run time over the course of 8 months were carried out for different soils. The results found for the 3% IC experiments were used to estimate the ignition temperatures needed for higher ICs, reducing the number of experiments required for finding the critical ignition temperature at those given inorganic contents. The minimum critical ambient temperature ($T_{a,c}$) is defined as the temperature for which thermal runaway leads to ignition. If the soil failed to reach ignition the experiment was repeated with a fresh sample at a higher temperature. If the soil reached ignition, then the experiment was repeated with a fresh sample at a lower temperature. The experiments were carried out until $T_{a,c}$ for ignition was located within ± 2.5 °C for each tested soil. At least two experiments were conducted at each IC and basket size condition.

Fig. 3.6 shows an example of successful soil ignition. The sample before and after self-heating ignition is shown visually as well. The mass of the organic content is reduced by 94% and what remains are char and ash (IC). The temperature profile at the centre of the soil where thermal runaway is seen, along with the reference ambient temperature T_a , are plotted in the figure.



Figure 3.3: Peat (left) and sand (right) are mixed to create the appropriate inorganic content ratios of the samples.

3.4 Results

Table 3.2 shows the obtained critical ignition temperatures for the different basket sizes and different IC. A detailed summary of all experiments is presented in the Appendices 3.A-3.D. The critical ignition data found in experiments was used to make a

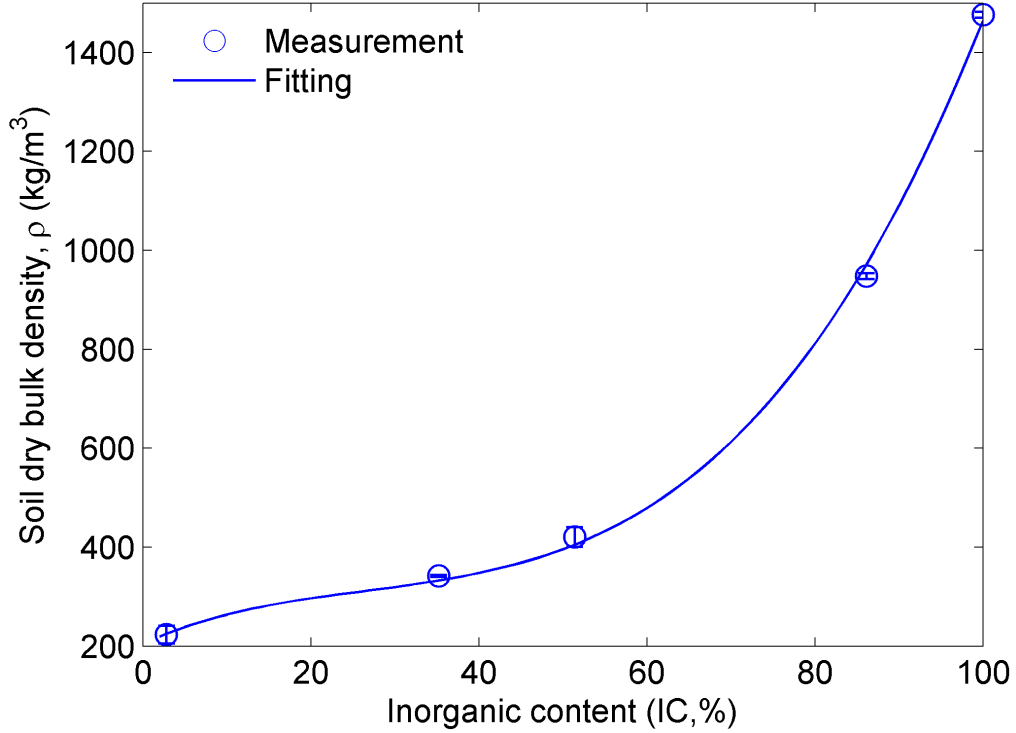


Figure 3.4: Density of soil samples with increasing IC.

Table 3.1: Number of experiments carried out for different soil IC and basket sizes.

IC (%)	Basket cube length (cm)			
	5.1	7.6	10.2	15.2
3%	4	4	2	8
35%	2	2	2	-
51%	2	3	2	-
86%	3	3	2	-

$\ln(\delta_c T_{a,c}/L^2)$ vs $1/T_{a,c}$ plot, and to calculate the best linear fit for each inorganic content value (Fig. 3.7). The slope of the straight line corresponds to $-E/R$, while the y-intercept is f/Rk . If the plot of $\ln(\delta_c T_{a,c}^2 L^2)$ against $1/T_{a,c}$ (Eq. (1.3)) is a straight line, it validates the Frank-Kamenetskii theory. As seen in Table 3.3, $R^2 > 0.94$ for all tested soil samples, confirming the validity of the Frank-Kamenetskii theory and 1-step Arrhenius reactions for the self-heating ignition of soil.

The slopes in Fig. 3.7 give the effective activation energies for the soil. The y-intercept of these lines allows the calculation of thermal parameters in Eq. (1.3). A summary of the activation energies for varying inorganic content is given in Table 3.3, with R^2 calculated from the linear fit for each line. The error bounds are calculated using the fits that would give the highest and the lowest possible effective activation energy from the experimental data obtained (largest possible errors).

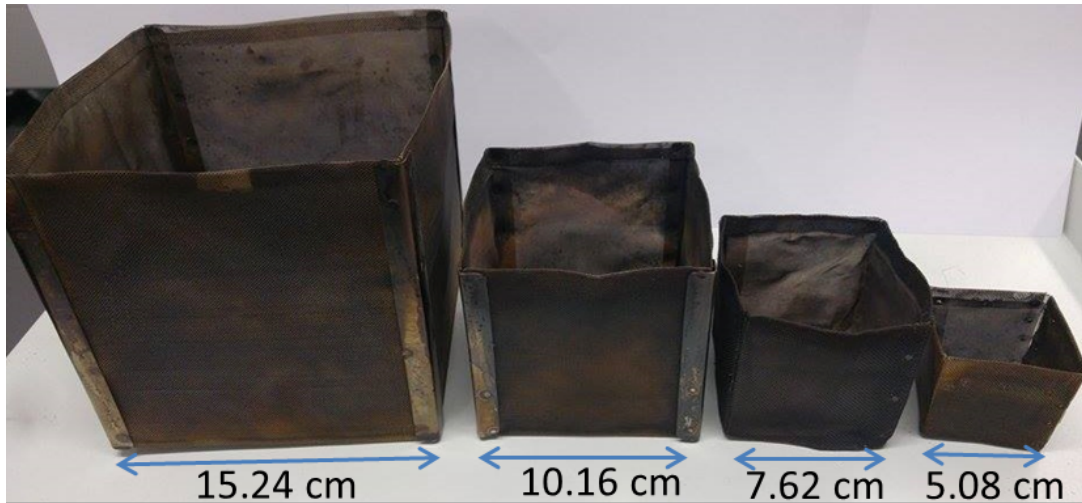


Figure 3.5: Experimental setup for studying self-heating of a sample placed at the centre of the thermostatically controlled oven with thermocouples for measuring the ambient and soil temperatures (left) and meshed test baskets (right).

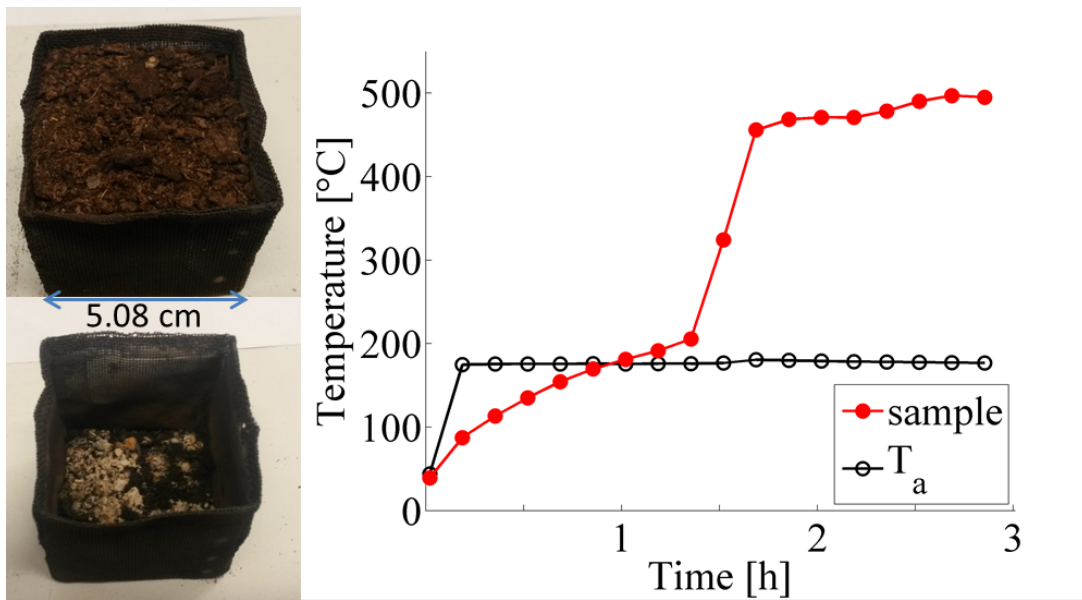
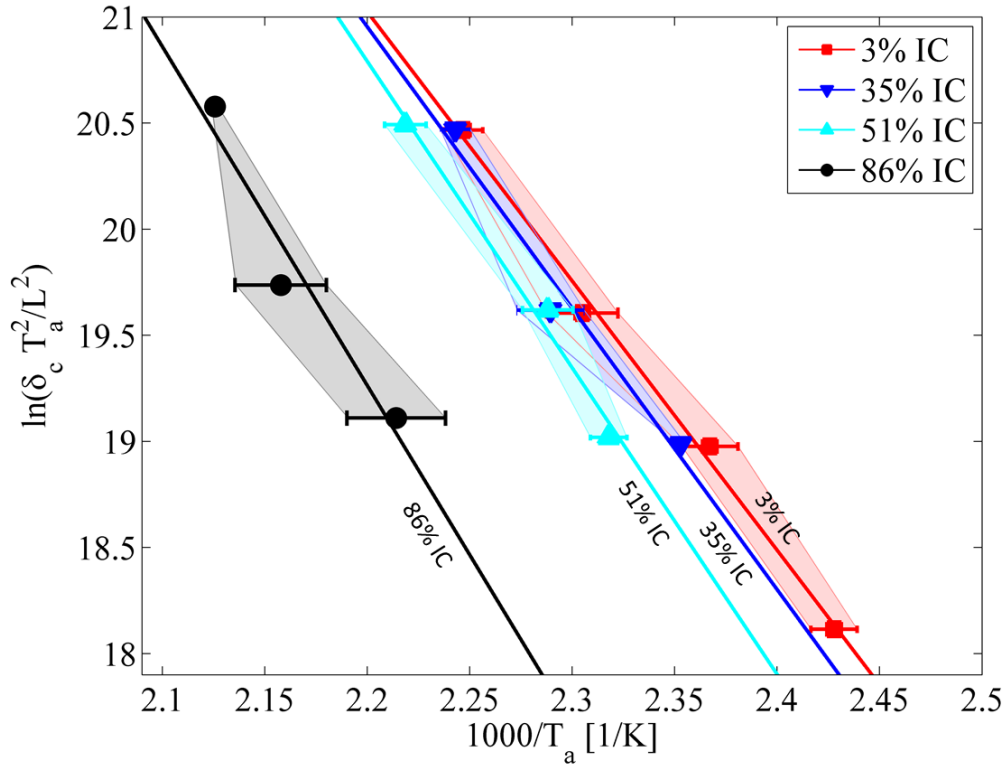


Figure 3.6: Soil sample before (top left) and after (bottom left) ignition. Temperature profile in the centre of the soil sample shows clear thermal runaway at $t=1.4$ h, with the ambient temperature (T_a) shown for reference.

The results found in this work help determine the effect of soil type and IC on self-heating ignition. I report a clear increase in ambient temperature required for ignition as the IC increases.

Table 3.2: The critical ignition temperatures found for different soil IC and basket sizes.

IC (%)	Basket cube length (cm)			
	5.1	7.6	10.2	15.2
3%	172 ± 2 °C	161 ± 3 °C	150 ± 3 °C	139 ± 2 °C
35%	173 ± 2 °C	164 ± 3 °C	152 ± 1 °C	-
51%	178 ± 2 °C	164 ± 2 °C	158 ± 2 °C	-
86%	197 ± 1 °C	190 ± 5 °C	179 ± 5 °C	-

**Figure 3.7:** Frank-Kamenetskii plot for soil with different IC ranging from 3% to 86%. Experimental error is estimated based on temperature measurements in Table 3.2. The linear fits have $R^2 > 0.94$ (Table 3.3).

3.5 Upscaling for natural soil layers

The properties in Table 3.3 can be used in the Frank-Kamenetskii theory to upscale the laboratory results to natural soil systems. Carbon-rich soil ecosystems are typically very wide, kilometres in length, but no deeper than 50 m [79,80]. Because the width is at least an order of magnitude larger than the depth, these systems behave as semi-infinite slabs, and critical ignition temperatures can be calculated for various depths by Eq. (1.3) with $\delta_c = 0.878$ [32]. The upscaling of the results assumes that oxygen is present in the porous soil, as it is needed for the self-heating to take place. This means, for example,

Table 3.3: Effective activation energy E and y-axis intercepts of Fig. 3.7 calculated using Eq. (1.3) for increasing values of IC. The R^2 values of the linear fits used to calculate these is included.

IC (%)	E (kJ/mol)	$\ln(QEf/Rk)$	R^2
3	105.5 (−9.3,+17.5)	48.9 (−2.6,+4.9)	0.995
35	110.2 (−7.7,+13.1)	50.1 (−2.1,+3.7)	0.970
51	120.1 (−17.6,+34.3)	52.6 (−4.8,+9.3)	0.985
86	132.8 (−27.5,+62.8)	54.4 (−6.9,+16.2)	0.943

that soil would not be waterlogged and that the entire depth being considered has oxygen access.

Possible ambient temperature ranging between 0 °C and 40 °C are considered because this range includes temperatures found in the natural environment (day and night, winter and summers in boreal and tropical regions). Temperatures below 0 °C can be found in the boreal regions, where the water in the soil can freeze. Because of the complexity of the melting process, upscaling results below 0 °C would not be meaningful.

Fig. 3.8 shows the upscaled results for the natural soil layers. For example, at ambient temperature of 40 °C, the soil with a low IC (e.g. peat) can self-ignite with a minimum thickness (L_{min}) of 8.8 m. As soil IC increases to 86%, the minimum soil thickness for self-ignition raises to 1.8 km which would be impossible to find in nature as organic soil depth reaches a maximum of about 50 m [79]. For IC between 3% and 35% the minimum thickness for self-ignition does not change significantly. However, as IC increases above 35% the minimum thickness increases significantly. As natural soil systems have thickness from ~ 0.1 m to 50 m, minimum critical ignition temperatures were calculated with respect to IC in Fig. 3.8. A dotted line representing the 50 m thick soil layer is plotted to show intersection values for varying IC. Anything below that means self-heating is expected, above means it is not expected. For a 50m thick soil layer, the critical ambient temperature is 14 °C for IC = 3% (i.e. peat soil), but as high as 50 °C for IC = 86%. At shallower thicknesses like 20 m, the minimum ambient temperature needed for ignition varies by 45 °C between the natural peat (3% IC) and the high-mineral soil (86% IC). In Fig. 3.8 (right) a dotted line representing 40 °C is plotted. If a given soil thickness curve does not intersect the line, we do not expect self-heating ignition to happen for that given thickness as T_a required would be too high to be found in natural conditions. For example, for soil systems ~ 1 m and ~ 5 m thick, self-heating ignition is not expected because even for 3% IC ambient temperatures required are greater than 40 °C. I estimate that the critical IC for a T_a of 40 °C and soil thickness of 50 m is 68%. Because those are extreme values of temperature and thickness, no self-heating ignition of soil can be expected above the 68% threshold of inorganic content.

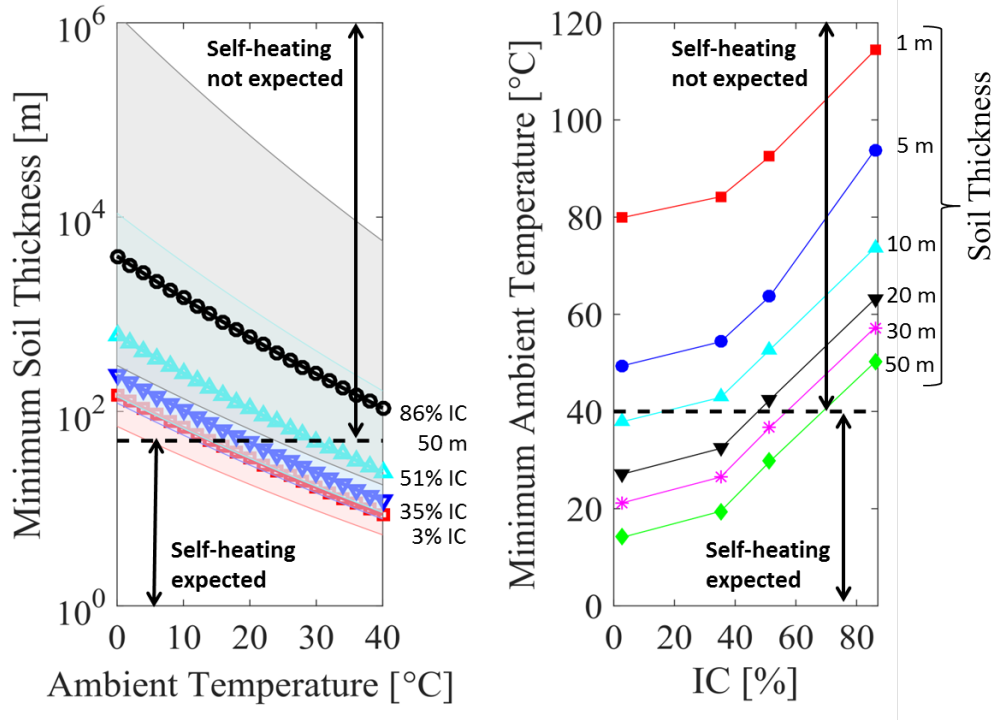


Figure 3.8: Upscaled results of soil depths required for self-ignition for ambient temperature between 0 °C and 40 °C for IC between 3% and 86%. Error show the worst-case scenario in terms of experimental measurements (Table 3.3). On the right, critical ambient ignition temperatures for six different soil thicknesses vs IC.

3.6 Conclusions

In this chapter, bench-scale experiments were conducted to determine the self-ignition criteria for soil samples with different IC values. The experiments predict and quantify the environmental temperature conditions necessary for the onset of smouldering fires in carbon-rich soil systems such as histosols or gelisols. Experimental results show that as the IC in the soil increases, the critical ambient temperature for self-ignition increases. Using the Frank-Kamenetskii theory, it is found that the effective activation energy for the soil increases from 105 kJ/mol to 133 kJ/mol as IC increases from 3% to 86%, indicating a significant reduction in reactivity and ignitability. I report a clear increase in the ambient temperature required for ignition as the IC increases.

By upscaling the bench-scale experiments to natural ecosystem sizes, the minimum ambient temperature and soil layer thickness for self-heating ignition are predicted. For a 50 m thick soil layer, the minimum ambient temperature is estimated to be as low as 14 °C for IC=3%, but as high as 50 °C for IC =86%. The maximum IC possible for self-ignition at 40 °C for the maximum natural thickness of peat, 50 m, was estimated to be 68%. Wildfires in carbon-rich ecosystems are a hazard, and determining the ignition conditions is important. This chapter is the first in-depth experimental quantification of self-heating ignition of soil, showing that it is indeed possible that wildfires are initiated

by self-heating of some soil types at the right conditions.

Appendices

3.A Experimental data from 3% inorganic content soil self-heating ignition cubic basket experiments

Table 3.4: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of 3% IC soil. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and soil sample temperatures. The data reported includes the dates of experiments, volume of soil basket being tested, inorganic content, ambient oven temperature, bulk density of the soil and if the sample ignited or not.

Date experiment was carried out	03/08/15	03/08/15	04/08/15	19/08/15	30/03/15	21/08/15	22/08/15	25/08/15	10/08/15
Volume of basket being tested (mL)	131	131	131	131	442	442	442	442	1049
Inorganic content(%)	3	3	3	3	3	3	3	3	3
Oven reference temperature (°C)	165.7	170.2	175.1	174.0	149.7	156.1	157.6	164.1	147.0
Bulk density of fuel (kg/m ³)	201	201	201	210	199	212	213	212	238
Ignition (Yes/No)	N	N	Y	Y	N	N	N	Y	N
Date experiment was carried out	21/08/15	26/03/15	28/03/15	23/08/15	24/08/15	01/09/15	03/09/15	21/03/16	
Volume of basket being tested (mL)	1049	3540	3540	3540	3540	3540	3540	3540	
Inorganic content(%)	3	3	3	3	3	3	3	3	
Oven reference temperature (°C)	151.9	146.5	128.6	132.0	135.2	137.0	136.5	140.8	
Bulk density of fuel (kg/m ³)	238	216	217	236	239	239	229	238	
Ignition (Yes/No)	Y	Y	N	N	N	N	N	Y	

3.B Experimental data from 35% inorganic content soil self-heating ignition cubic basket experiments

Table 3.5: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of 35% IC soil. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and soil sample temperatures. The data reported includes the dates of experiments, volume of soil basket being tested, inorganic content, ambient oven temperature, bulk density of the soil and if the sample ignited or not.

Date experiment was carried out	27/04/16	29/04/16	01/06/16	08/06/16	14/06/16	16/06/16
Volume of basket being tested (mL)	131	131	442	442	1049	1049
Inorganic content (%)	35	35	35	35	35	35
Oven reference temperature (°C)	174.3	171.4	160.7	166.9	152.4	151.6
Bulk density of fuel (kg/m ³)	340	342	343	340	343	343
Ignition (Yes/No)	Y	N	N	Y	Y	N

3.C Experimental data from 51% inorganic content soil self-heating ignition cubic basket experiments

Table 3.6: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of 51% IC soil. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and soil sample temperatures. The data reported includes the dates of experiments, volume of soil basket being tested, inorganic content, ambient oven temperature, bulk density of the soil and if the sample ignited or not.

Date experiment was carried out	01/09/15	01/09/15	11/09/15	15/09/15	18/09/15	22/09/15	22/03/16
Volume of basket being tested (mL)	131	131	442	442	442	1049	1049
Inorganic content(%)	51	51	51	51	51	51	51
Oven reference temperature (°C)	179.8	175.7	171.4	166.4	161.7	156.8	160.1
Bulk density of fuel (kg/m ³)	401	401	424	423	425	439	438
Ignition (Yes/No)	Y	N	Y	Y	N	N	Y

3.D Experimental data from 86% inorganic content soil self-heating ignition cubic basket experiments

Table 3.7: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of 86% IC soil. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and soil sample temperatures. The data reported includes the dates of experiments, volume of soil basket being tested, inorganic content, ambient oven temperature, bulk density of the soil and if the sample ignited or not.

Date experiment was carried out	08/01/16	11/01/16	18/01/16	07/09/15	11/09/15	17/09/15	28/04/16	18/05/16
Volume of basket being tested (mL)	131	131	131	442	442	442	1049	1049
Inorganic content(%)	86	86	86	86	86	86	86	
Oven reference temperature (°C)	201.1	197.1	197.8	176.2	185.7	195.2	173.8	183.5
Bulk density of fuel (kg/m ³)	953	954	954	945	940	949	947	947
Ignition (Yes/No)	Y	N	Y	N	N	Y	N	Y

Chapter 4

Quantifying reactivity of biochar as a function of the pyrolysis reactor temperature using self-heating ignition properties

Summary ¹

Biomass and torrefied biomass are an important part of the fuel mix for fossil fuel power plants, and their worldwide use is projected to grow significantly. At the same time biochar, originated from pyrolysis of biomass, is being used for soil amendment and carbon sequestration. However, there are fire safety issues with these materials. Both biochar and torrefied biomass are produced from biomass through pyrolysis in a reactor under controlled conditions. Different reactor temperatures produce different pyrolyzed biomass, leading to materials with different properties and exothermic reactivity. Biomass, biochar and torrefied biomass are reactive porous media, and therefore can undergo self-heating. The more reactive the material, the more prone it is to self-heat. Fire risk is associated with production, transport, handling and storage of these materials. Spontaneous ignition of pyrolyzed biomass has already lead to accidental fires like the fuel storage units at Tilbury Power Plant (UK) which ignited in 2012. Using basket experiments in a thermostatically controlled laboratory oven I experimentally measured the different ignition temperatures of softwood pellets and softwood biochar produced at reactor temperatures ranging from 350 to 800 °C. By investigating self-heating behaviour of these samples I quantify the different reactivities based on reactor temperature for the first time. In total, 92 experiments were carried out with 567 h of oven run time. The results show that softwood biochar is the most prone to self-heating when produced at reactor temperature of 450 °C. Furthermore, the experiments show that the reactivity of the softwood is not a monotonic function of pyrolysis reactor temperature. I show that there is an optimal reactor temperature for self-heating, at 450 °C. Furthermore, at

1. This chapter is based on “F. Restuccia, O. Mašek, R. M. Hadden, G. Rein (2017) *Quantifying reactivity of biochar as a function of the pyrolysis reactor temperature using self-heating ignition properties*, (to be submitted to **Bioresource Technology**).”

reactor temperatures higher than 600 °C the biochar is less reactive than the original feed-stock sample. This work improves the understanding of the fire risks posed by biomass pyrolysis and their impact on self-heating, providing insights necessary for successful and safe application of these products.

4.1 Introduction

Biomass, plant-based materials collected by humans which are not used for food or feed, have historically been waste material or used as a form of energy source, especially in the form of wood. So, over the past number of years, biomass has become an important part of the fuel mix for fossil fuel power plants, and its use is projected to grow significantly [81]. Torrefied biomass, a product of biomass pyrolysis, is a possible replacement for coal, as it could integrate into existing coal power plants, enabling power plants to generate clean energy without an expensive conversion process [82]. At the same time biochar, charcoal produced from the pyrolysis of biomass, is being used for soil amendment for very acidic soils. Furthermore, carbon remains sequestered in biochar for centuries, so sustainable biochar production allows for atmospheric carbon sequestration. However, there are fire safety issues associated with both biomass and biochar. Both biochar and torrefied biomass are solid biomass pyrolysis products. They are derived biomass through pyrolysis in a reactor under controlled conditions. Different reactor temperatures produce different pyrolyzed biomass, leading to materials with different properties and reactivities [83]. For reactor temperatures below 350°C, this solid material is called torrefied biomass. For temperatures greater than 350°C, this solid material is called biochar [83].

Reactive porous media such as wood, biomass, biochar, organic soils and coal have small free spaces (i.e. pores, voids) embedded in the solid together with a presence of a carbon-rich component [43]. This allows the media to be permeable to air, and greatly increases its surface area per unit volume making the organic media reactive by allowing oxidation to take place when oxygen is present [84]. Such reactive porous media have been shown to undergo self-heating [1,31]. Self-heating is the tendency of certain porous fuels to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures [1]. In biomass, this process typically starts by exothermic biological reactions, which cannot go beyond 70 °C [85]. The further exothermicity is then dominated by slow exothermic oxidation at low temperatures but the reaction alone is insufficient to raise the material temperature. The temperature rise is determined by the balance between the rate of heat generation and the rate of heat losses [86]. These exothermic reactions can lead to ignition, leading to smouldering or flaming fires and can be hazardous. The more reactive the material, the more prone it is to self-heat.

Fire initiated by self-heating ignition is a well-known problem for many porous reactive media, and has been reported and studied for materials such as chemically activated

carbon, sawdust, wood, coal, organic soils, [31,35,87] as well as soils and shale as shown in Chapters 2 and 3. Some work has been carried out on the self-heating ignition properties of biomass utilising thermogravimetric analysis (TGA) on a variety of materials such as poplar wood and wheat straw [88–91]. TGA is very useful for determining kinetics, but is not sufficient to characterise self-heating, as the assumption for TGA measurements is that the sample can be considered 0D. In reality, self-heating requires understanding of the heat distribution in space as self-heating will occur at the centre of a sample. Therefore analysis is required to be able to analyse the bulk behaviour of biomass self-heating ignition. Some of this work is present in literature: Garcia et al [92] carried out some of these bulk property studies on the self-heating ignition properties of biomass dust, and its propensity to ignite in storage conditions where oxygen is present and the environmental temperature is elevated enough. Jones et al [46] studied self-heating ignition properties using (TGA) coupled with basket experiments for a variety of biomass feedstock including olive residue, sugars, and sunflower husks. Some work was also carried out to predict self-heating ignition of biomass by analysing emission products [68].

Torrefied biomass and biochar can be produced at a variety of pyrolysis reactor temperatures. Fire risk is associated with its production, transport, handling and storage. Spontaneous ignition of pyrolyzed biomass has already lead to accidental fires, for example biomass storage units at Tilbury Power Plant (UK) ignited in 2012 and the biomass storage silos at Avedøre (Denmark) ignited in 2016, both potentially due to self-heating [93,94]. Most recently in Decemebr 2017 two generation units at Drax power station were shut due to a fire in it's biomass pellet fuel delivery conveyor belt [95]. However there is no work present in the literature quantifying the critical ignition thresholds for torrefied biomass and biochar, and the propensity of biomass and biochar to self-heating as a function of reactor temperatures. This work aims to fill this gap, using softwood feedstock and biochar produced in a range of reactor temperatures to quantify the function of reactor temperature to propensity to self-heat.

4.2 Theory

4.2.1 Biochar reactivity

In-depth studies of biomass pyrolysis have been previously carried out in literature to determine the pyrolysis effect of the three major components of biomass cellulose, hemicellulose and lignin [96,97]. They showed that at heating rates lower than 100 °C/min biomass decomposes first by hemicellulose decomposition, then cellulose decomposition and finally lignin which decomposes more slowly. Moisture evaporation will occur at temperatures below 110 °C. For the decomposition, hemicellulose was found to have most of its weight loss in the temperature range between 220 °C and 315 °C, cellulose in the temperature range between 315 °C and 400 °C, and lignin as a slower process with only 67 % of it's weight lost by 850°C [96].

Biochar is defined as a porous carbonaceous solid produced by the thermochemical conversion of organic materials in the absence of oxygen. Because of its production temperatures above 350 °C, lignin is the main component of biochar produced from biomass. Biochar also contains aromatic-aliphatic organic compounds of complex structure which include residual volatiles, and ash. Finally, there are voids in the biochar structure formed as pores (macro, meso and micropores), cracks and morphologies of cellular biomass origin making biochar a reactive porous structure [98]. This porous structure makes biochar prone to self-heating ignition.

4.3 Experimental setup

To carry out this experimental work on self-heating ignition of softwood biomass pellets and biochar, a series of biochars were produced in a bench-scale pyrolysis reactor at the UK Biochar Research Centre at the University of Edinburgh by our collaborator Ondřej Mašek. The reactor is a rotary kiln pyrolysis reactor, with pyrolysis temperatures between 350 °C and 800 °C. The biochars used for this experimental work were produced from a softwood pellet feedstock pyrolysed in a reactor at 350 °C, 400 °C, 450 °C, 550 °C, 600 °C, 700 °C and 800 °C. At reactor temperatures below 350 °C the product would not be biochar so temperatures below that threshold were not considered. These samples are presented in Fig. 4.1, and show different physical properties in terms of diameter, average length and bulk density. A summary of these characteristics is presented in Table 4.1. As can be seen in the table the density and diameter of the pellets reduces with increasing pyrolysis temperature as more of the softwood pyrolyses, but for pyrolysis above temperatures of 450 °C the bulk density and diameter of the particle does not change as significantly as up to 450 °C. This was also seen in Fig. 4.1 visually as the particles become much darker and smaller. Elemental analysis of the biochars and biomass is presented in Table 4.2, where it can be seen the percentage of weight of the biochar is increasingly carbon with increasing reactor temperature. This agrees with results from literature [99]. Water, ash and carbon in dry ash free basis (Cdaf) for the softwood and its biochar are calculated using the TGA data presented in 4.4.2. The carbon in dry ash free basis is calculating according to the BSI standard EN 15296:2011 [100]. Results are presented in Table 4.3, where it can be seen that for all the biochars carbon content is above 61 %, and biochars above 700 are purely carbon apart from water and ash.

The laboratory setup to determine the minimum critical ambient temperature for self-heating $T_{a,c}$ that leads to self-ignition was constructed following the experimental methodology used in all chapters of this thesis, presented in Ch 1 section 1.4. Fig. 4.2 shows the three basket sizes filled with softwood feedstock pellets as sample representations of a typical basket setup. The pellets were packed into cubic shaped wire mesh baskets of three different sizes to ensure sufficient data could be measured to assess if the assumption of Arrhenius reactions necessary to adopt Frank-Kamenetskii theory could

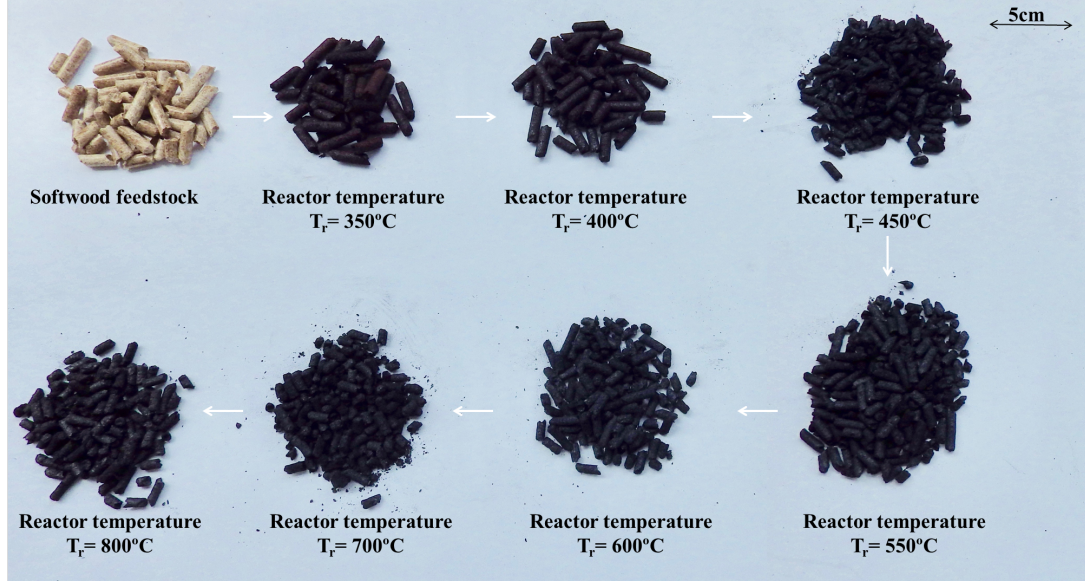


Figure 4.1: Softwood samples used, with feedstock and various biochars produced in pyrolysis reactors at temperatures ranging from 350°C to 800°C.

Table 4.1: Physical properties of softwood biomass and biochar pellets produced at various reactor temperatures used for experiments.

Physical Properties	density (kg/m ³)	pellet length (mm)	pellet diameter (mm)
Softwood Feedstock	531	21.8	5.8
produced at $T_r = 350^\circ\text{C}$	400	21.7	5.6
produced at $T_r = 400^\circ\text{C}$	396	19.0	5.4
produced at $T_r = 450^\circ\text{C}$	295	17.9	4.3
produced at $T_r = 550^\circ\text{C}$	289	20.3	4.1
produced at $T_r = 600^\circ\text{C}$	284	13.6	4.2
produced at $T_r = 700^\circ\text{C}$	274	13.5	4.3
produced at $T_r = 800^\circ\text{C}$	255	14.1	4.2

be applied. As in the previous chapters, I selected cube shaped baskets as it is the shape most easily adaptable to increasing geometry size in a rectangular oven without making the larger samples approach the oven walls. The baskets were made of 0.5 mm diameter wire mesh with volumes of 131, 442 and 1049 cm³. These baskets ensure a good range of sizes for the largest possible temperature range given at the laboratory scale, between 90 °C and 200 °C for these softwood samples. As the basket size increases the critical ignition temperature reduces because of the ratio of heat losses to the environment to heat generated by chemical reactions decreases [35], therefore the larger the baskets in the experimental setup, the more accurate the predictions that can be extracted from the results when upscaling to large stockpile sizes. To analyse the results, Frank-Kamenetskii theory was adopted as detailed in Ch 1 section 1.2.

Table 4.2: Elemental analysis of the biomass and biochars produced at various reactor temperatures.

Element Weight %	C	H	N
Softwood Feedstock	45.80	6.43	<0.3
produced at $T_r = 350^\circ\text{C}$	58.78	5.35	<0.3
produced at $T_r = 400^\circ\text{C}$	58.68	5.59	<0.3
produced at $T_r = 450^\circ\text{C}$	76.76	3.80	<0.3
produced at $T_r = 550^\circ\text{C}$	82.27	3.17	<0.3
produced at $T_r = 600^\circ\text{C}$	84.01	2.83	<0.3
produced at $T_r = 700^\circ\text{C}$	86.31	2.55	<0.3
produced at $T_r = 800^\circ\text{C}$	89.61	1.70	0.38

Table 4.3: Water, ash and carbon in dry ash free basis (Cdaf) for the biomass and biochars calculated using the TGA data presented in section 4.4.2.

Element	Water Weight %	Ash	Cdaf
Softwood feedstock	5.45	0.87	48.9
produced at $T_r = 350^\circ\text{C}$	4.18	2.66	63.1
produced at $T_r = 400^\circ\text{C}$	2.27	1.69	61.1
produced at $T_r = 450^\circ\text{C}$	4.17	1.81	81.6
produced at $T_r = 550^\circ\text{C}$	3.83	3.03	88.3
produced at $T_r = 600^\circ\text{C}$	3.99	3.20	90.5
produced at $T_r = 700^\circ\text{C}$	4.57	9.03	99.9
produced at $T_r = 800^\circ\text{C}$	3.60	6.60	99.8

In total, 92 experiments were carried out with 567 h of oven run time. A summary of the experiments carried out is presented in Table 4.4. If the softwood failed to reach ignition the experiment was repeated with a fresh sample at a higher temperature. If the softwood reached ignition, then the experiment was repeated with a fresh sample at a lower temperature. The experiments were carried out until $T_{a,c}$ for ignition was located within $\pm 4^\circ\text{C}$ for each tested biomass. A minimum of two experiments were conducted at each basket size for each softwood sample.

In addition to the basket experiments, thermogravimetric analysis was conducted for each sample to provide information on the reaction kinetics of each sample at the microscale. Furthermore the conductivity of the softwood feedstocks and each biochar produced were measured for a range of temperatures between 65°C and 165°C . This was carried out to provide more data on the physical properties of the samples, so as to be able to extract more data from the self-heating basket experiments.



Figure 4.2: Experimental setup for studying self-heating of a biomass sample placed at the centre of the thermostatically controlled oven with thermocouples for measuring the ambient and biomass temperatures (left) and meshed experiment baskets filled with softwood feedstock (right).

Table 4.4: Number of experiments carried out for each type of softwood biochar and basket sizes.

Pellet type	Basket length l (cm)		
	5.1	7.6	10.2
Softwood Feedstock	4	4	3
produced at $T_r = 350^\circ\text{C}$	3	3	2
produced at $T_r = 400^\circ\text{C}$	9	2	3
produced at $T_r = 450^\circ\text{C}$	9	3	2
produced at $T_r = 550^\circ\text{C}$	4	3	2
produced at $T_r = 600^\circ\text{C}$	5	3	3
produced at $T_r = 700^\circ\text{C}$	8	3	3
produced at $T_r = 800^\circ\text{C}$	5	3	3

4.4 Results and discussion

4.4.1 Basket experiments results

Minimum ignition temperature, the lowest oven temperature required for ignition, was found for each basket for each sample type and is shown in Fig. 4.3.

As can be noted the lowest ignition temperature occurs for softwood biochar pyrolysed in a reactor at 450°C . As mentioned in Section 4.2, biomass pyrolysis above 400°C leaves mainly lignin in the biochar [96]. This can explain the increase in reactivity and proneness to self-heating ignition around the temperature of 450°C reactor temperature because the biochar is almost pure lignin. As reactor temperature further increases

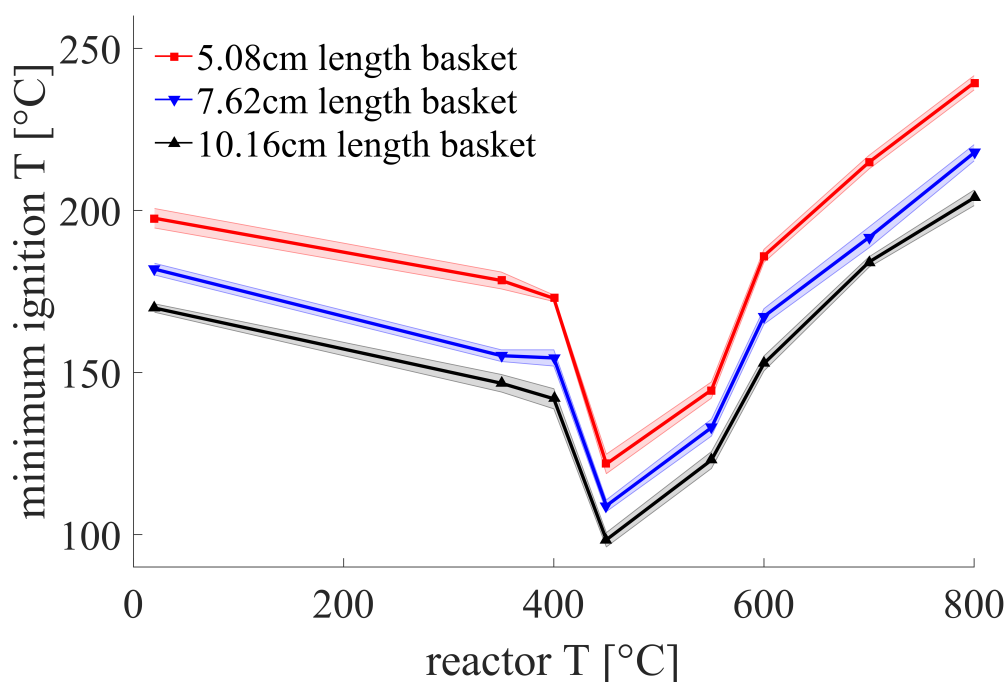


Figure 4.3: Minimum ignition temperature for softwood feedstock and biochar between 350 °C and 800 °C for three basket sizes. Experimental error is estimated based on temperature error bounds on each individual set of experiments.

then the lignin also begins to decompose and we are left with less reactive carbon in the biochar. However the density and dimensions of the biochar pellets do not have significant changes above this temperature as shown in Table 4.1 and therefore there is less reactive material in the bulk system and the self-heating tendency decreases. For the explored basket sizes, for reactor temperatures above 600 °C the biochar becomes less prone to self-heating than the original softwood feedstock. These results show that the lowest ignition temperature for softwood biochar is not a monotonic function of the reactor temperature. In fact, after a gradual increase in reactivity with softwood produced at reactor temperatures of 350 °C and 400 °C there is a significant increase in reactivity for reactor temperatures of 450 °C, and then again a sharp decrease in reactivity for reactor temperatures above 550 °C. This result demonstrates that there is a very narrow range of reactor temperatures which produce softwood that is far more reactive than the rest of the reactor temperatures, and that maximum in reactivity lies at reactor temperature of 450 °C.

Plotting the minimum ignition temperature for one basket size (10.16cm length basket) for all the biochars with respect to the carbon dry free ash allows a comparison of the effect of total carbon content with the critical ignition temperature and is done in Fig. 4.4. The results show that the peak at 450 °C is not solely caused by the carbon content, as the V shape seen in Fig. 4.3 is also clearly present in this plot.

Conductivity was measured experimentally using a guarded heat flow meter at various

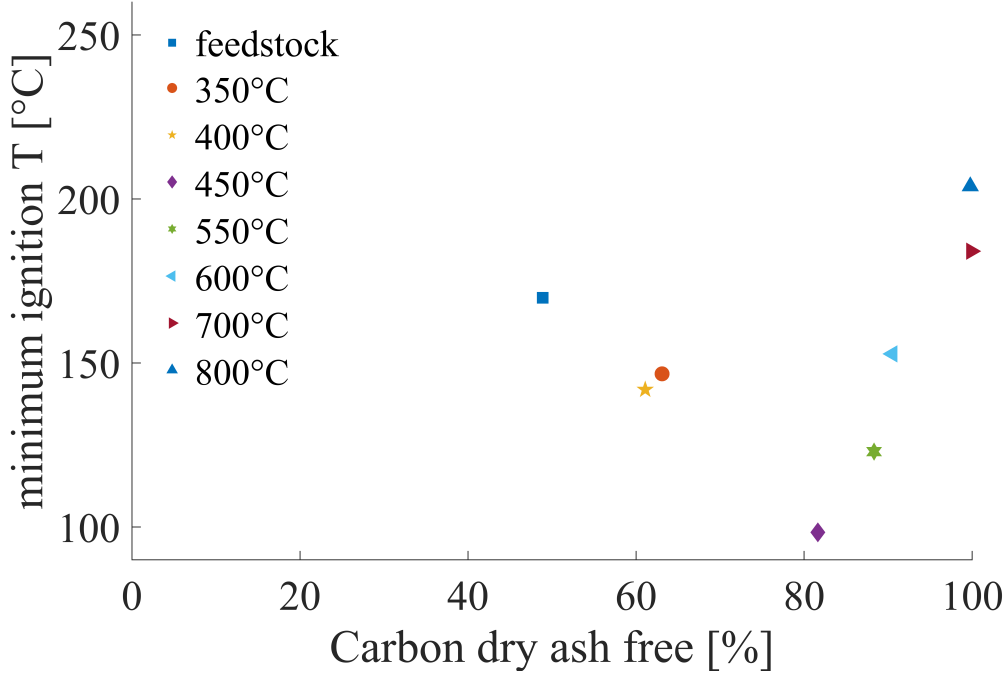


Figure 4.4: Minimum ignition temperature for softwood feedstock and biochar between 350 °C and 800°C for a fixed basket size plotted vs carbon dry ash free.

temperatures, and was shown to be linear between 65 and 165 °C. The most conductive of the softwood was the feedstock. The lowest thermal conductivity was found to be for softwood produced at reactor temperatures of 450 °C. The percentage difference in thermal conductivity between the softwood produced at reactor temperatures of 450 °C and the softwood feedstock, so between least and most reactive, was 27 %. This helps to further explain why this particular softwood biochar is most prone to self-heating, as the material acts as a good insulator, preserving the heat produced from the exothermic reactions within the centre of the sample and reducing the amount of cooling to the ambient. The summary of the conductivity measurements is presented in Table 4.5.

To use Frank-Kamenetskii theory of criticality to extract a one-step kinetic model and thermal parameters from the basket experiments the data was used to make a $\ln(\delta_c T_{a,c}/L^2)$ vs $1/T_{a,c}$ plot (Fig. 4.5). In this plot, the slope of the straight line corresponds to $-E/R$. If the plot of $\ln(\delta_c T_{a,c}^2 L^2)$ against $1/T_{a,c}$ (Eq. (1.3)) is a straight line, it validates the Frank-Kamenetskii theory. As seen in Table 4.6, $R^2 > 0.975$ for all tested softwood samples, confirming the linearity of the slopes and therefore the validity of the Frank-Kamenetskii theory and 1-step global reactions assumption. Taking slopes in Fig. 4.5 gives the effective activation energies for the biomass. The y-intercept of these lines allows the calculation of thermal parameters in Eq. (1.2) $\ln(\frac{QE_f}{Rk})$. As can be seen in Fig. 4.5, 5 of the 8 softwoods tested have similar slopes and ignition behaviour, namely feedstock and softwood produced at temperatures of 350 °C, 400 °C, 600 °C and 700 °C.

The thermal conductivity values of the softwood produced at the various reactor tem-

Table 4.5: Thermal conductivity measurements for the biomass samples conducted at 3 temperatures, with resulting fit equation. The R^2 values of the linear fits through these points is included.

k for biomass type	65°C (W/mK)	115°C (W/mK)	165°C (W/mK)	R^2 (-)
Softwood feedstock	0.1107	0.1228	0.1436	0.977
produced at $T_r = 350^\circ\text{C}$	0.0936	0.1060	0.1147	0.990
produced at $T_r = 400^\circ\text{C}$	0.1030	0.1060	0.1145	0.933
produced at $T_r = 450^\circ\text{C}$	0.0807	0.0893	0.1004	0.995
produced at $T_r = 550^\circ\text{C}$	0.0904	0.0917	0.0940	0.976
produced at $T_r = 600^\circ\text{C}$	0.0903	0.1004	0.1055	0.964
produced at $T_r = 700^\circ\text{C}$	0.0853	0.0919	0.0974	0.997
produced at $T_r = 800^\circ\text{C}$	0.1027	0.1139	0.1192	0.960

peratures is one of the required physical parameters in this equation. Conductivity values were used for a temperature of 115 °C to ensure moisture effects were not encountered, as the self-heating experiments were carried out above 100 °C, but so that the value was in the range of experimental measurements carried out in the basket experiments. The values were therefore taken from Table 4.5 at 115 °C. By using these thermal conductivities, and plugging in the value of the universal gas constant R , I can isolate the (Qf) which is effectively a pre-exponential factor.

The results can therefore isolate all the thermal and kinetic parameters and a summary of all of these parameters is presented in Table 4.6, with R^2 calculated from the linear fit for each line. The error bounds are calculated using the fits that would give the highest and the lowest possible effective activation energy from the experimental data obtained (largest possible errors). The linear fits all have $R^2 > 0.975$, validating the Arrhenius reaction assumption. A detailed summary of all experimental results are presented in Appendices 4.A-4.H.

4.4.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out in air with a heating rate of 10 K/min for all the softwood feedstock and biochar samples. The heating rate was chosen to have slow heating and therefore avoid thermal effects influencing experimental results. The reason for carrying out these measurements was to compare oxidative reactivity in microscale experiments so as to be able to have a link between the bulk scale experiments presented in this work and kinetics. Fig. 4.6 shows thermogravimetric analysis in air of the different softwood biomasses and biochar measured in this work. All the samples display an initial reduction in mass due to drying of the softwood around 100 °C, then a large reduction in mass between 200 °C and 400 °C for the softwood feedstock, a less pronounced reduction in the same temperature range for biochar produced

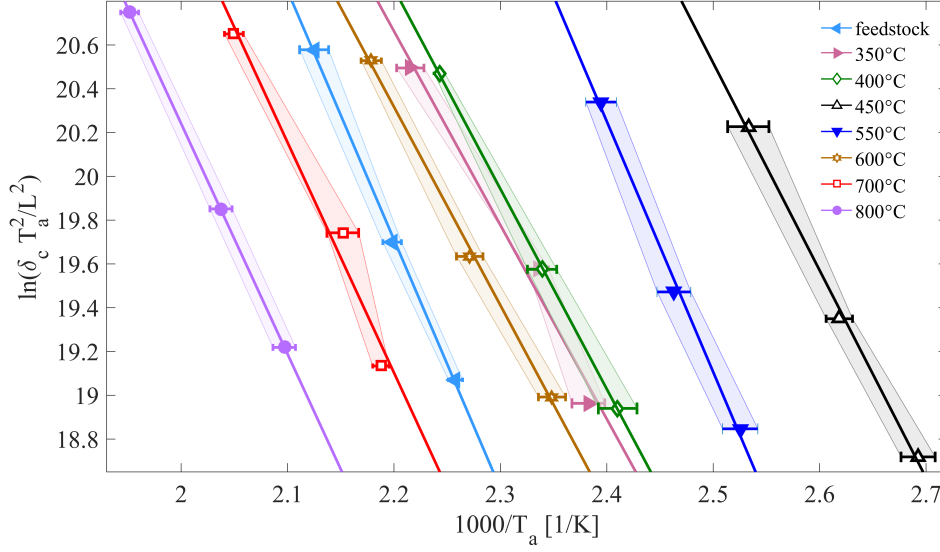


Figure 4.5: Frank-Kamenetskii plot for softwood feedstock and biochar between 350 °C and 800 °C. Experimental error is estimated based on error bounds on each individual set of experiments. The linear fits all have $R^2 > 0.975$ (Table 4.6).

Table 4.6: Effective activation energy E , pre-exponential factor Qf , conductivity k extracted from frank-kamenestkiiplot (Fig. 4.7) calculated using Eq. (1.3). The R^2 values of the linear fits used to calculate these is included.

biomass type	E (kJ/mol)	k (W/mK)	Qf (W/m ³)	R^2 (-)
Softwood feedstock	94.52	0.1228	$2.86 \cdot 10^{14}$	0.999
produced at $T_r = 350^\circ\text{C}$	73.65	0.1060	$3.28 \cdot 10^{12}$	0.982
produced at $T_r = 400^\circ\text{C}$	76.01	0.1060	$7.19 \cdot 10^{12}$	1.000
produced at $T_r = 450^\circ\text{C}$	78.76	0.0893	$1.48 \cdot 10^{14}$	0.997
produced at $T_r = 550^\circ\text{C}$	95.18	0.0917	$4.27 \cdot 10^{15}$	0.996
produced at $T_r = 600^\circ\text{C}$	75.37	0.1004	$3.38 \cdot 10^{12}$	0.998
produced at $T_r = 700^\circ\text{C}$	87.44	0.0919	$1.93 \cdot 10^{13}$	0.975
produced at $T_r = 800^\circ\text{C}$	87.51	0.1139	$9.26 \cdot 10^{12}$	1.000

at pyrolysis temperatures of 350 °C and 400 °C, and then insignificant mass loss in the same temperature range for the biochar produced above 450 °C. This conforms to the theory presented in section 2, where the hemicellulose and cellulose for biochars produced in a pyrolysis reactor above 450 °C are already reduced to a minimum and therefore the sample is made up of mostly lignin at this stage. All samples then present a steady mass loss above 400 °C. This can be further confirmed when analysing the mass loss rate of the samples calculated from the TGA of the biomasses several interesting trends can be clearly identified as seen in Fig. 4.7. Biochars produced above 450 °C all show reaction peaks at the same temperatures, with the only difference being the size of these mass loss

peaks: the peak size decreases with increasing biochar pyrolysis temperature, and this can be explained by the fact that at high pyrolysis temperatures (600 °C and above) a lot of the lignin has pyrolysed [96], and we have less carbon present for oxidation reactions to take place. The characteristic temperatures where these mass losses occur are reported in Table 4.7, where it can be seen that for all the biochar apart from 350 °C the characteristic temperatures for mass loss and end of combustion increase with increasing pyrolysis temperature. When softwood is pyrolysed at very high temperatures, above 700 °C, the TGA curve does not plateau for the duration of the analysis.

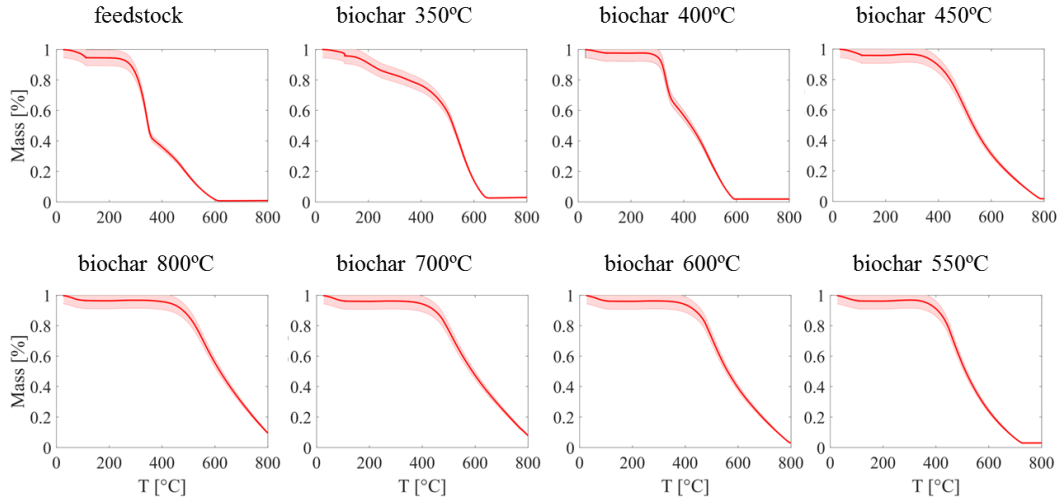


Figure 4.6: Thermogravimetric analysis in air of the different softwood biomass and biochar samples carried out with a heating rate of 10 K/min. Each plot represents mass % as a function of temperature with error clouds taking into account experimental error.

Table 4.7: Characteristic temperatures for mass loss from Fig. 4.6.

Element	T characteristic 1 Temperature °C	T characteristic 2
Softwood feedstock	260	600
produced at $T_r = 350^\circ\text{C}$	120	650
produced at $T_r = 400^\circ\text{C}$	300	690
produced at $T_r = 450^\circ\text{C}$	330	790
produced at $T_r = 550^\circ\text{C}$	350	725
produced at $T_r = 600^\circ\text{C}$	350	795
produced at $T_r = 700^\circ\text{C}$	350	810
produced at $T_r = 800^\circ\text{C}$	380	815

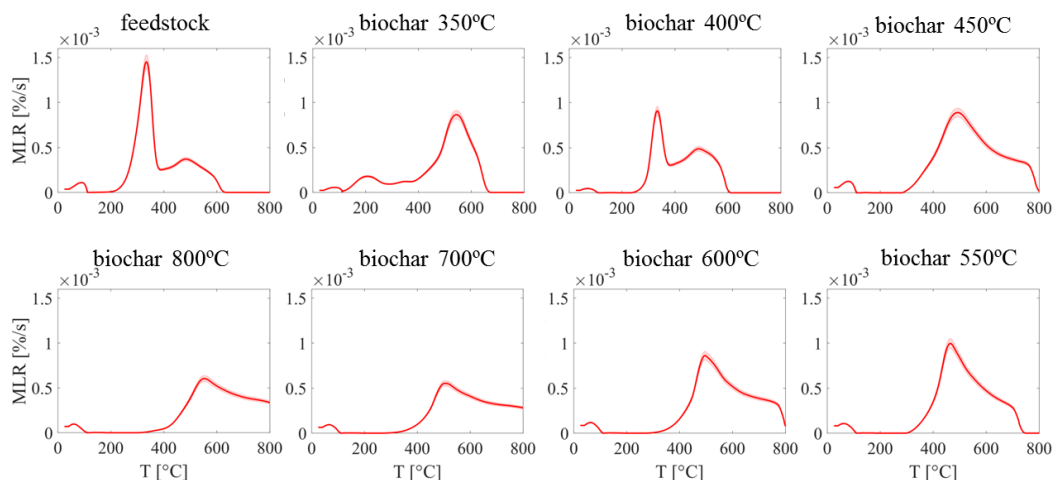


Figure 4.7: Mass loss rates calculated from thermogravimetric analysis in air for softwood biomass and biochars samples. Each plot represents mass loss %/s as a function of temperature with error clouds taking into account experimental error.

4.4.3 Upscaling of results

The results presented in this work can be used together with Frank-Kamenetskii theory to upscale the laboratory results to large biomass and biochar stockpiles of cubic size. Some examples of such systems are standard domestic biomass storage units (10 m^3) or open top container trucks (30 m^3) for transport. The upscaled results are presented in Figure 4.8 for a temperature range from $-10 \text{ }^\circ\text{C}$ to $40 \text{ }^\circ\text{C}$ for softwood feedstock and softwood biochar produced at pyrolysis reactor temperatures between $350 \text{ }^\circ\text{C}$ and $800 \text{ }^\circ\text{C}$. The temperature range of upscaling was chosen to span the range of ambient temperatures expected in power plants. Some significant results from this figure are that softwood biochar pellets produced at $450 \text{ }^\circ\text{C}$ of the dimensions of even a standard domestic biomass storage unit (2.2 m cube height) will ignite from self-heating at ambient temperatures as low as $20 \text{ }^\circ\text{C}$. On the other hand biochar produced at high pyrolysis reactor temperatures like $800 \text{ }^\circ\text{C}$ would not ignite from self-heating in containers of the same size even for temperatures of $70 \text{ }^\circ\text{C}$. Softwood feedstock is similarly safe for handling when stored in spaces smaller than 8000 m^3 for temperatures below $40 \text{ }^\circ\text{C}$. This shows that for biochar transport storage and handling the production mechanism is very important, as there is large variation in the biochar's propensity to self-ignite. As shown experimentally softwood biochar produced at $450 \text{ }^\circ\text{C}$ is the most prone to self-heating ignition, even for relatively modest storage sizes of (10 m^3), and therefore particular care must be taken when transporting and storing said softwood. The upscaling requires oxidizer to be present for the reactions to take place, but in the example of domestic storage or open-top truck transport oxygen is readily available.

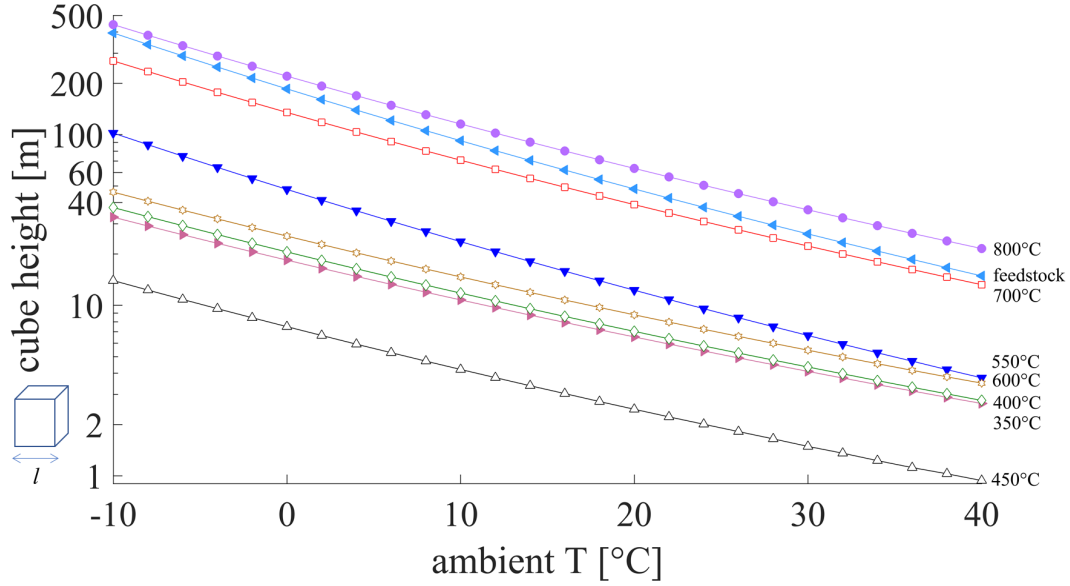


Figure 4.8: Upscaled results of cubic biomass and biochar piles required for self-ignition for ambient temperature between $-10\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ based on the thermal and kinetic parameters found in self-heating basket experiments (Table 4.6).

4.5 Conclusion

In this chapter, bench-scale experiments were conducted to determine the effect of pyrolysis reactor temperature used in the production of biochar on the propensity to ignite for self-heating for that given material. Softwood was pyrolysed at seven different pyrolysis reactor temperatures and basket experiments, thermogravimetric analysis and physical parameter measurements were carried out for each biochar product as well as the original softwood feedstock. Self-heating basket experiments quantified the ignition temperature for 3 given critical volumes for self-ignition criteria for the biochars. The results show that the reactivity of the softwood is not a monotonic function of pyrolysis reactor temperature. In fact, results show that biochar produced at a reactor temperature of $450\text{ }^{\circ}\text{C}$ is the most prone to self-heating, and that the reactivity of the softwood increases with reactor temperature up to $450\text{ }^{\circ}\text{C}$ but then significantly decreases and for reactor temperatures above $550\text{ }^{\circ}\text{C}$ the softwood is less reactive than the feedstock. Using the Frank-Kamenetskii theory to extract thermal and kinetic parameters, effective activation energies with pre-exponential factors were determined for each biochar sample and were summarised in Table 4.6. Results showed that for reactor temperatures above $600\text{ }^{\circ}\text{C}$ the biochar was less prone to self-heating than the original softwood feedstock. Thermal conductivity measurements of the different biochars also show that the least conductive of the softwoods is the one produced at reactor temperature of $450\text{ }^{\circ}\text{C}$, while the feedstock softwood being the most conductive.

The bench-scale experiments were extended to large scale systems to compare to real storage and transport sizes using the experimentally measured effective activation

energies and thermal parameters. This shows that softwood biochar produced at pyrolysis reactor temperatures of 450 °C is prone to self-heating ignition at ambient temperatures as low as 20 °C for dimensions as small as domestic biomass storage sizes, making it a fire hazard. This chapter is the first in-depth experimental quantification of self-heating ignition of biomass and biochar as a function of pyrolysis reactor temperature used for production, giving kinetic and thermal parameters that can be used to calculate safe sizes for transport and storage of softwood biomass and softwood biochars. The work shows that it is very important to know at what conditions biochar is produced as its proneness to self-heating ignition varies dramatically with biochar production temperature.

Appendices

4.A Experimental data from self-heating ignition cubic basket experiments for softwood feedstock

Table 4.8: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood feedstock biomass pellets. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biomass basket being tested, ambient oven temperature, bulk density of the biomass, duration of experiment and if the sample ignited or not.

Date experiment was carried out	08/11/16	11/11/16	14/11/16	15/11/16	16/11/16	16/11/16
Volume of basket being tested (mL)	131	131	131	131	131	442
Oven reference temperature (°C)	166.0	184.9	200.5	194.6	163.8	170.0
Bulk density of fuel (kg/m ³)	534	531	530	527	573	583
Duration (s)	10435	20400	21405	28735	26225	57970
Ignition (Yes/No)	N	N	Y	N	N	N

Date experiment was carried out	23/11/16	24/11/16	06/12/16	07/12/16	08/12/16
Volume of basket being tested (mL)	442	442	1049	1049	1049
Oven reference temperature (°C)	183.7	180.1	165.1	168.5	171.2
Bulk density of fuel (kg/m ³)	583	588	626	626	626
Duration (s)	66495	68320	65790	62975	54290
Ignition (Yes/No)	Y	N	N	N	Y

4.B Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 350 °C

Table 4.9: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 350 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	26/01/17	27/01/17	30/01/17	27/01/17	30/01/17	27/01/17	30/01/17	31/01/17	31/01/17	01/02/17
Volume of basket being tested (mL)	131	131	131	131	131	131	131	442	442	1049
Oven reference temperature (°C)	181.0	171.8	175.8	157.0	148.3	153.3	144.0	149.4	149.4	149.4
Bulk density of fuel (kg/m ³)	404	399	398	414	412	408	472	472	472	472
Duration (s)	7995	6850	10560	22385	14350	16740	640202	66090	66090	66090
Ignition (Yes/No)	Y	N	N	Y	N	N	N	N	N	Y

4.C Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 400 °C

Table 4.10: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 400 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out										
Volume of basket being tested (mL)	23/01/17	23/01/17	23/01/17	23/01/17	23/01/17	23/01/17	23/01/17	24/01/17	24/01/17	24/01/17
Oven reference temperature (°C)	131	131	131	131	131	131	131	131	131	131
Bulk density of fuel (kg/m ³)	126.0	135.4	144.5	154.2	164.5	172.4	182.0	182.0	182.0	182.0
Duration (s)	397	390	396	403	399	396	395	396	396	395
Ignition (Yes/No)	7245	6545	6090	5740	9770	8015	6480	8015	8015	6480
Date experiment was carried out										
Volume of basket being tested (mL)	25/01/17	03/02/17	25/01/17	26/01/17	25/01/17	26/01/17	25/01/17	26/01/17	26/01/17	30/01/17
Oven reference temperature (°C)	131	131	442	442	442	152.0	144.9	1049	1049	1049
Bulk density of fuel (kg/m ³)	176.0	173.3	157.0	152.0	152.0	410	473	134.2	134.2	138.8
Duration (s)	394	396	413	410	410	410	473	465	465	469
Ignition (Yes/No)	6595	8950	17605	15045	15045	57880	57880	57320	57320	53200
Date experiment was carried out										
Volume of basket being tested (mL)	25/01/17	03/02/17	25/01/17	26/01/17	25/01/17	26/01/17	25/01/17	26/01/17	26/01/17	30/01/17
Oven reference temperature (°C)	131	131	442	442	442	152.0	144.9	1049	1049	1049
Bulk density of fuel (kg/m ³)	176.0	173.3	157.0	152.0	152.0	410	473	134.2	134.2	138.8
Duration (s)	394	396	413	410	410	410	473	465	465	469
Ignition (Yes/No)	6595	8950	17605	15045	15045	57880	57880	57320	57320	53200

4.D Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 450 °C

Table 4.11: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 450 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out									
Volume of basket being tested (mL)	06/12/16	06/12/16	07/12/16	07/12/16	07/12/16	07/12/16	08/12/16	08/12/16	08/12/16
Oven reference temperature (°C)	131	131	131	131	131	131	131	131	131
Bulk density of fuel (kg/m ³)	180.4	171.7	162.2	154.1	292	294	123.5	296	110.7
Duration (s)	288	301	297	5830	3605	5330	6600	290	7615
Ignition (Yes/No)	Y	Y	Y	Y	Y	Y	Y	Y	N
Date experiment was carried out									
Volume of basket being tested (mL)	08/12/16	09/12/16	12/12/16	13/12/16	14/12/16	14/12/16	14/12/16	15/12/16	15/12/16
Oven reference temperature (°C)	131	131	442	442	442	442	1049	1049	1049
Bulk density of fuel (kg/m ³)	116.1	120.1	107.5	116.1	110.2	110.2	96.2	100.6	100.6
Duration (s)	297	301	334	333	333	333	368	367	367
Ignition (Yes/No)	6055	11270	20720	11925	16910	16910	64360	57960	57960
	N	N	N	Y	Y	Y	N	Y	Y

4.E Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 550 °C

Table 4.12: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 550 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	15/12/16	15/12/16	15/12/16	15/12/16	16/12/16	16/12/16	16/12/16	19/12/16	19/12/16	20/12/16
Volume of basket being tested (mL)	131	131	131	131	442	442	442	1049	1049	1049
Oven reference temperature (°C)	128.5	142.1	152.2	147.1	135.6	125.5	130.3	120.4	125.5	125.5
Bulk density of fuel (kg/m ³)	285	291	290	291	314	312	311	345	347	347
Duration (s)	5215	4975	5380	4815	12740	11170	12685	52270	17520	17520
Ignition (Yes/No)	N	N	Y	Y	Y	N	N	N	N	Y

4.F Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 600 °C

Table 4.13: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 600 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	02/02/17	02/02/17	02/02/17	02/02/17	02/02/17	03/02/17
Volume of basket being tested (mL)	131	131	131	131	131	442
Oven reference temperature (°C)	160.4	169.9	188.0	179.0	184.0	174.0
Bulk density of fuel (kg/m ³)	285	285	285	283	283	306
Duration (s)	4980	5040	4620	4595	4080	13095
Ignition (Yes/No)	N	N	Y	N	N	Y

Date experiment was carried out	06/02/17	07/02/17	02/02/17	06/02/17	07/02/17
Volume of basket being tested (mL)	442	442	1049	1049	1049
Oven reference temperature (°C)	164.8	169.7	150.4	160.2	155.1
Bulk density of fuel (kg/m ³)	308	306	330	329	329
Duration (s)	14400	23605	53775	58720	63315
Ignition (Yes/No)	N	Y	N	Y	Y

4.G Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 700 °C

Table 4.14: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 700 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	17/11/16	22/11/16	23/11/16	24/11/16	24/11/16	25/11/16	28/11/16
Volume of basket being tested (mL)	131	131	131	131	131	131	131
Oven reference temperature (°C)	161.2	170.3	183.7	189.0	199.2	207.6	217.0
Bulk density of fuel (kg/m ³)	281	272	271	274	273	269	281
Duration (s)	21570	16560	14345	6000	11085	10700	10980
Ignition (Yes/No)	N	N	N	N	N	N	Y
Date experiment was carried out	28/11/16	29/11/16	30/11/16	30/11/16	30/11/16	01/12/16	03/12/16
Volume of basket being tested (mL)	131	442	442	442	1049	1049	1049
Oven reference temperature (°C)	212.8	204.8	188.5	194.9	172.9	182.4	185.7
Bulk density of fuel (kg/m ³)	274	293	295	298	325	326	324
Duration (s)	10875	27305	26880	58205	19250	69185	16295
Ignition (Yes/No)	N	Y	N	Y	N	N	Y

4.H Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 800 °C

Table 4.15: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 800 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	08/02/17	08/02/17	08/02/17	08/02/17	08/02/17	09/02/17
Volume of basket being tested (mL)	131	131	131	131	131	442
Oven reference temperature (°C)	216.1	233.2	251.0	241.6	237.2	224.1
Bulk density of fuel (kg/m ³)	256	252	256	257	256	264
Duration (s)	4510	3755	2830	3350	3150	4740
Ignition (Yes/No)	N	N	Y	Y	N	Y

Date experiment was carried out	09/02/17	09/02/17	09/02/17	10/02/17	13/02/17
Volume of basket being tested (mL)	442	442	1049	1049	1049
Oven reference temperature (°C)	215.3	220.3	206.3	201.5	207.1
Bulk density of fuel (kg/m ³)	264	264	278	280	281
Duration (s)	6495	9595	63255	28970	27780
Ignition (Yes/No)	N	Y	Y	N	Y

Chapter 5

Self-heating and ignition behaviour of torrefied biomass and biochar from softwood pellets, wheat pellets and rice husks

Summary ¹

Torrefied biomass and biochar are increasingly utilised for energy production, carbon sequestration and soil amendment. Different natural fuels are used for the production of torrefied biomass and biochar, including softwood pellets, wheat pellets, and rice husk. Each natural fuel source has different characteristic properties. Using basket experiments in a laboratory oven, I experimentally measured the different self-heating ignition temperatures of softwood pellets, rice husks and wheat straw pellets and their respective biochar produced at temperatures of 450 °C, 550 °C and 700 °C. By investigating self-heating behaviour as a function of pyrolysis reactor temperature for each sample I was able to quantify the different reactivities for the three different biomasses and compare their properties with respect to one another. 130 self-heating basket experiments were carried out with 791 h of oven run time. I found that softwood produced at reactor temperatures of 450 °C is the most prone of the three fuels to self-heating ignition. Wheat and softwood pellet feedstock present different self-heating ignition behaviour, with the softwood more prone to self-heating. However the wheat and softwood torrefied biomass show similar self-heating ignition properties when produced at reactor temperatures of 450 °C and 550 °C. Torrefied rice husk produced at reactor temperatures of 450 °C and 550 °C is shown to be less reactive than its softwood and wheat pellet counterparts, but at reactor temperatures of 700 °C has similar reactivity behaviour to softwood. The most reactive biochar produced at a reactor temperature of 700 °C is the wheat biochar, being more prone to self-heating ignition than its feedstock counterpart. This work helps quantify the fire risks posed by biomass and biochar for three different types of fuels and

1. This chapter is based on “F. Restuccia, O. Mašek, R. M. Hadden, G. Rein (2017) *Self-heating and ignition behaviour of torrefied biomass and biochar from softwood pellets, wheat pellets and rice husks*, (to be submitted to **Bioresource Technology**).”

their individual self-heating properties, highlighting the differences arising from using different biomass feedstock natural sources to provide the biochar and what effect this has on the biochar's relative fire risk. This work helps provide the necessary knowledge for safe handling and storage of these torrefied materials depending on their origin and production temperature.

5.1 Introduction

Biomass, plant-based materials collected by humans that are not used for food, have historically been waste material or used as a form of energy source, in the form of wheat, wood, rice and other materials. Therefore over time biomass has become an important part of the fuel mix for fossil fuel power plants, and its use is projected to grow significantly [81]. As shown in literature feasibility studies, torrefied biomass, which is a product of biomass pyrolysis, is a possible replacement for coal, because it could integrate into existing coal power plants, enabling them to generate clean energy without requiring expensive power plant conversions [82]. Biochar, charcoal produced from the pyrolysis of biomass, is also being used for soil amendment for very acidic soils. In addition, because carbon remains sequestered in biochar for centuries, a sustainable production of biochar can be used for atmospheric carbon sequestration. Both biochar and torrefied biomass are solid biomass pyrolysis products. They are derived from biomass through pyrolysis in a reactor under controlled conditions. Products differ based on reactor temperatures, with different temperatures leading to products with different properties and reactivities [83]. When produced at temperatures greater than 350 °C, this solid material is called biochar. When produced at reactor temperatures below 350 °C, this solid product is called torrefied biomass [83].

Biomass and biochar have a large application potential, however there are fire safety issues associated with both which have to be addressed. Materials such as wood, biomass, biochar, organic soils, coal and shale are all forms of reactive porous media. Their structure presents small free spaces (pores) embedded in the solid together with a carbon-rich component [43]. This makes the media permeable to oxygen, and greatly increases its surface area per unit volume making the organic media reactive because in the presence of oxygen the material will oxidize [84]. Because of this, such reactive porous media are known to undergo self-heating [1,31]. Self-heating is the tendency of certain porous fuels to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures [1]. In biomass, this process typically starts by exothermic biological reactions, which cannot go beyond 70 °C [85]. The further exothermicity is then dominated by slow exothermic oxidation at low temperatures but the reaction alone is insufficient to raise the material temperature. The temperature rise is determined by the balance between the rate of heat generation and the rate of heat losses [86]. These exothermic reactions can lead to ignition, leading to smouldering or flaming fires and can be hazardous. The

more reactive the material, the more prone it is to self-heating.

Fire initiated by self-heating ignition has been identified as a problem for many porous reactive media and has been studied and reported before. Literature exists on self-heating ignition for materials such as coal and biomass [87], and shale and organic soils from my work in Ch 2-3. For biomass, fire risk is associated with its production, transport, handling and storage. Spontaneous ignition of pyrolyzed biomass has already lead to accidental fires. Some more widely reported cases of biomass self-heating ignition are the biomass storage units at Tilbury Power Plant (UK), which ignited in 2012, and the biomass storage silos at Avedøre (Denmark), which ignited in 2016 [93, 94]. In the past, work was carried out to study the self-heating ignition properties of biomass utilising thermogravimetric analysis (TGA) on a variety of materials such as wood, wheat, olive cake and sunflower husk [88–91]. TGA is very useful for determining kinetics, but is not sufficient to characterise self-heating, as the assumption for TGA measurements is that the sample can be considered 0D. Self-heating requires a study of the heat distribution in space as self-heating will occur at the centre of a sample. Therefore to have a better understanding of the bulk behaviour of the material on self-heating ignition, TGA alone is not sufficient. Some work on this is present in literature: Garcia et al [92] carried out some of these bulk property studies on the self-heating ignition properties of biomass dust, and how likely it is to ignite when in storage conditions which have oxygen access. Jones et al [46] studied self-heating ignition properties using (TGA) coupled with basket experiments for a variety of biomass feedstock including olive residue, sugars, and sunflower husks to capture the impact of the low activation energy of certain materials to the increase in self-heating ignition risks. Some work used biomass emission products to then predict self-heating ignition of biomass by analysing emission products [68]. In my recent work, presented in Ch 4, I carry out an analysis to quantify the effect of softwood torrefied biomass and biochar produced at different pyrolysis reactor temperatures on self-heating ignition properties, showing that for softwood there is a specific range of pyrolysis temperature for which the biochar is most prone to self-heating ignition.

Torrefied biomass and biochar can be produced at a variety of pyrolysis reactor temperatures from a variety of fuels. My previous work, in Ch 4, has already shown that the pyrolysis reactor temperature is an important parameter when studying how prone biochar is to self-heating ignition. However it has been shown in literature that the physiochemical properties of the products of pyrolysis reactors are not only dependent on reactor temperature, but also the starting organic material [101]. There is no current literature on the effect of torrefaction of biomass on self-heating ignition, and how that effect will change depending on the original feedstock material. This work aims to fill this gap, using wheat, softwood and rice husk feedstock and biochar produced at reactor temperatures of 450 °C, 550 °C and 700°C to quantify the function of reactor temperature to propensity to self-heat for each of these starting organic materials and therefore compare the propensity of self-heating of the biomass and biochars produced from these

different organic materials.

5.2 Experimental setup

The theory used for this work is described in Ch 1 and is the same as that used for previous chapters. For this work, a comparison of three different kinds of biomass was carried out to determine self-heating ignition of torrefied biomass and biochar produced from softwood, wheat biomass pellets, and rice husks. The biochars were produced from a softwood pellet feedstock, wheat pellet feedstock, and rice husk feedstock pyrolysed in a rotary kiln reactor at 450 °C, 550 °C and 700 °C at the UK Biochar Research Centre at the University of Edinburgh by our collaborator Ondřej Mašek. The experimental data on softwood presented in this chapter was first introduced in Chapter 4, whilst the data on wheat pellets and rice husks is novel to the study given in this current chapter. The samples used in the experiments are presented in Fig. 5.1, and show different physical properties in terms of diameter, average length and bulk density of each. A summary of these characteristics is presented in Table 5.1. For all three natural fuels the density and diameter decreased significantly after the feedstock was placed in the pyrolysis reactor, but once pyrolysed the bulk density and diameter of the particle does not change as significantly between the reactor temperatures of 450 °C to 700 °C. The rice husk samples were significantly smaller than the wheat and softwood pellets. Elemental analysis was carried out for all of the biochars and biomass feedstock to compare the CHN composition of each and is presented in Table 5.2. For softwood and wheat, the amount of carbon present in the char increases with increasing reactor temperature which agrees with results in literature [99, 102]. For rice husks, the amount of carbon decreases above the reactor temperature of 450 °C as more of the rice husk converts into oil, in agreement with what has been shown before in literature [103, 104]. The highest amount of carbon is present in the softwood samples. Water, ash and Carbon in dry ash free basis (C_{daf}) for the biomass and biochars are calculated using the TGA data presented in 5.3.2. The Carbon in dry ash free basis is calculating according to the BSI standard EN 15296:2011 [100]. Results are presented in Table 5.3, where it can be seen that for rice husk the amount of C_{daf} is significantly higher than the total carbon found in the elemental analysis, due to the high amount of ash produced in rice husk combustion. Furthermore, biochars pyrolysed at temperatures above 700 °C are purely carbon (apart from water and ash) for wheat and softwood, but not for rice husk.

The laboratory setup to determine the minimum critical ambient temperature for self-heating $T_{a,c}$ is the same as that used in Ch 4. The pellets were packed into cubic shaped wire mesh baskets of three different sizes to ensure sufficient data could be measured to assess if the assumption of Arrhenius reactions necessary to adopt Frank-Kamenetskii theory could be applied. As in my previous work, I selected cube shaped baskets as it is the shape most easily adaptable to increasing geometry size in a rectangular oven without



Figure 5.1: Biomass and biochar samples used, with feedstock and various biochars produced in a pyrolysis reactors at temperatures of 450 °C, 550 °C, and 700 °C for softwood, wheat, and rice husk.

making the larger samples approach the oven walls. The baskets were made of 0.5 mm diameter wire mesh with volumes of 131, 442 and 1049 cm³. These baskets ensure a good range of sizes for the largest possible temperature range given at the laboratory scale, between 90 °C and 200 °C for these biomass and biochar samples.

In total, 130 experiments were carried out with 791 h of oven run time. If the biomass sample failed to reach ignition the experiment was repeated with a fresh sample at a higher temperature. If the sample reached ignition, then the experiment was repeated with a fresh sample at a lower temperature. The experiments were carried out until $T_{a,c}$ for ignition was located within ± 4 °C for each tested biomass. A minimum of two experiments were conducted at each basket size for each softwood sample. A summary of the experiments carried out is presented in Table 5.4.

In addition to basket experiments, the thermal conductivity for all 12 sample types was measured using a guarded heat flow meter for temperatures of 65 °C, 115 °C and 165 °C in order to analyse how thermally insulating each material is, as decreasing thermal conductivity enhances the likelihood of a material to ignite from self-heating. Furthermore, thermal conductivity values can be used to determine pre-exponential factors using the basket experiment data. Finally, to provide information on the reaction kinetics at the

Table 5.1: Physical properties of softwood, wheat, and rice husk biomass and biochar used for experiments.

Physical Properties	Density (kg/m ³)	Pellet length (mm)	pellet diameter (mm)
Softwood feedstock	531	21.8	5.8
Softwood biochar produced at $T_r = 450^\circ\text{C}$	295	17.9	4.3
Softwood biochar produced at $T_r = 550^\circ\text{C}$	289	20.3	4.1
Softwood biochar produced at $T_r = 700^\circ\text{C}$	274	13.5	4.3
Wheat feedstock	389	15.2	6.5
Wheat biochar produced at $T_r = 450^\circ\text{C}$	215	9.6	5.0
Wheat biochar produced at $T_r = 550^\circ\text{C}$	204	11.0	4.8
Wheat biochar produced at $T_r = 700^\circ\text{C}$	255	9.1	4.6
Rice husk feedstock	110	7.7	1.6
Rice husk biochar produced at $T_r = 450^\circ\text{C}$	82	5.4	0.4
Rice husk biochar produced at $T_r = 550^\circ\text{C}$	77	5.3	0.6
Rice husk biochar produced at $T_r = 700^\circ\text{C}$	95	5.5	0.4

Table 5.2: Elemental analysis of the biomass and biochars arranged by feedstock type.

Element	C	H	N
	Weight %		
Softwood feedstock	45.80	6.43	<0.3
Softwood biochar produced at $T_r = 450^\circ\text{C}$	76.76	3.80	<0.3
Softwood biochar produced at $T_r = 550^\circ\text{C}$	82.27	3.17	<0.3
Softwood biochar produced at $T_r = 700^\circ\text{C}$	86.31	2.55	<0.3
Wheat feedstock	42.66	6.20	0.39
Wheat biochar produced at $T_r = 450^\circ\text{C}$	60.00	3.19	1.25
Wheat biochar produced at $T_r = 550^\circ\text{C}$	68.40	2.83	0.81
Wheat biochar produced at $T_r = 700^\circ\text{C}$	77.44	2.22	<0.3
Rice husk feedstock	36.47	5.17	<0.3
Rice husk biochar produced at $T_r = 450^\circ\text{C}$	48.94	2.58	0.52
Rice husk biochar produced at $T_r = 550^\circ\text{C}$	46.97	1.98	<0.3
Rice husk biochar produced at $T_r = 700^\circ\text{C}$	41.51	1.30	<0.3

microscale of each pyrolysed biomass from the three feedstock sources, thermogravimetric analysis was conducted for each sample.

Table 5.3: Water, ash and Carbon in dry ash free basis (Cdaf) for the biomass and biochars calculated using the TGA data presented in section 5.3.2.

Element	Water Weight %	Ash	Cdaf
Softwood feedstock	5.45	0.87	48.9
Softwood biochar produced at $T_r = 450\text{ }^{\circ}\text{C}$	4.17	1.81	81.6
Softwood biochar produced at $T_r = 550\text{ }^{\circ}\text{C}$	3.83	3.03	88.3
Softwood biochar produced at $T_r = 700\text{ }^{\circ}\text{C}$	4.57	9.03	99.9
Wheat feedstock	4.61	4.87	47.1
Wheat biochar produced at $T_r = 450\text{ }^{\circ}\text{C}$	4.49	19.50	78.9
Wheat biochar produced at $T_r = 550\text{ }^{\circ}\text{C}$	3.31	20.81	90.1
Wheat biochar produced at $T_r = 700\text{ }^{\circ}\text{C}$	3.43	18.71	99.5
Rice husk feedstock	3.74	21.04	48.5
Rice husk biochar produced at $T_r = 450^{\circ}\text{C}$	3.56	39.87	86.5
Rice husk biochar produced at $T_r = 550^{\circ}\text{C}$	2.56	47.52	94.1
Rice husk biochar produced at $T_r = 700^{\circ}\text{C}$	2.33	49.4	86.0

Table 5.4: Number of experiments carried out for each type of biomass and biochar, ordered on the basis of feedstock type and basket sizes.

Pellet type	Basket length (cm)		
	5.1	7.6	10.2
Softwood Feedstock	4	4	3
Softwood biochar produced at $T_r = 450\text{ }^{\circ}\text{C}$	9	3	2
Softwood biochar produced at $T_r = 550\text{ }^{\circ}\text{C}$	4	3	2
Softwood biochar produced at $T_r = 700\text{ }^{\circ}\text{C}$	8	3	3
Wheat Feedstock	4	3	2
Wheat biochar produced at $T_r = 450\text{ }^{\circ}\text{C}$	6	3	2
Wheat biochar produced at $T_r = 550\text{ }^{\circ}\text{C}$	4	3	3
Wheat biochar produced at $T_r = 700\text{ }^{\circ}\text{C}$	2	3	3
Rice husk Feedstock	7	3	2
Rice husk biochar produced at $T_r = 450^{\circ}\text{C}$	4	3	2
Rice husk biochar produced at $T_r = 550^{\circ}\text{C}$	6	3	2
Rice husk biochar produced at $T_r = 700^{\circ}\text{C}$	6	3	3

5.3 Results and discussion

5.3.1 Basket experiments results

For all 12 sample types, the minimum ignition temperature required for ignition was found for all three basket sizes. Fig. 5.2 shows the results of these experiments

for samples produced from softwood feedstock. As can be noted the lowest ignition temperature occurs for softwood biochar produced at a reactor temperature of 450 °C. Softwood biochar produced at a reactor temperature of 550 °C is still more prone to self-heating ignition than the feedstock, but the biochar produced at a reactor temperature of 700 °C is the least prone to self-heating ignition.

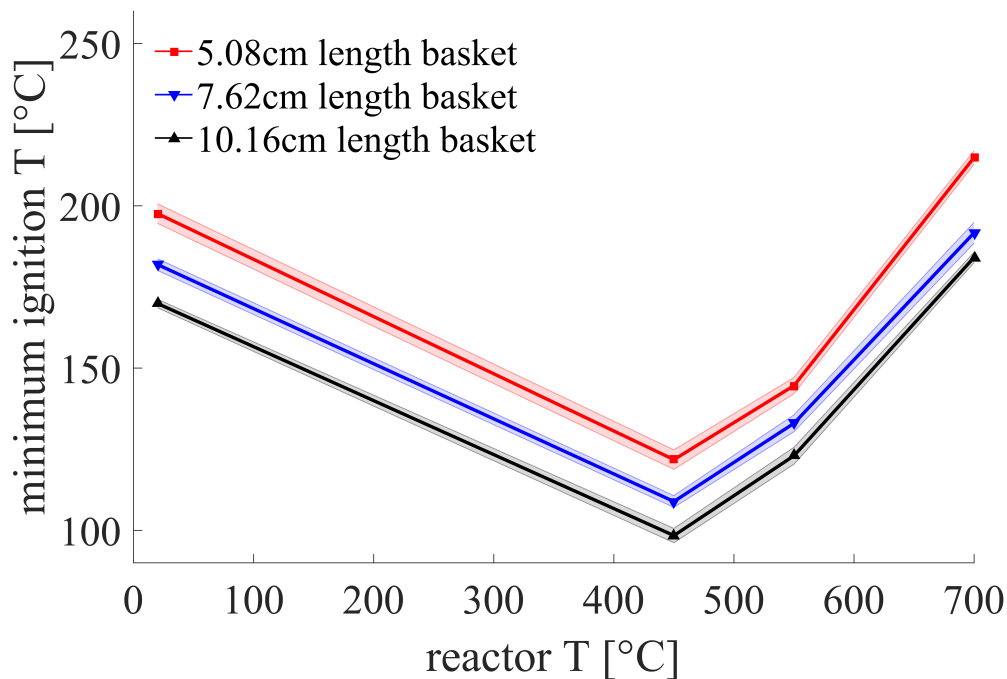


Figure 5.2: Minimum ignition temperature for softwood feedstock and biochar produced at 450 °C, 550 °C, and 700 °C for three basket sizes. Experimental error is estimated based on temperature error bounds on each individual set of experiments.

Similarly, Fig. 5.3 shows the results of the basket experiments for the samples produced from wheat feedstock. As can be noted the lowest ignition temperature occurs for wheat biochar produced at a reactor temperature of 450 °C, like for the softwood samples. Wheat biochar produced at reactor temperature of 550 °C is still more prone to self-heating ignition than the wheat feedstock, like for the biochar produced at reactor temperature of 700 °C which is less prone to self-heating ignition than the other biochars but still more than the feedstock.

Similarly, Fig. 5.4 shows the results of the basket experiments for the samples produced from rice husk feedstock. The lowest ignition temperature occurs for rice biochar produced at a reactor temperature of 450 °C, like for both the softwood and the wheat samples. Rice biochar produced at a reactor temperature of 550 °C is less prone to self-heating ignition than the rice feedstock, which is a different behaviour with respect to the wheat and softwood equivalents. The biochar produced at reactor temperature of 700 °C is the least prone to self-heating. The rice products are generally less prone to self-heating, resulting in higher minimum ignition temperatures for same sized boxes and

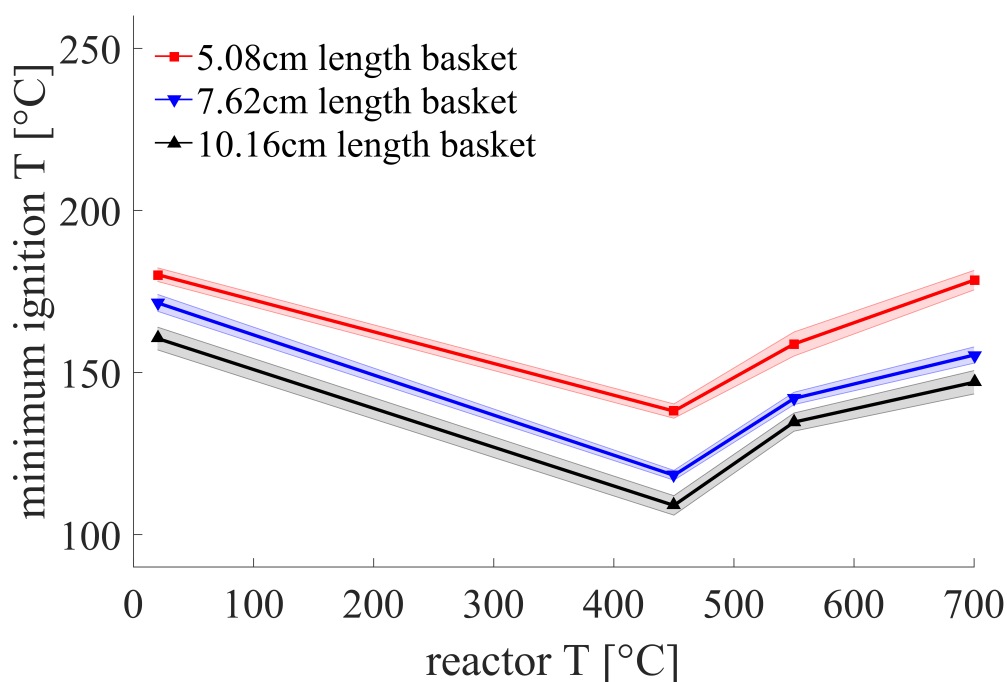


Figure 5.3: Minimum ignition temperature for wheat feedstock and biochar produced at 450 °C, 550 °C, and 700 °C for three basket sizes. Experimental error is estimated based on temperature error bounds on each individual set of experiments.

same reactor temperatures when compared to both the softwood and wheat products. For the 10.16 cm length cube box, the difference in ignition temperature for the rice and softwood biochar produced at 450 °C is over 40 °C, making the self-heating ignition behaviour of the biochar produced from different biomass materials significantly different.

Plotting the minimum ignition temperature for one basket size (10.16cm length basket) for all the biochars with respect to the carbon dry free ash allows a comparison of the effect of total carbon content with the critical ignition temperature. This has already been done for the softwood in Ch 4, and is done for wheat in Fig. 5.5 and rice husk in Fig. 5.6. The results for wheat show that the peak at 450 °C is not solely caused by the carbon content, as the V shape seen in Fig. 5.3 is also clearly present in this plot, and behaves very similarly to the softwood seen in Ch 4. The rice husks have a slightly different behaviour, as the carbon content of rice husk produced at pyrolysis temperatures of 550 °C has a higher carbon dry ash free content than the one produced at 700 °C, causing the shape not to follow the same V shape as the previous two materials. However the trend of a local minimum at 450 °C production temperature is still found for rice husk.

Conductivity of the different biochars produced from different feedstocks also varies. Therefore conductivity was measured experimentally using the guarded heat flow meter method at various temperatures, and was shown to be linear within our measured temperature range between 65 and 165 °C for all biomass products, irrespective of the

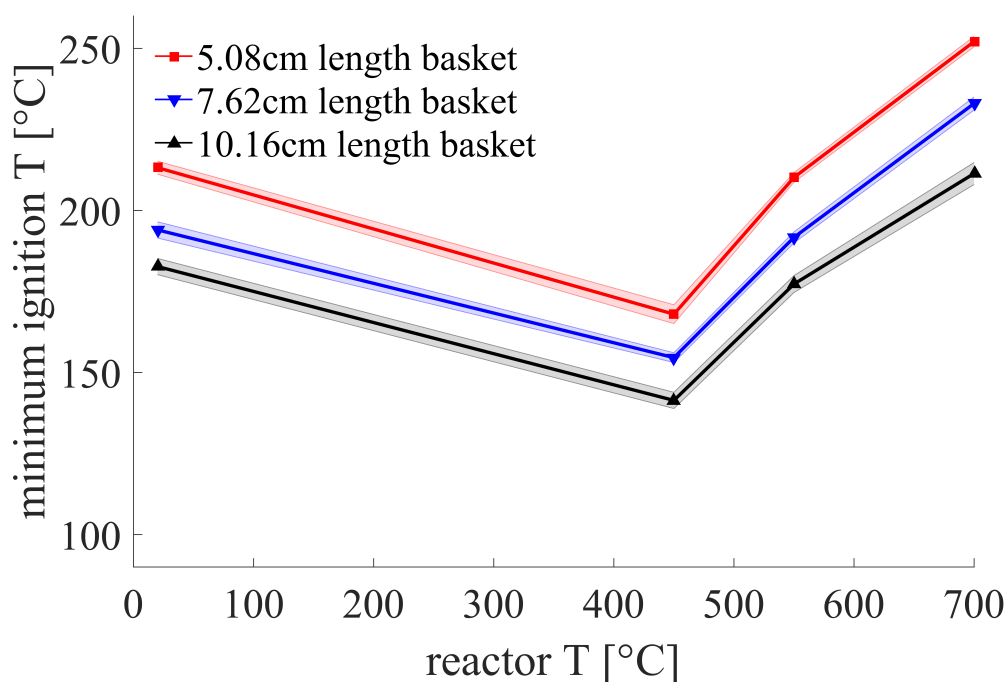


Figure 5.4: Minimum ignition temperature for rice husk feedstock and biochar produced at 450 °C, 550 °C, and 700 °C for three basket sizes. Experimental error is estimated based on temperature error bounds on each individual set of experiments.

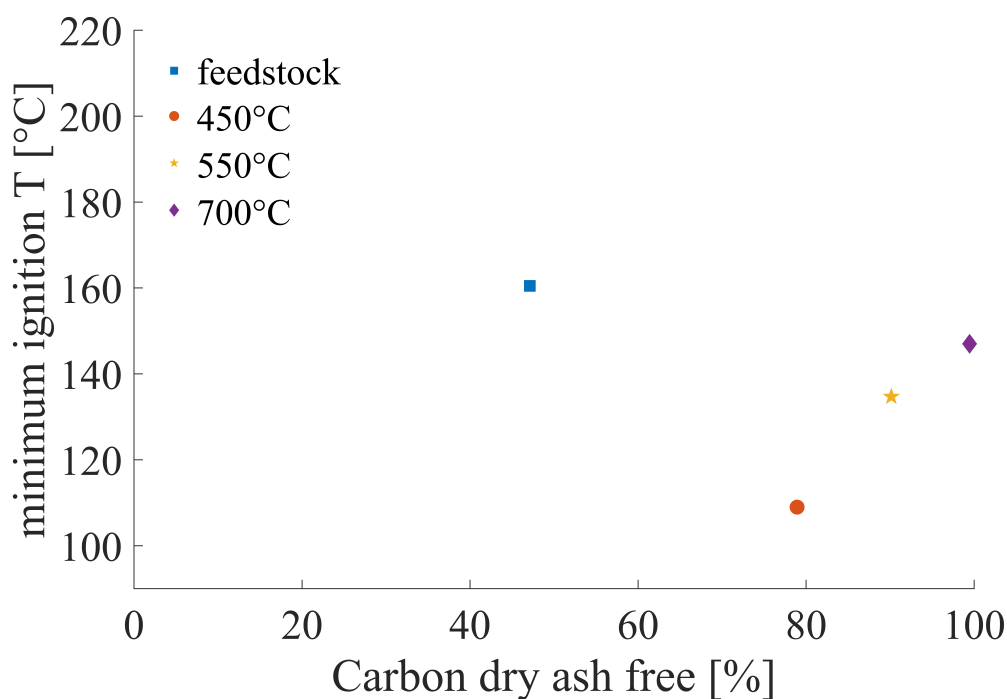


Figure 5.5: Minimum ignition temperature for wheat feedstock and biochar between 450 °C and 700 °C for a fixed basket size plotted vs carbon dry ash free.

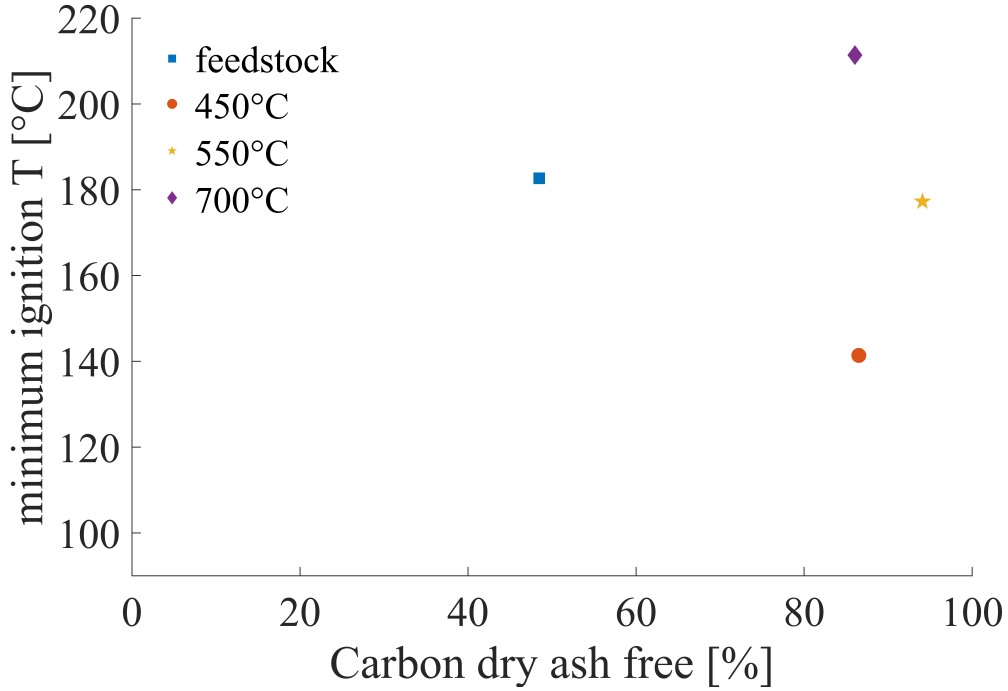


Figure 5.6: Minimum ignition temperature for rice husk feedstock and biochar between 450 °C and 700°C for a fixed basket size plotted vs carbon dry ash free.

biomass used. A summary of the conductivity measurements is presented in Table 5.5 divided by type of biomass feedstock material. Some patterns were found in the conductivity properties: for both wheat and softwood the most conductive of material was the feedstock, with the biochar produced at 450 °C the least conductive and biochars produced at higher reactor temperatures increasing in thermal conductivity, but staying below the thermal conductivity of the feedstock. Between wheat and softwood, wheat is slightly more conductive. The fact that the biochar was produced at 450 °C contributes to why the biochar produced at this temperature is the most prone to ignite, as the exothermic reactions at the core of the sample cannot be as effectively cooled by the ambient temperature due to the fact that the surrounding biochar acts as a good insulator. On the other hand, for rice husk the thermal conductivity behaviour observed from the experiments is different, as the least conductive of the samples is the rice feedstock, with increasing thermal conductivity with respect to increasing reactor temperature.

Using the experimental results from the basket experiments and the Frank-Kamenetskii theory of criticality it is possible to extract a one-step kinetic model and thermal parameters by plotting $\ln(\delta_c T_{a,c}/L^2)$ vs $1/T_{a,c}$. This was done for softwood (Fig. 4.5 from Ch 4), wheat (Fig. 5.7) and rice (Fig. 5.8). In these plots, the slope of the straight line corresponds to $-E/R$. Taking slopes in each figure gives the effective activation energies for each biomass. The y-intercept of these lines allows the calculation of thermal parameters in Eq. 1.3 from Ch 1, $\ln(\frac{QE_f}{Rk})$. A few observations from these plots are that for both softwood, wheat, and rice husks the characteristics of the slopes of the feedstock

Table 5.5: Thermal conductivity measurements for the biomass samples conducted at 3 temperatures, with resulting fit equation. The R^2 values of the linear fits through these points are included.

k for biomass type	65 °C (W/mK)	115 °C (W/mK)	165 °C (W/mK)	R^2 (-)
Softwood feedstock	0.1107	0.1228	0.1436	0.977
Softwood biochar produced at $T_r = 450^\circ\text{C}$	0.0807	0.0893	0.1004	0.995
Softwood biochar produced at $T_r = 550^\circ\text{C}$	0.0904	0.0917	0.0940	0.976
Softwood biochar produced at $T_r = 700^\circ\text{C}$	0.0853	0.0919	0.0974	0.997
Wheat feedstock	0.1397	0.1502	0.1715	0.963
Wheat biochar produced at $T_r = 450^\circ\text{C}$	0.0881	0.0908	0.0980	0.935
Wheat biochar produced at $T_r = 550^\circ\text{C}$	0.0879	0.0977	0.1061	0.998
Wheat biochar produced at $T_r = 700^\circ\text{C}$	0.1082	0.1186	0.1243	0.971
Rice husk feedstock	0.1055	0.1129	0.1239	0.990
Rice husk biochar produced at $T_r = 450^\circ\text{C}$	0.1256	0.1360	0.1424	0.981
Rice husk biochar produced at $T_r = 550^\circ\text{C}$	0.1266	0.1469	0.1588	0.977
Rice husk biochar produced at $T_r = 700^\circ\text{C}$	0.1222	0.1350	0.1469	1.000

and biochar produced at reactor temperatures of 700 °C are quite similar. Using the thermal conductivity data presented in Table 5.5, I can remove an unknown from the thermal parameters. The conductivity values were taken at 115 °C to ensure I did not encounter moisture effects, as the experiments were carried out above 100 °C, so that the value was in the range of experimental measurements carried out in the basket experiments. This allows me to isolate (Qf) which is effectively a pre-exponential factor. The results can therefore isolate all the thermal and kinetic parameters and a summary of all of these parameters is presented in Table 5.6, with R^2 calculated from the linear fit for each line. The error bounds are calculated using the fits that would give the highest and the lowest possible effective activation energy from the experimental data obtained (largest possible errors). A detailed summary of all experimental results are presented in Appendices 5.A-5.L.

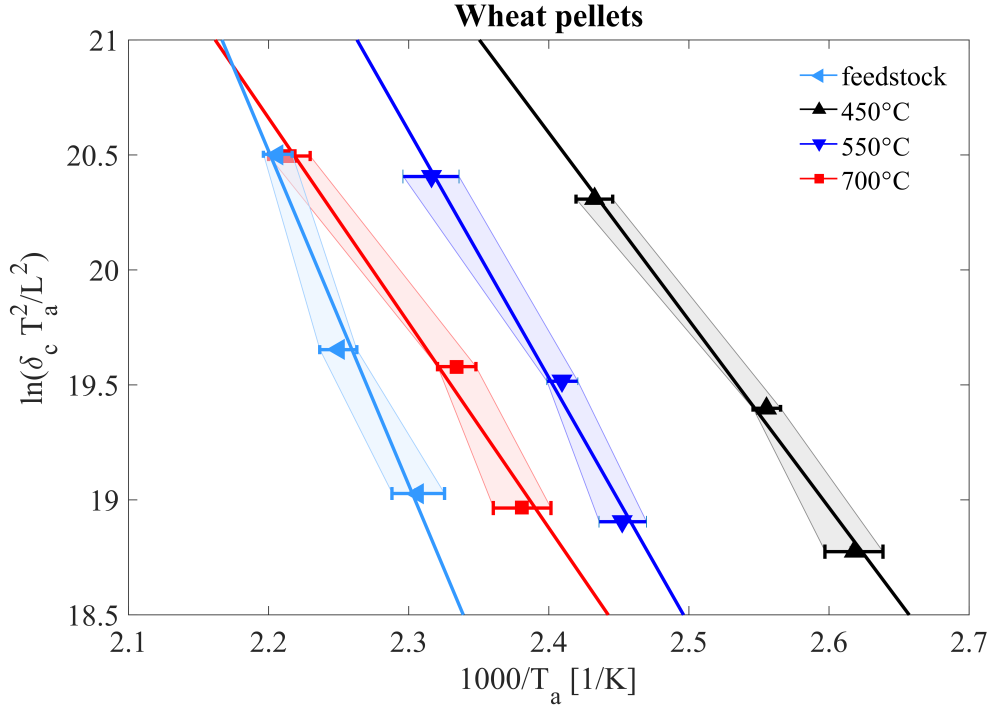


Figure 5.7: Frank-Kamenetskii plot for wheat feedstock and biochar produced at 450 °C, 550 °C, and 700°C. Experimental error is estimated based on error bounds on each individual set of experiments. The linear fits all have $R^2 > 0.972$ (Table 5.6).

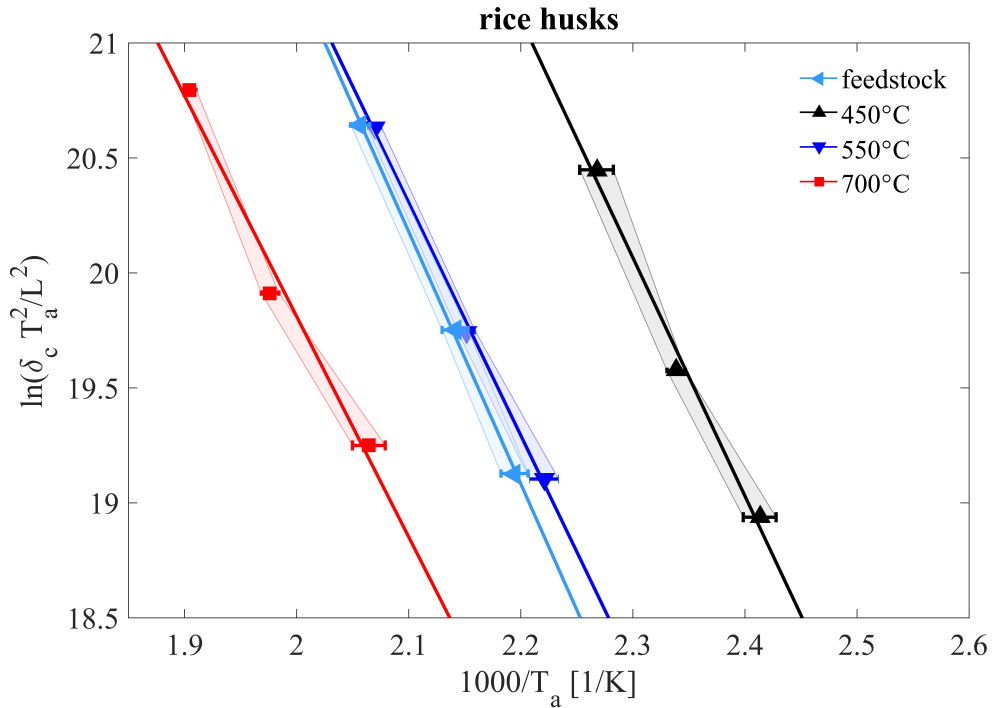


Figure 5.8: Frank-Kamenetskii plot for rice husk feedstock and biochar produced at 450 °C, 550 °C, and 700°C. Experimental error is estimated based on error bounds on each individual set of experiments. The linear fits all have $R^2 > 0.982$ (Table 5.6).

Table 5.6: Effective activation energy E , pre-exponential factor Qf , conductivity k extracted from Frank-Kamenestkii plot (Fig. 5.7-5.8 and from Ch 4 for softwood) calculated using Eq. (1.3). The R^2 values of the linear fits used to calculate these are included.

biomass type	E (kJ/mol)	k (W/mK)	Qf (W/m ³)	R^2 (-)
Softwood feedstock	94.52	0.1228	$2.86 \cdot 10^{14}$	0.999
Softwood biochar produced at $T_r = 450^\circ\text{C}$	78.76	0.0893	$1.48 \cdot 10^{14}$	0.997
Softwood biochar produced at $T_r = 550^\circ\text{C}$	95.18	0.0917	$4.27 \cdot 10^{15}$	0.996
Softwood biochar produced at $T_r = 700^\circ\text{C}$	87.44	0.0919	$1.93 \cdot 10^{13}$	0.975
Wheat feedstock	120.68	0.1502	$6.22 \cdot 10^{17}$	0.972
Wheat biochar produced at $T_r = 450^\circ\text{C}$	67.76	0.0908	$3.06 \cdot 10^{12}$	0.994
Wheat biochar produced at $T_r = 550^\circ\text{C}$	92.20	0.0977	$4.21 \cdot 10^{14}$	0.989
Wheat biochar produced at $T_r = 700^\circ\text{C}$	74.09	0.1186	$4.08 \cdot 10^{12}$	0.982
Rice husk feedstock	91.20	0.1129	$6.02 \cdot 10^{13}$	0.999
Rice husk biochar produced at $T_r = 450^\circ\text{C}$	86.18	0.1360	$1.53 \cdot 10^{14}$	0.989
Rice husk biochar produced at $T_r = 550^\circ\text{C}$	84.17	0.1469	$1.63 \cdot 10^{13}$	0.998
Rice husk biochar produced at $T_r = 700^\circ\text{C}$	79.75	0.1350	$1.21 \cdot 10^{12}$	0.980

5.3.2 Thermogravimetric analysis

To compare these self-heating basket experiments to the oxidative reactivity carried out in microscale experiments, thermogravimetric analysis (TGA) was carried out in air with a heating rate of 10 K/min for all the feedstock and biochar samples. This allows a link between bulk scale experiments and kinetics. The heating rate was chosen to have slow heating and to reduce thermal effects on the kinetic measurements. Fig. 5.9 shows the results of the mass loss found in each sample from TGA. All the samples display an initial reduction in mass due to drying of the softwood around 100 °C, then a large reduction in mass between 200 °C and 400 °C. Mass loss continues until 600 °C for all the samples. Just for the softwood biochars the mass loss continues in the 600 °C to 800 °C temperature range. Differences can be seen in the mass loss of the different materials: rice husk has a significantly higher residue than wheat and softwood. For rice husk feedstock the residue is just over 20% of the initial mass, while for softwood feedstock it is negligible, close to 0%, and for wheat feedstock around 5%. This significant difference in residue is also found for the biochars, where for rice biochars the residue mass ranges from 40% to 50% of the original mass, compared to wheat biochar which has around 20% residue mass and softwood biochar with negligible residue. The characteristic temperatures where these mass losses occur are reported in Table 5.7, where it can be seen that for all the materials both the first and second characteristic temperature increase with increasing pyrolysis temperature. For softwood, these temperatures are the highest, while lowest for the rice husk.

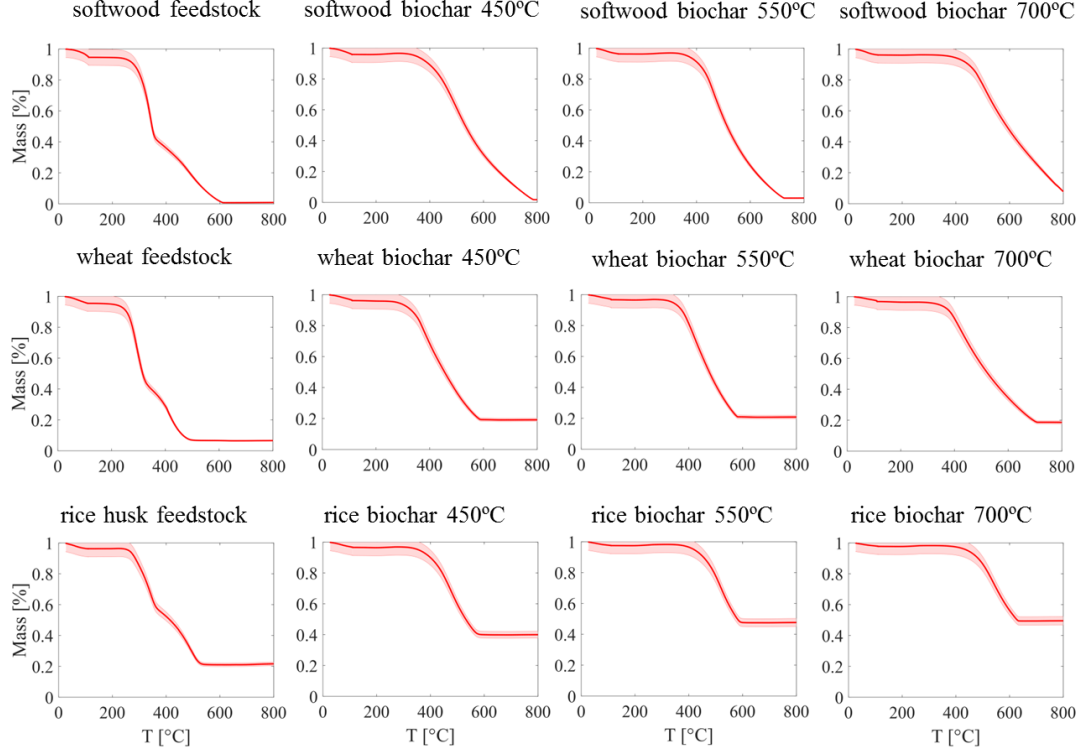


Figure 5.9: Thermogravimetric analysis in air of the softwood, wheat, and rice husk biomass and biochar samples carried out with a heating rate of 10 K/min. Each plot represents mass % as a function of temperature with error clouds taking into account experimental error.

Table 5.7: Characteristic temperatures for mass loss from Fig. 5.9.

Element	T characteristic 1 Temperature °C	T characteristic 2
Softwood feedstock	260	650
Softwood biochar produced at $T_r = 450$ °C	330	790
Softwood biochar produced at $T_r = 550$ °C	350	725
Softwood biochar produced at $T_r = 700$ °C	350	810
Wheat feedstock	200	500
Wheat biochar produced at $T_r = 450$ °C	270	680
Wheat biochar produced at $T_r = 550$ °C	310	580
Wheat biochar produced at $T_r = 700$ °C	320	700
Rice husk feedstock	240	550
Rice husk biochar produced at $T_r = 450$ °C	300	600
Rice husk biochar produced at $T_r = 550$ °C	350	600
Rice husk biochar produced at $T_r = 700$ °C	400	630

Analysing the mass loss rate (MLR) of the samples calculated from the TGA of the

biomasses, several trends can be clearly identified and are presented in Fig. 5.10. All three type of feedstock present two peaks around 350 °C and 450 °C the first corresponding to a large loss of hemicellulose and cellulose, the second to a loss of lignin [96]. The biochars do not present these two peaks, as they are all produced at reactor temperatures above 450 °C, therefore past the decomposition of the hemicellulose and cellulose. Therefore one peak is seen, decomposition of the lignin [96]. For the rice husk all biochars show peaks of mass loss rates at the same temperature, around 550 °C, and of the same magnitude. The wheat biochar shows similarly sized peaks but at a slightly lower temperature just above 400 °C. Finally the softwood shows peaks of a higher magnitude than both the wheat and the softwood, around 500 °C. For all the biochars, the magnitude of the MLR tends to decrease with increasing biochar pyrolysis temperature, and this can be explained by the fact that at high pyrolysis temperatures (600 °C and above) a lot of the lignin has already pyrolysed [96], and we have less carbon present for oxidation reactions to take place.

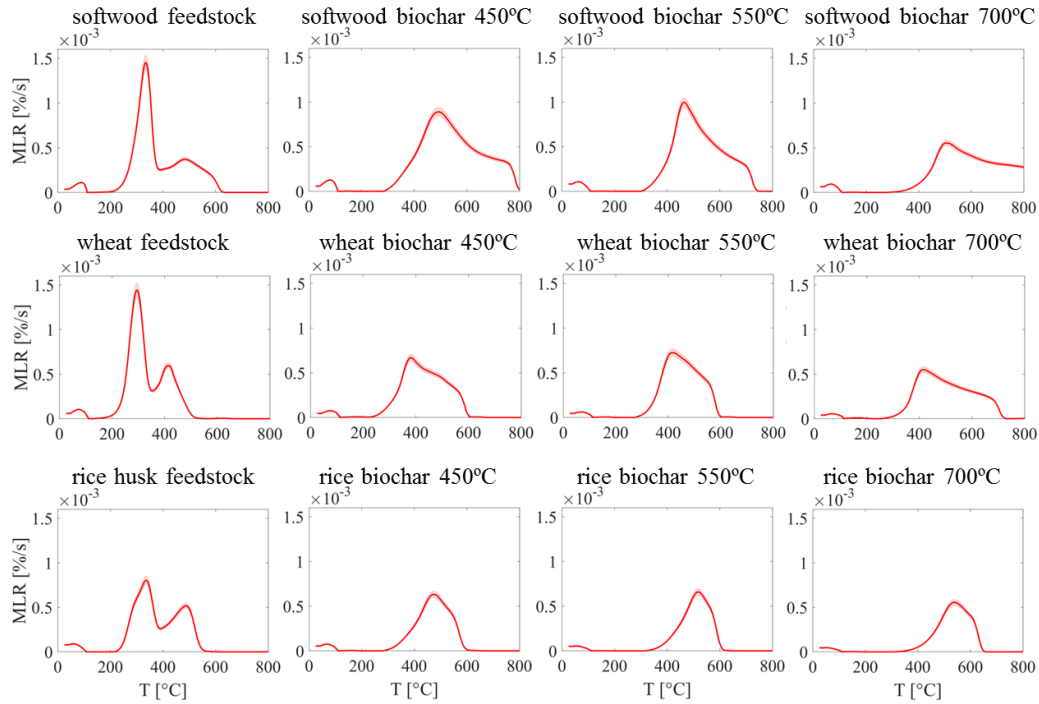


Figure 5.10: Mass loss rates calculated from thermogravimetric analysis in air for softwood biomass and biochars samples. Each plot represents mass loss %/s as a function of temperature with error clouds taking into account experimental error.

5.3.3 Upscaling of results

The thermal properties and kinetics obtained from the experimental campaign can be extended to larger biomass and biochar stockpiles of cubic size to quantify possibility of self-heating ignition at environmental temperature ranges that can be found in power

plant storage silos or domestic biomass storage units, from $-10\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$. For reference, the sizes of such storage and transport systems can range from standard domestic biomass storage units (10 m^3) or open top container trucks (30 m^3) for transport to large power plant storage silos. Using Frank-Kamenetskii theory I upscale the results for all 12 types of sample used in this study, and present them based on the different original feedstock: softwood products in Fig. 5.11, wheat products in Fig. 5.12 and rice husk products in Fig. 5.13.

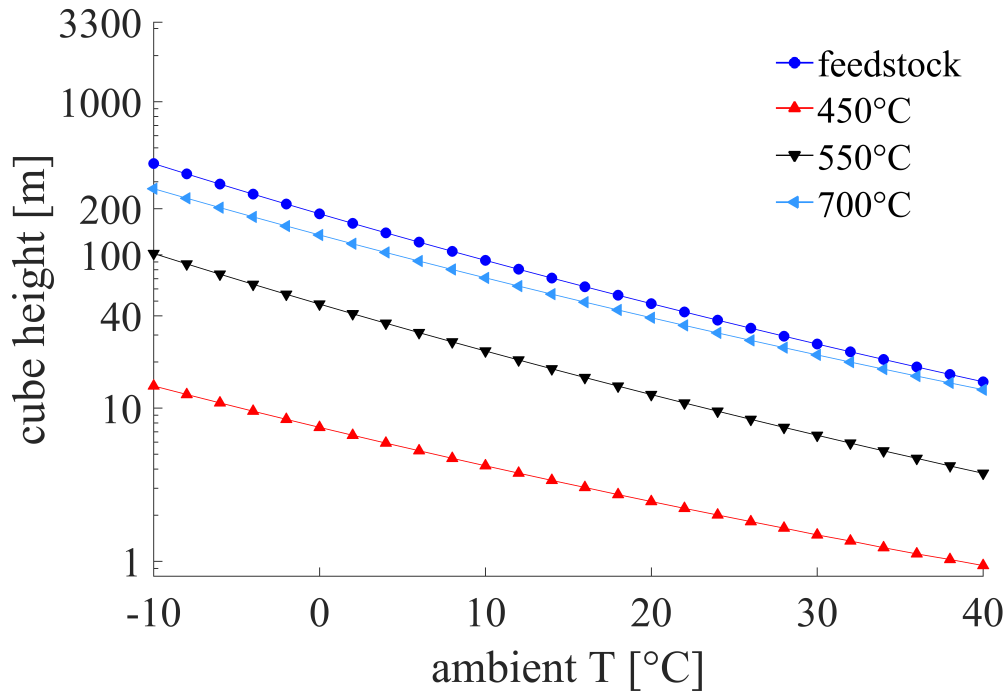


Figure 5.11: Upscaled results of cubic softwood biomass and biochar piles required for self-ignition at ambient temperature between $-10\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ based on the thermal and kinetic parameters found in self-heating basket experiments (Table 5.6).

Some significant results from Fig. 5.11 are that softwood biochar pellets produced at $450\text{ }^{\circ}\text{C}$ of the dimensions of even a standard domestic biomass storage unit (2.2 m cube height) will ignite from self-heating at ambient temperatures as low as $20\text{ }^{\circ}\text{C}$. Biochar produced at reactor temperature of $550\text{ }^{\circ}\text{C}$ would not ignite from self-heating in containers of the same size, but would be at the threshold for ignition in an open top container for temperatures of $44\text{ }^{\circ}\text{C}$, just above the temperature range considered for this upscaling. Softwood feedstock and biochar produced at $700\text{ }^{\circ}\text{C}$ would not be a risk to ignition in the entire temperature range being studied at any of these sizes, even for temperatures as high as $70\text{ }^{\circ}\text{C}$.

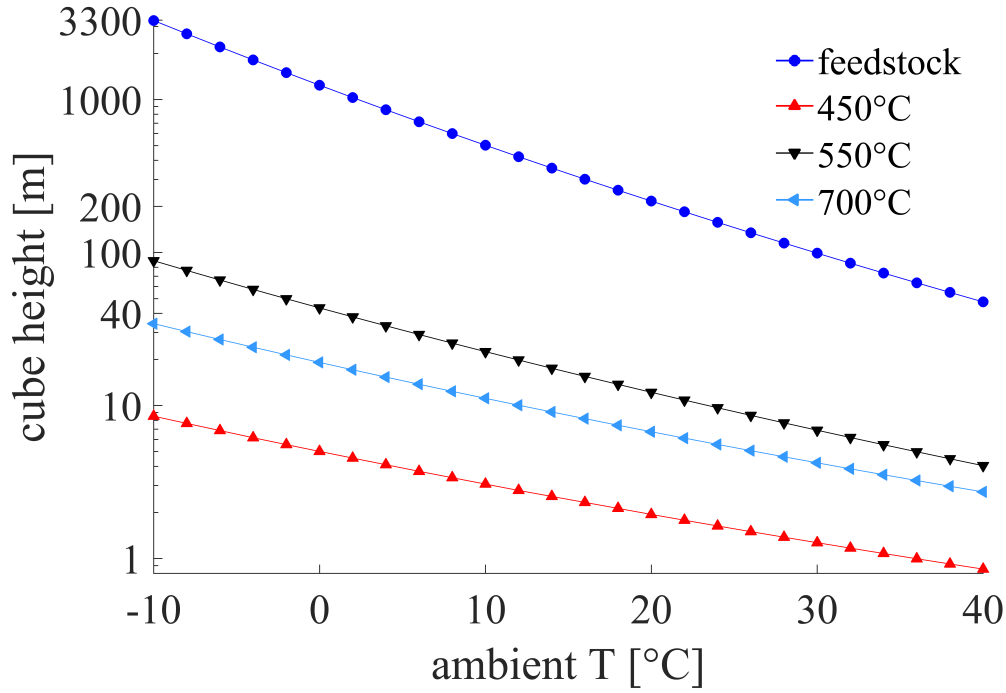


Figure 5.12: Upscaled results of cubic wheat biomass and biochar piles required for self-ignition at ambient temperature between -10 °C and 40 °C based on the thermal and kinetic parameters found in self-heating basket experiments (Table 5.6).

When analysing the upscaling results for wheat biochar, shown in Fig. 5.12, a similar ignition trend to that of softwood is found for the biochar pellets produced at 450 °C. For a sample of the dimensions of even a standard domestic biomass storage unit (2.2 m cube height) will ignite from self-heating at ambient temperatures as low as 16 °C. Biochar produced at a reactor temperature of 550 °C would not ignite from self-heating in a container of the same size, nor an open top container for temperatures up to 40 °C. Similarly, feedstock would require a much larger critical size to ignite at temperatures below 40 °C. However, and quite differently than the result found for softwood, wheat biochar produced at 700 °C would be at risk of self-heating ignition in volumes the size of open top containers for temperatures around 38 °C.

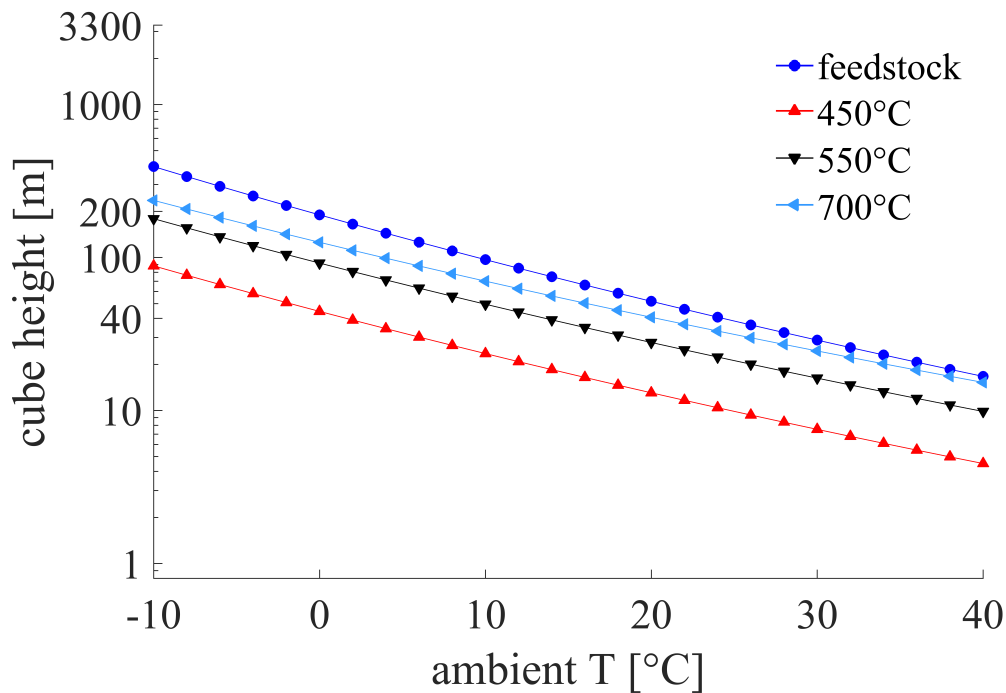


Figure 5.13: Upscaled results of cubic rice husk biomass and biochar piles required for self-ignition for ambient temperature between -10 °C and 40 °C based on the thermal and kinetic parameters found in self-heating basket experiments (Table 5.6).

The upscaling of the rice husk pile sizes (Fig. 5.13) shows that for all analysed samples, i.e. rice husk feedstock and biochar produced at reactor temperatures of 450 °C, 550 °C and 700 °C the required size for self-heating ignition is well above the threshold of both domestic size storage units and open top containers in the temperature range between -10 °C and 40 °C, meaning these samples are less prone to self-heating ignition in these typical environmental conditions and sizes with respect to both the softwood and wheat biomass and biochars.

5.4 Conclusions

Self-heating of torrefied biomass can cause fires and is a common problem associated with the transport, storage and handling of biomass. This study investigates experimentally and for the first time the self-heating and ignition conditions for torrefied biomass produced at 3 different pyrolysis reactor temperatures for softwood, wheat and rice husk torrefied biomass. The Frank-Kamenetskii theory of ignition criticality shows that a one-step global reaction mechanism applies for all these torrefied biomasses, as the linear fits to Frank-Kamenetskii plots all have $R^2 > 0.972$. It was shown that the torrefied biomass produced at a reactor temperature of 450 °C is the most prone to self-heating ignition regardless of the natural feedstock source. However different feedstock sources showed different proness to self-heating ignition. For the experimental laboratory bench-

scale studies the fuel most prone to self-heating ignition was softwood, but softwood and wheat showed very similar characteristics. The rice husk was shown to be overall less prone to self-heating ignition, with an upscaling analysis showing that at typical temperature ranges found in areas like power plant storage the required pile size of rice husk or one of its biochar products is well above what is found in standard domestic storage or open-top transport containers. A few key differences found between the wheat and softwood biochars is that wheat biochar produced at 700 °C is much more prone to self-heating ignition than its softwood counterpart.

The bench-scale experiments were extended to large scale systems to compare to real storage and transport sizes using the experimentally measured effective activation energies and thermal parameters. This shows that both wheat and softwood biochar produced at pyrolysis reactor temperatures of 450 °C are prone to self-heating ignition at ambient temperatures as low as 16 °C and 20 °C respectively, for dimensions as small as domestic biomass storage sizes. This chapter is the first in-depth experimental comparison of self-heating ignition of different biomasses and biochars as a function of both pyrolysis reactor temperature used for production and natural feedstock source. This work highlights the differences between torrefied biomass produced from rice husk, wheat pellets, or softwood pellets giving kinetic and thermal parameters that can be used to calculate safe sizes for transport and storage of softwood biomass and softwood biochars. The work shows that for fire safety and hazard assessment it is very important to know at what conditions biochar is produced in addition to its feedstock type as its proneness to self-heating ignition varies dramatically with biochar production temperature and that variation is dependent on the original biomass source, as the trends observed for a specific pyrolysis temperature change when analysing different feedstock sources.

Appendices

5.A Experimental data from self-heating ignition cubic basket experiments for softwood feedstock

Table 5.8: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood feedstock biomass pellets. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biomass basket being tested, ambient oven temperature, bulk density of the biomass, duration of experiment and if the sample ignited or not.

Date experiment was carried out	08/11/16	11/11/16	14/11/16	15/11/16	16/11/16	16/11/16
Volume of basket being tested (mL)	131	131	131	131	131	442
Oven reference temperature (°C)	166.0	184.9	200.5	194.6	163.8	170.0
Bulk density of fuel (kg/m ³)	534	531	530	527	573	583
Duration (s)	10435	20400	21405	28735	26225	57970
Ignition (Yes/No)	N	N	Y	N	N	N

Date experiment was carried out	23/11/16	24/11/16	06/12/16	07/12/16	08/12/16
Volume of basket being tested (mL)	442	442	1049	1049	1049
Oven reference temperature (°C)	183.7	180.1	165.1	168.5	171.2
Bulk density of fuel (kg/m ³)	583	588	626	626	626
Duration (s)	66495	68320	65790	62975	54290
Ignition (Yes/No)	Y	N	N	N	Y

5.B Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 450 °C

Table 5.9: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 450 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	06/12/16	06/12/16	07/12/16	07/12/16	07/12/16	07/12/16	08/12/16	08/12/16
Volume of basket being tested (mL)	131	131	131	131	131	131	131	131
Oven reference temperature (°C)	180.4	171.7	162.2	154.1	292	294	123.5	110.7
Bulk density of fuel (kg/m ³)	288	301	297	5830	5330	296	290	290
Duration (s)	3440	6110	3605	5830	5330	6600	7615	7615
Ignition (Yes/No)	Y	Y	Y	Y	Y	Y	Y	N

Date experiment was carried out	08/12/16	09/12/16	12/12/16	13/12/16	14/12/16	14/12/16	14/12/16	15/12/16
Volume of basket being tested (mL)	131	131	442	442	442	442	1049	1049
Oven reference temperature (°C)	116.1	120.1	107.5	116.1	110.2	96.2	100.6	100.6
Bulk density of fuel (kg/m ³)	297	301	334	333	333	368	367	367
Duration (s)	6055	11270	20720	11925	16910	64360	57960	57960
Ignition (Yes/No)	N	N	N	Y	Y	N	Y	Y

5.C Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 550 °C

Table 5.10: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 550 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	15/12/16	15/12/16	15/12/16	15/12/16	16/12/16	16/12/16	16/12/16	19/12/16	19/12/16	20/12/16
Volume of basket being tested (mL)	131	131	131	131	442	442	442	442	1049	1049
Oven reference temperature (°C)	128.5	142.1	152.2	147.1	135.6	125.5	130.3	120.4	125.5	
Bulk density of fuel (kg/m ³)	285	291	290	291	314	312	311	345	347	
Duration (s)	5215	4975	5380	4815	12740	11170	12685	52270	17520	
Ignition (Yes/No)	N	N	Y	Y	Y	N	N	N	N	Y

5.D Experimental data from self-heating ignition cubic basket experiments for softwood produced at reactor temperatures of 700 °C

Table 5.11: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood biochar pellets produced in a pyrolysis reactor at a temperature of 700 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	17/11/16	22/11/16	23/11/16	24/11/16	24/11/16	25/11/16	28/11/16
Volume of basket being tested (mL)	131	131	131	131	131	131	131
Oven reference temperature (°C)	161.2	170.3	183.7	189.0	199.2	207.6	217.0
Bulk density of fuel (kg/m ³)	281	272	271	274	273	269	281
Duration (s)	21570	16560	14345	6000	11085	10700	10980
Ignition (Yes/No)	N	N	N	N	N	N	Y

Date experiment was carried out	28/11/16	29/11/16	30/11/16	30/11/16	30/11/16	01/12/16	03/12/16
Volume of basket being tested (mL)	131	442	442	442	1049	1049	1049
Oven reference temperature (°C)	212.8	204.8	188.5	194.9	172.9	182.4	185.7
Bulk density of fuel (kg/m ³)	274	293	295	298	325	326	324
Duration (s)	10875	27305	26880	58205	19250	69185	16295
Ignition (Yes/No)	N	Y	N	Y	N	N	Y

5.E Experimental data from self-heating ignition cubic basket experiments for wheat feedstock biomass

Table 5.12: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of wheat feedstock biomass pellets. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biomass sample temperatures. The data reported includes the dates of experiments, volume of biomass basket being tested, ambient oven temperature, bulk density of the biomass, duration of experiment and if the sample ignited or not.

Date experiment was carried out	21/12/16	21/12/16	22/12/16	22/12/16	22/12/16	21/12/16	22/12/16	22/12/16	21/12/16	03/01/17	04/01/17	04/01/17	05/01/17
Volume of basket being tested (mL)	131	131	131	131	131	131	131	131	442	442	442	1049	1049
Oven reference temperature (°C)	171.7	190.7	182.2	178.1	158.5	168.9	174.0	164.0	157.0	157.0	157.0	157.0	157.0
Bulk density of fuel (kg/m ³)	384	391	391	388	423	423	424	457	450	450	450	450	450
Duration (s)	8715	6220	17655	9205	57735	55280	18495	49065	60460	60460	60460	60460	60460
Ignition (Yes/No)	N	Y	Y	N	N	N	Y	Y	N	N	Y	Y	N

5.F Experimental data from self-heating ignition cubic basket experiments for wheat produced at reactor temperatures of 450 °C

Table 5.13: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of wheat biochar pellets produced in a pyrolysis reactor at a temperature of 450 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	22/09/16	23/09/16	26/09/16	27/09/16	05/10/16	09/01/17
Volume of basket being tested (mL)	131	131	131	131	131	131
Oven reference temperature (°C)	170.1	158.6	149.4	140.3	132.5	135.9
Bulk density of fuel (kg/m ³)	212	212	210	210	213	232
Duration (s)	19245	12200	12425	23670	15900	4570
Ignition (Yes/No)	Y	Y	Y	Y	N	Y

Date experiment was carried out	17/10/16	18/10/16	19/10/16	27/10/16	02/11/16
Volume of basket being tested (mL)	442	442	442	1049	1049
Oven reference temperature (°C)	119.8	110.2	116.8	106.0	111.9
Bulk density of fuel (kg/m ³)	240	240	240	284	290
Duration (s)	65365	17620	14720	71710	26615
Ignition (Yes/No)	Y	N	N	N	Y

5.G Experimental data from self-heating ignition cubic basket experiments for wheat produced at reactor temperatures of 550 °C

Table 5.14: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of wheat biochar pellets produced in a pyrolysis reactor at a temperature of 550 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	20/10/16	20/10/16	26/10/16	01/11/16	31/10/16
Volume of basket being tested (mL)	131	131	131	131	442
Oven reference temperature (°C)	141.0	155.1	166.2	162.5	143.9
Bulk density of fuel (kg/m ³)	207	205	200	201	221
Duration (s)	11395	14245	29105	15820	24300
Ignition (Yes/No)	N	N	Y	Y	Y

Date experiment was carried out	03/11/16	04/11/16	07/11/16	09/11/16	10/11/16
Volume of basket being tested (mL)	442	442	1049	1049	1049
Oven reference temperature (°C)	134.2	140.1	122.9	137.5	131.8
Bulk density of fuel (kg/m ³)	223	219	244	256	256
Duration (s)	15855	14540	21235	63945	29765
Ignition (Yes/No)	N	N	N	Y	N

5.H Experimental data from self-heating ignition cubic basket experiments for wheat produced at reactor temperatures of 700 °C

Table 5.15: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of wheat biochar pellets produced in a pyrolysis reactor at a temperature of 700 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	15/09/16	16/09/16	19/09/16	20/09/16	21/09/16	03/10/16	06/10/16	12/10/16
Volume of basket being tested (mL)	131	131	442	442	442	1049	1049	1049
Oven reference temperature (°C)	175.5	181.5	162.5	152.9	157.8	134.1	143.3	150.6
Bulk density of fuel (kg/m ³)	254	256	263	259	262	293	295	305
Duration (s)	11735	18090	28645	21210	36205	62705	62985	56275
Ignition (Yes/No)	N	Y	Y	N	Y	N	N	Y

5.I Experimental data from self-heating ignition cubic basket experiments for rice husk feedstock biomass

Table 5.16: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of rice husk biomass feedstock. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biomass sample temperatures. The data reported includes the dates of experiments, volume of biomass basket being tested, ambient oven temperature, bulk density of the biomass, duration of experiment and if the sample ignited or not.

Date experiment was carried out		20/12/16		20/12/16		02/01/17		02/01/17		02/01/17		02/01/17	
Volume of basket being tested (mL)		131	131	131	131	131	131	131	131	131	131	131	131
Oven reference temperature (°C)		155.0	173.2	182.9	201.0	211.2	220.2	211.2	211.2	211.2	211.2	211.2	220.2
Bulk density of fuel (kg/m ³)		108	106	111	113	109	112	109	109	109	109	109	112
Duration (s)		5610	6275	6050	4825	7690	3870	7690	7690	7690	7690	7690	3870
Ignition (Yes/No)		N	N	N	N	N	N	N	N	N	N	N	Y
Date experiment was carried out		03/01/17		03/01/17		03/01/17		04/01/17		05/01/17		06/01/17	
Volume of basket being tested (mL)		131	442	442	442	442	1049	442	442	1049	1049	1049	1049
Oven reference temperature (°C)		215.1	201.3	191.5	196.5	180.2	185.1	196.5	196.5	180.2	185.1	185.1	185.1
Bulk density of fuel (kg/m ³)		111	113	113	113	113	119	113	113	118	118	118	119
Duration (s)		6230	8260	7600	10575	22015	24125	10575	10575	22015	24125	24125	24125
Ignition (Yes/No)		Y	Y	N	Y	N	Y	Y	Y	N	N	Y	Y

5.J Experimental data from self-heating ignition cubic basket experiments for rice husk produced at reactor temperatures of 450 °C

Table 5.17: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of rice husk biochar produced in a pyrolysis reactor at a temperature of 450 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	17/10/60	09/01/17	09/01/17	17/10/60	09/01/17	17/10/60	17/10/17	10/01/17	17/10/17	17/10/17	10/01/17	17/10/17	17/10/17	17/10/17
Volume of basket being tested (mL)	131	131	131	131	131	131	131	131	131	131	131	131	131	131
Oven reference temperature (°C)	153.1	170.9	162.0	162.0	165.1	153.1	153.1	162.5	156.0	143.9	1049	1049	1049	1049
Bulk density of fuel (kg/m ³)	83	82	82	82	81	83	83	83	83	99	93	93	93	93
Duration (s)	3360	2645	13900	13900	3835	10535	9520	8650	54535	58015				
Ignition (Yes/No)	N	Y	N	N	N	N	N	Y	Y	Y	Y	Y	Y	N

5.K Experimental data from self-heating ignition cubic basket experiments for rice husk produced at reactor temperatures of 550 °C

Table 5.18: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of rice husk biochar produced in a pyrolysis reactor at a temperature of 550 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out									
Volume of basket being tested (mL)	131	131	131	131	131	131	131	131	131
Oven reference temperature (°C)	162.8	181.1	198.6	208.7	216.4	211.7			
Bulk density of fuel (kg/m³)	76	75	81	74	79	76			
Duration (s)	4245	2895	3135	2940	3190	2070			
Ignition (Yes/No)	N	N	N	N	Y	Y			Y
Date experiment was carried out									
Volume of basket being tested (mL)	442	442	442	1049	1049				
Oven reference temperature (°C)	198.5	190.0	193.4	179.9	174.7				
Bulk density of fuel (kg/m³)	81	82	82	97	92				
Duration (s)	5340	14120	10530	49880	21915				
Ignition (Yes/No)	Y	N	Y	Y	N				

5.L Experimental data from self-heating ignition cubic basket experiments for rice husk produced at reactor temperatures of 700 °C

Table 5.19: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of rice husk biochar produced in a pyrolysis reactor at a temperature of 700 °C. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biochar basket being tested, ambient oven temperature, bulk density of the biochar, duration of experiment and if the sample ignited or not.

Date experiment was carried out	16/01/17	16/01/17	16/01/17	16/01/17	16/01/17	16/01/17	17/01/17
Volume of basket being tested (mL)	131	131	131	131	131	131	131
Oven reference temperature (°C)	217.3	227.9	237.3	244.0	253.7	250.5	
Bulk density of fuel (kg/m ³)	98	92	96	94	98	92	
Duration (s)	3495	3075	7310	4010	2480	3005	
Ignition (Yes/No)	N	N	N	N	Y	N	N

Date experiment was carried out	17/01/17	17/01/17	17/01/17	17/01/17	17/01/17	18/01/17	19/01/17
Volume of basket being tested (mL)	442	442	442	1049	1049	1049	1049
Oven reference temperature (°C)	235.0	227.1	231.0	218.4	214.8	208.0	
Bulk density of fuel (kg/m ³)	98	101	99	114	109	114	
Duration (s)	4245	11555	5460	57515	24660	60060	
Ignition (Yes/No)	Y	N	Y	Y	Y	N	N

Chapter 6

Particle size effect on self-heating ignition of biomass

Summary¹

Biomass might become an important fuel source for future power generation worldwide. However safety considerations and fire hazards need to take into account the different ignition behaviour of this new fuel source because biomass piles are prone to self-heating and can lead to fires. When storing and transporting biomass, it is usually in the form of pellets which vary in diameter but are usually desired to be in the order of 7 mm for power generation. However, pellets tend to break up into smaller particles below 2 mm in diameter and even into dust down to the μm size, therefore the particles present in the pile of a storage silo or transport containers can vary from mm to μm . For self-heating, size of particles matters but the topic is poorly studied. Studies of self-heating ignition of biomass in literature each have a different size, and so it is not possible to understand the effect of size range. This chapter experimentally studies for the first time the self-heating ignition properties of 4 different particle sizes of the same biomass, wheat, in the range from 6.5 mm diameter to 300 μm . Experiments are done in an isothermal oven to find minimum ignition temperatures as a function of sample size, like for the work in Ch 2-5, and the experimental results are analysed using Frank-Kamenetskii theory. The results show increasing self-heating ignition as the particle size decreases. Dust is more prone to self-heating ignition, and for an environmental temperature of 40 °C ignites for a cubic pile of length 12.35 m, compared to 41.55 m length pile required for coarse particles. This chapter demonstrates that particle size is an important property for biomass self-heating ignition, and quantifies thermal and kinetic parameters for different sizes of wheat. It shows that the size of particles needs to be carefully considered.

1. This chapter is based on “F. Restuccia, N. Fernandez-Anez, G. Rein (2017) *Particle size effect on self-heating ignition of biomass*, **Proceedings of the Combustion Institute 2018** (submitted).”

6.1 Introduction

In the current era, different fuel options are being studied to shift away from the traditional fossil fuel energy market. This is driven by a need to reduce carbon emissions. Fossil fuels emit carbon-compound gases that increase the global greenhouse effect and decrease the quality of air. The need to decrease these carbon emissions has brought on the development of many protocols and regulations worldwide. The European Union member states are working towards 2020 targets, which established that by the year 2020 greenhouse gas emissions should be reduced by 20%, renewable energy should represent 20% of the European final energy consumption, and energy efficiency should increase by 20% [16]. In this scenario, the role of biomass as an alternative energy source becomes crucial to achieve these targets.

Biomass presents properties that require extensive characterisation Because of its natural origin and considerable variation with source. One of the fuel characteristics that is particularly important for safety and fire hazards is the ignition tendency of the materials. Most of these fuels come in bulk, but produce particles of many sizes all the way down to dust by abrasion or friction during their handling. The effect of small particles and dust has to be taken into account as their behaviour can be considerably different from that of large particles. The demarcation from small particle to dust size is not well defined, but in practice any solid particle with a particle diameter of less than 500 μm is considered dust [8].

The physical and chemical characteristics of the sample can impact the tendency of the material to ignite. Focusing on particle size, some work has been done on the flammability of several solid fuels studying its influence on the minimum explosion concentration, minimum ignition energy and minimum ignition temperature [105, 106]. However none of this work focused on self-heating ignition.

One of the most dangerous processes associated with dust and pellet stockpiles is the risk of fires. These fires can be caused by self-heating ignition. Self-heating ignition is defined as the tendency a porous solid fuel has to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures [1, 31]. Knowledge of the tendency of materials to self-ignite is essential to power plants that handle, store, or process biomass resources [89]. Critical conditions for self-heating in stored bulk materials could be determined with laboratory-scale methods such as adiabatic calorimetry, hot plate experiments and isothermal oven tests as seen in literature [31, 46, 107, 108] and in Ch 2-5. The influence of particle size on the storage of materials has to consider the following two countering properties: When the particle size increases, the gaps between the particles with oxidizer present increase, so self-heating ignition becomes easier since oxidation is promoted. But on the other hand, air is less conductive than the material, decreasing the heat transfer and therefore the chance of self-heating ignition [109].

For self-heating, the reactivity of coal is proportional to the average surface area to

volume ratio of the sample, A/V , with a decreasing particle size corresponding to an increase in the reactivity and propensity to self-heating ignition [18, 61]. As biomass comes in different sizes and shapes, the existing literature on self-heating ignition of biomass is not carried out at one uniform size. It is often assumed that the particle size plays an important role on self-heating ignition conditions, but there is no experimental quantification of this influence in the literature. Some work has been previously carried out to determine the self-heating ignition characteristics of biomass with constant particle size [46, 89, 92, 110]. This chapter aims to fill these literature gaps by experimentally studying for the first time the self-heating ignition properties of 4 different particle size ranges to quantify the different self-heating characteristics of wheat biomass with varying particle size.

6.2 Experimental methodology

To carry out this experimental work on self-heating ignition we use wheat biomass particles. The reason for choosing wheat biomass is that I have carried out extensive work with wheat biomass in Ch 5, and therefore have detailed elemental and physical parameters such as the thermal conductivity which allow the extraction of more thermal and kinetic parameters from the experimental data reported in this chapter. The biomass was in the form of pellets made of compressed wheat with varying sizes between 2.6 mm diameter and 6.5 mm diameter. The pellets were grinded using a hand blender and separated into different size distributions using mechanical sieves. A series of 4 particle size distributions was produced based on particle diameter. The first was made of unground pellets, of diameter between 6.5 mm and 2.6 mm (coarse particles). The second were particles with a diameter distribution between 2.6 mm and 2 mm (medium particles), the third between 2 mm and 1 mm (fine particles), and the fourth between 1 mm and 300 μm (dust). These distributions span all particle sizes from pellet size all the way down to dust size. These sample distribution sets are presented in Fig. 6.1. Elemental analysis was already carried out for the wheat in Ch 5, and resulted in 42.66% C, 6.20% H, and 0.39% N.

These particle size distributions were individually tested to determine the minimum critical ambient temperature for self-heating, $T_{a,c}$, that leads to self-ignition for each distribution. A laboratory setup was constructed following the procedure described in Ch 1, section 1.4. At least two experiments were conducted at each particle size and basket size condition. This experimental setup is the same as the one used in Ch 2-5. A summary of the experiments carried out is presented in Table 6.1.

The bulk density found when using these materials in basket experiments for the different particle size distributions is presented in Fig. 6.2. It is clear from the figure that the loose particles all have very similar bulk densities, while the pellets have a higher density, due to the fact that they are produced by compressing wheat. Furthermore, the

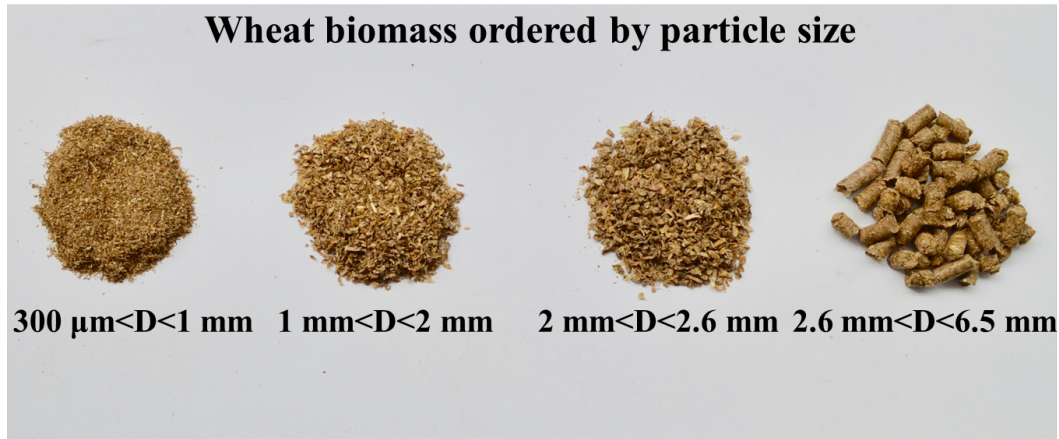


Figure 6.1: Different sized wheat biomass, ordered by increasing particle size.

Table 6.1: Number of experiments carried out for each particle distribution range of wheat biomass.

particle distribution size	Basket length	
	5.1 cm	7.6 cm
Pellets, 2.6 mm < D < 6.5 mm	2	2
2 mm < D < 2.6 mm	2	2
1 mm < D < 2 mm	3	3
300 μm < D < 1 mm	3	2

thermal conductivity of the wheat pellets was already measured in Ch 5 and was found to be 0.1715 W/mK at 165 °C. The temperature chosen for the conductivity value is based on the range of temperatures measured in this experimental work. Furthermore, previous work has shown that thermal conductivity differences are less than 10 % between coarse and fine particles of biomass [111], so this measured value was used for all the particle size distributions.

6.3 Results

Given the same ambient reference temperature, different particles will ignite or not ignite from self-heating depending on the particle size distributions. This is highlighted in Fig. 6.3, where given the same oven reference temperature of 183.7 °C the finest particles, with particle size 300 μm < D < 1 mm, shown by the red curve undergo thermal runaway and ignite while the larger particles, with size 2.6 mm < D < 6.5 mm, will not reach thermal runaway as can be seen by the blue curve in the figure.

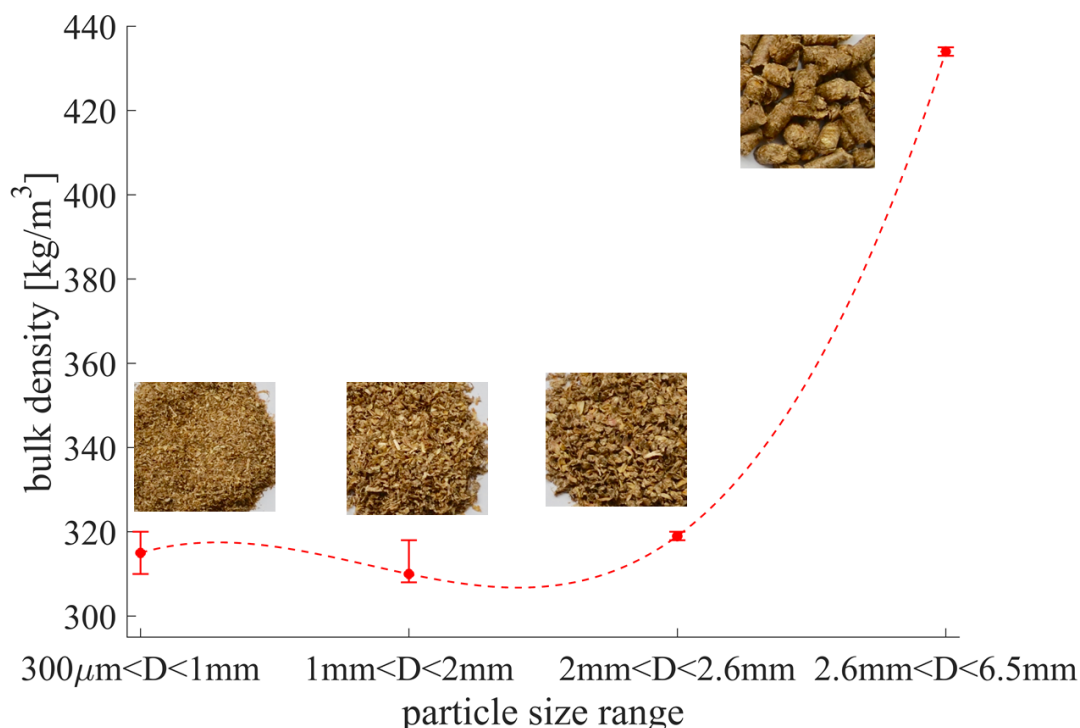


Figure 6.2: Density of the different sized wheat biomass particles, ordered by increasing particle size, with a trendline to show increasing density at pellet sized particle distributions.

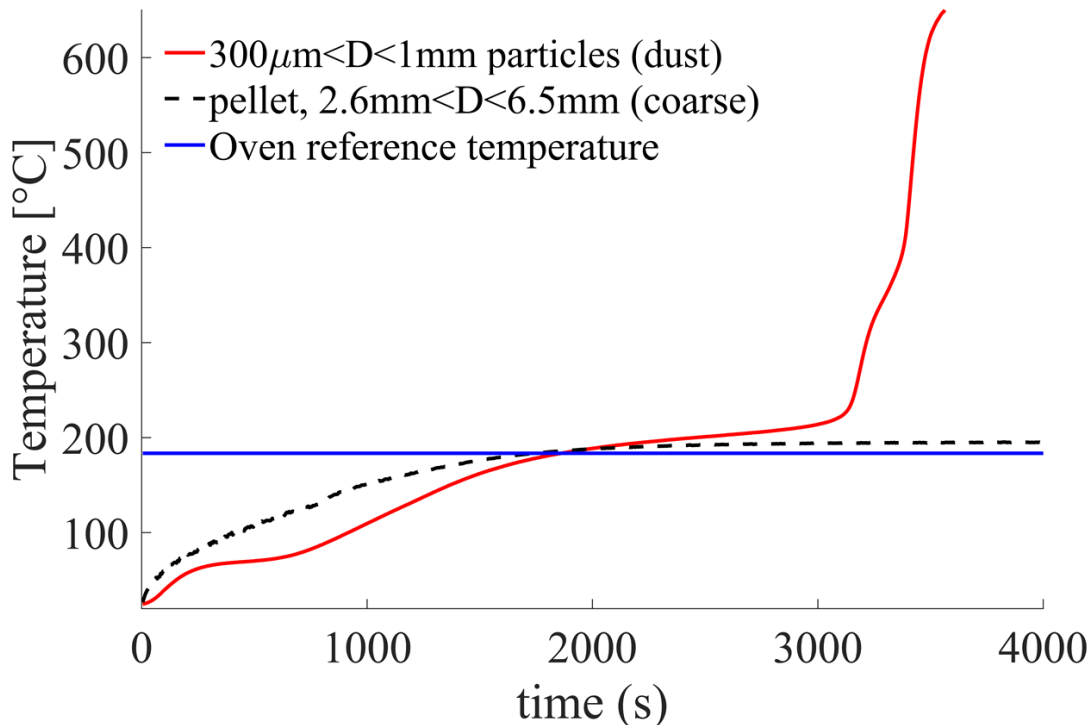


Figure 6.3: A comparison of ignition vs no ignition for two samples tested in 5.08 cm length baskets made up of samples of different particle size distributions placed in the same oven environment of 183.7 °C. The basket with particles in the $300\mu\text{m} < D < 1\text{mm}$ particle size range ignite due to self-heating, and is clear from the thermal runaway seen on the red line. The particles in the pellet size range ($2.6\text{mm} < D < 6.5\text{mm}$) however do not ignite, and no thermal runaway is seen.

Results from all the basket experiments are summarised in Fig. 6.4. The minimum ignition temperature required for ignition decreased with decreasing particle size. This trend applied to all the 4 distributions studied, with the pellet size ($2.6 \text{ mm} < D < 6.5 \text{ mm}$) and $2 \text{ mm} < D < 2.6 \text{ mm}$ particles igniting from self-heating at the same temperatures. The pellet has higher density, as shown earlier in Fig. 6.2, so this increase in fuel present per given volume might be offsetting the effect of decreasing particle size. However for $1 \text{ mm} < D < 2 \text{ mm}$ particles there is a clear decrease in ignition temperature, and an even more significant drop in temperature required for ignition for the particles in the $300 \mu\text{m} < D < 1 \text{ mm}$ particle size distribution. For this size distribution, the smallest being tested, at volumes of 442 cm^3 there is a $6.3 \text{ }^\circ\text{C}$ difference in the minimum ignition temperature with respect to the $2.6 \text{ mm} < D < 6.5 \text{ mm}$ sized wheat pellets. This is 52 % greater than the maximum uncertainties in measurement, showing it is indeed a particle size effect, and not experimental error.

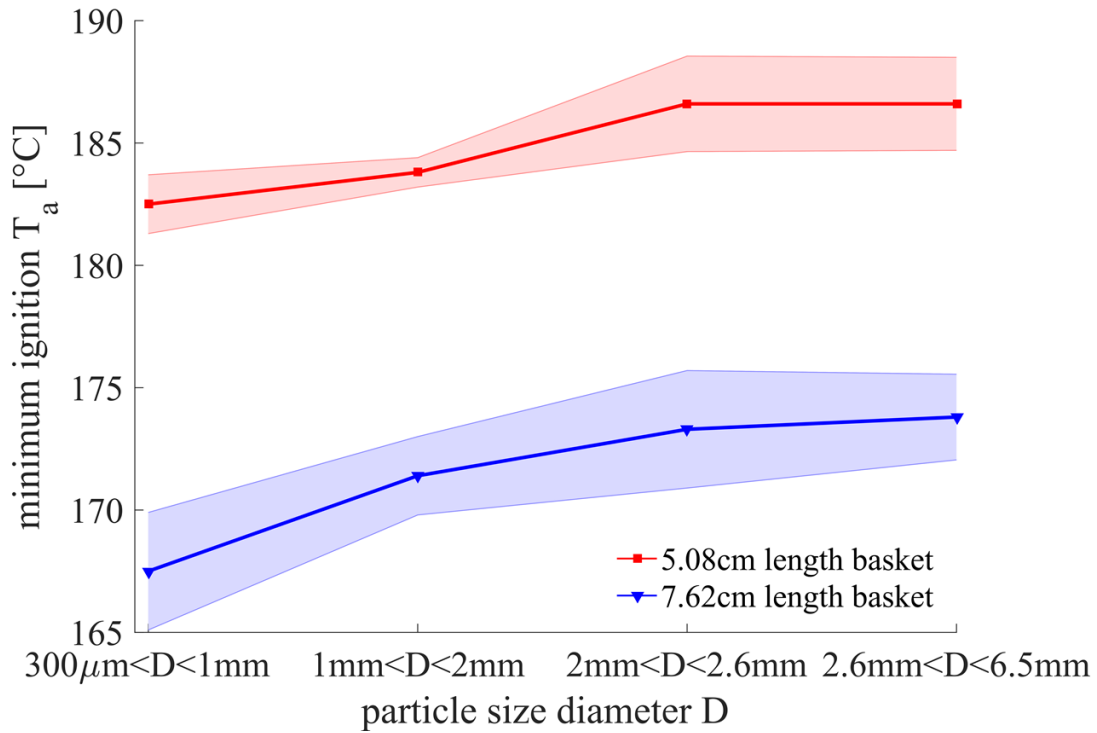


Figure 6.4: The experimentally found minimum ignition temperatures plotted with respect to the four studied particle size distributions, with separate lines for the two different box sizes.

6.4 Frank-Kamenetskii analysis

Using Frank-kamenetskii analysis, presented in Ch 1, section 1.2, I plotted the critical ignition temperatures for the two basket sizes found for the experiments in all four particle size distributions tested in a $\ln(\delta_c T_{a,c}/L^2)$ vs $1/T_{a,c}$ plot. For this wheat biomass, Arrhenius reaction was shown to be a valid approximation in Ch. 5, Table 5.5, where a

R^2 value of 0.972 was found for the wheat feedstock pellets. The slope of the straight line through the critical ignition temperatures and sizes of different sized boxes, for the same particle size distribution, corresponds to $-E/R$; The y-intercept can be used to obtain Qf . The plot is shown in Fig. 6.5. From this figure, it can be seen that the pellets, $2.6 \text{ mm} < D < 6.5 \text{ mm}$, and the 2nd largest particles ($2 \text{ mm} < D < 2.6 \text{ mm}$) have almost identical slopes and almost overlap completely. The smallest particle sizes however have a distinct behaviour and are at the right hand side of the plot.

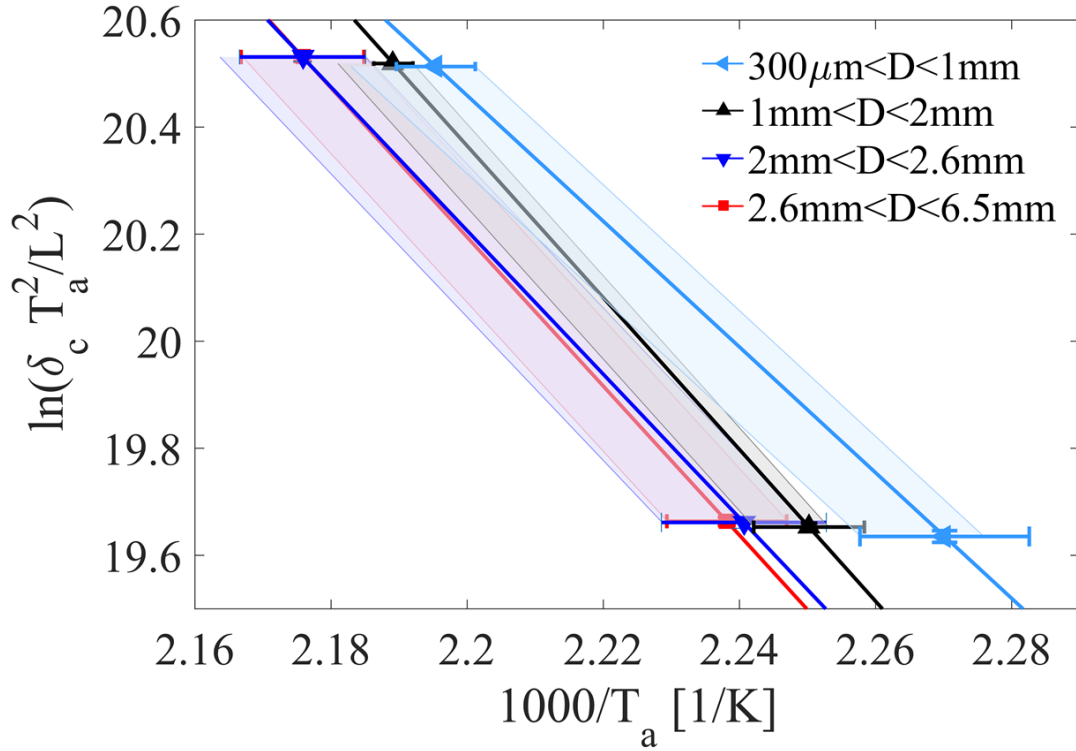


Figure 6.5: Frank-Kamenetskii plot of self-heating ignition properties for the four wheat biomass particle size distributions.

Effective activation energies and pre-exponential factors were extracted using the Frank-Kamenetskii theory and the experimental data, and are presented in Table 6.2. Although the upper and lower bounds for activation energies are large, due to the worst-case calculation of errors based on the upper and lower experimental bounds on each basket size measurement from Fig. 6.5, several trends are observed. The first three distributions, $2.6 \text{ mm} < D < 6.5 \text{ mm}$, $2 \text{ mm} < D < 2.6 \text{ mm}$ and $1 \text{ mm} < D < 2 \text{ mm}$ have similar activation energies ranging between 111.5 kJ/mol and 117.9 kJ/mol. However the finest particles going to dust size, $300 \text{ } \mu\text{m} < D < 1 \text{ mm}$, have a significantly lower activation energy at 97.6 kJ/mol.

The thermal and kinetic parameters were used to upscale the results to ambient temperatures closer to what is typically found in the environment, between 10 °C and 40 °C for the four particle sizes studied in this experimental campaign and is shown in Fig. 6.6. The results of the upscaling show that the smallest particles are considerably more

Table 6.2: Effective activation energy E and pre-exponential factor Qf extracted from Frank-Kamenestkii plot (Fig. 6.5) calculated using Eq. (1.3). The values in parenthesis are lower and upper bounds of activation energy and pre-exponential factors from error analysis

Particle distribution size	E (kJ/mol)	$\ln(Qf)$ (W/m^3)
Pellets, 2.6 mm<D<6.5 mm	115.7 (88.39,164.82)	$1.44 \cdot 10^{17}$ ($1.33 \cdot 10^{14}$, $4.65 \cdot 10^{22}$)
2 mm<D<2.6 mm	111.5 (82.1,169.6)	$4.98 \cdot 10^{16}$ ($2.76 \cdot 10^{13}$, $1.58 \cdot 10^{23}$)
1 mm<D<2 mm	117.9 (98.8,145.3)	$2.97 \cdot 10^{17}$ ($2.76 \cdot 10^{13}$, $3.43 \cdot 10^{20}$)
300 μm <D<1 mm	97.6 (77.1,131.2)	$1.86 \cdot 10^{15}$ ($9.75 \cdot 10^{12}$, $1.08 \cdot 10^{19}$)

prone to self-heating ignition at ambient temperatures than the pellet sized particles. The coarse, medium and fine particles, not down to the smallest particle size, all show similar sizes required for ignition, and this is due to their effective activation energies being very similar. The results show that for dust particle size (300 μm <D<1 mm), the required size for self-heating ignition at a given temperature is about 4 times smaller than for the other particle sizes studied. For the smallest particles the critical length required for self-heating ignition, at 40 °C, is of 12.35 m. For the coarse particles, a 41.55 m tall pile would be required for self-heating ignition at the same temperature. Attention must be paid to dealing with storage of finer particles, as 12.35 m height is considerably higher than what is found in domestic storage areas, but can be found in situations like silo storage for example. This shows that for determining risk and propensity of self-ignition for biomass, particle size present is very important and must be considered.

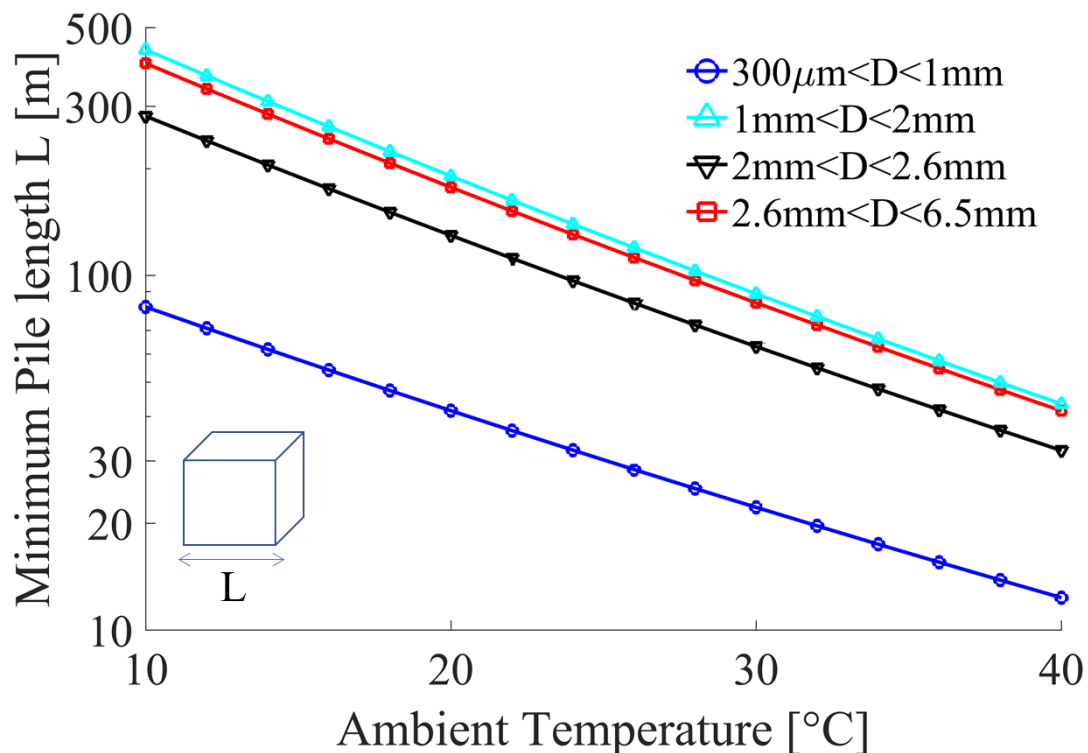


Figure 6.6: Upscaling the thermal properties and kinetics derived from the self-heating ignition basket experiments to larger scale sizes for the four particle size distributions. The upscaling is based on the parameters presented in Table 6.2.

6.5 Conclusions

Biomass comes in bulk form, but can erode into smaller particle sizes, down to dust size below $500 \mu\text{m}$. It is prone to self-heating ignition, and understanding the conditions required for it to ignite is fundamental. Extensive work exists on the study of different effects of size below the dust threshold ($500 \mu\text{m}$). However this is the first set of experimental work quantifying the effects of particle size on biomass self-heating ignition, from pellet size down to dust size. This study investigates experimentally the effect of particle diameter size on self-heating and ignition conditions for biomass using isothermal oven self-heating basket experiments. Previous work present in literature on coal ignition has shown that a decrease in particle size corresponds to an increase in reactivity and propensity to self-heating ignition. We show that this is true for biomass as well, where for a given volume, the critical temperature for self-heating ignition decreases with particle size. In fact, particle size has a large effect on reactivity, with the finest particles in the size distribution between $300 \mu\text{m}$ and 1 mm being more reactive than coarse pellets of diameter between 2.6 mm and 6.5 mm and presenting a smaller effective activation energy of 97.6 kJ/mol compared to 115.7 kJ/mol . This chapter shows that particles of size distribution between $300 \mu\text{m}$ and 1 mm ignite due to self-heating at significantly lower temperature and critical length in respect to the other 3 larger sizes studied.

This chapter provides the first experimental quantification of the varying self-heating conditions for wheat biomass as a function of particle size. The kinetic and thermal parameters found for different particle sizes and how that affects self-heating ignition contributes to understanding and predicting the onset of fires in biomass storage and handling, which is an important problem especially for the energy industry.

Appendices

6.A Experimental data from self-heating ignition cubic basket experiments for particle size effect measurement

Table 6.3: This table contains a complete set of experimental data from self-heating ignition cubic basket experiments of softwood feedstock biomass pellets. The experiments were carried out in a thermostatically controlled oven with thermocouples for measuring the ambient and biochar sample temperatures. The data reported includes the dates of experiments, volume of biomass basket being tested, ambient oven temperature, bulk density of the biomass, duration of experiment and if the sample ignited or not.

Particle size measured		2.6mm < D < 6.5mm	2.6mm < D < 6.5mm	2.6mm < D < 6.5mm	2.6mm < D < 6.5mm	2.6mm < D < 6.5mm	2mm < D < 2.6mm	2mm < D < 2.6mm	2mm < D < 2.6mm	1mm < D < 2mm	1mm < D < 2mm
Volume of basket being tested (mL)		131	131	442	442	442	131	131	442	442	131
Oven reference temperature (°C)		188.5	184.7	175.5	172	188.5	184.6	175.7	170.9	183.2	186.6
Bulk density of fuel (kg/m ³)		435	434	433	434	320	320	318	318	308	318
Duration (s)		2930	5795	5885	7175	2900	3780	6595	6815	4390	4245
Ignition (Yes/No)		Y	N	Y	N	Y	N	Y	N	N	Y
Date experiment was carried out		1mm < D < 2mm	1mm < D < 2mm	1mm < D < 2mm	1mm < D < 2mm	300µm < D < 1mm	300µm < D < 1mm	300µm < D < 1mm	300µm < D < 1mm	300µm < D < 1mm	300µm < D < 1mm
Volume of basket being tested (mL)		131	442	442	442	131	131	131	442	442	442
Oven reference temperature (°C)		184.4	174.4	169.8	173.0	183.7	178.5	181.3	169.9	165.1	
Bulk density of fuel (kg/m ³)		309	308	306	309	318	318	320	312	310	
Duration (s)		6525	7655	8730	7495	4035	4440	4200	8080	8245	
Ignition (Yes/No)		Y	Y	N	Y	Y	N	N	Y	N	

Chapter 7

Conclusions

7.1 Outcomes of the present research

Ignition of various reactive porous media due to low-temperature oxidation often leads to fires and safety hazards. The work in this thesis focused on quantifying self-heating ignition risks and properties, and quantifying the chemical kinetics and thermal properties of natural fuels such as shale, natural carbon-rich soils such as peat, and biochars from wheat, rice husks and softwood. I have focused on the effect of three main physical parameters: the origin of the reactive natural fuel, the particle size of the fuel and the carbon and inorganic contents. All work carried out in this thesis utilised the oven basket methodology presented in Ch. 1 to obtain experimental data, with over the duration of this thesis required a total of 287 oven basket experiments requiring 1705 hours of oven run time. The results showed some similarities and trends, summarised in Fig 7.1.

Activation energy vs carbon content is presented in Table 7.1 and Fig 7.1. From Fig 7.1 a few trends are clear. Higher carbon content results in a material more prone to self-heating ignition, as it has a lower effective activation energy. Low carbon content results in a material less prone to self-heating ignition. For both materials with high carbon content, such as biomass, and materials with a lower carbon content such as shale, the effective activation energy of a material is highly dependent on particle size, where an increase in particle size brings a sharp increase in effective activation energy. For the same material, this results in a material much more prone to self-heating ignition with decreasing particle size, as can be seen for the shale and wheat particles (circled with a dotted line). For the high carbon content materials, specifically biomass and biochar, the results closely match with the activation energy values found in literature, where biomass such as poplar wood, almond shell, wheat straw dust, aromatic plant waste, mesquite, sunflower husks and olive pits were found to have activation energies between 60 and 82 kJ/mol [46, 92]. In this thesis, the values for biomass and biochar were found to range from 67 to 120 kJ/mol, but the biomass studied was in pellet form and therefore has a higher activation energy than the dust and small particles studied in the literature. For

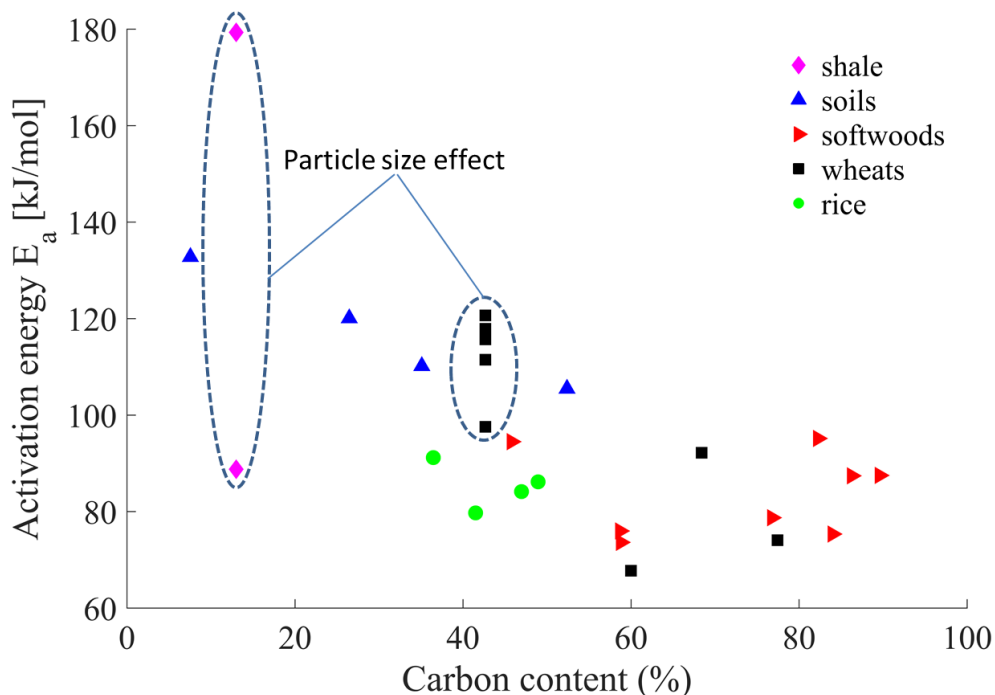


Figure 7.1: Effective activation energies for materials studied in thesis based on carbon content from self-heating experiment results. Information on each specific point can be found in Table 7.1.

lower carbon content materials, such as shale, the resulting activation energies for large sized particles, 179 kJ/mol, are much higher than the values found for coal dust in the literature, which typically range between 50 and 90 kJ/mol [19,20,23,24]. The shale rocks have a carbon content of only 13 % compared to the 60 to 80% found in coal. However the fine sized shale particles, with an activation energy of 89 kJ/mol, are comparable to those found in coal.

Several important conclusions arise from the work presented in this thesis. I experimentally investigated, for the first time in literature, the self-heating and ignition conditions for shale rock at various ambient temperatures and for different particle diameter sizes. I proposed enhanced experimental diagnostics for identification of self-heating ignition by adding two novel diagnostic tools valuable for studying samples of high inert content. This work contributes to understanding and predicting the onset of shale formation fires, which have been observed in nature. It was shown that particle size has a large effect on reactivity, with fine particles being more reactive than coarse particles and presenting a smaller effective activation energy of 88.79 kJ/mol compared to 179.36 kJ/mol, differing by almost a factor of two. This work goes on to show that the shale rock geological deposit (or mining pile) thickness required for ignition varies dramatically with shale particle size. For fine particles with size distribution below 2 mm, at 22 °C, ignition is possible for a thickness of 35 m. For coarse particles, which include particles up to 1.7 cm diameter, for the same temperature, a thickness of 358 km is required for ignition.

Table 7.1: Summary of effective activation energies found for different materials throughout this thesis.

Material	E_a kJ/mol	Carbon content %
Shale coarse	179.4	13
Shale fine	88.8	13
Soil 3% IC	105.5	52.4
Soil 35% IC	110.2	35.1
Soil 51% IC	120.1	26.5
Soil 86% IC	132.8	7.6
Softwood feedstock	94.5	45.8
Softwood biochar produced at $T_r = 350^\circ\text{C}$	73.7	58.8
Softwood biochar produced at $T_r = 400^\circ\text{C}$	76.0	58.7
Softwood biochar produced at $T_r = 450^\circ\text{C}$	78.8	76.8
Softwood biochar produced at $T_r = 550^\circ\text{C}$	95.2	82.3
Softwood biochar produced at $T_r = 600^\circ\text{C}$	75.4	84.0
Softwood biochar produced at $T_r = 700^\circ\text{C}$	87.4	86.3
Softwood biochar produced at $T_r = 800^\circ\text{C}$	87.5	89.6
Wheat feedstock	120.7	42.7
Wheat biochar produced at $T_r = 450^\circ\text{C}$	67.8	60.0
Wheat biochar produced at $T_r = 550^\circ\text{C}$	92.2	68.4
Wheat biochar produced at $T_r = 700^\circ\text{C}$	74.1	77.4
Rice husk feedstock	91.2	36.5
Rice husk biochar produced at $T_r = 350^\circ\text{C}$	86.2	48.9
Rice husk biochar produced at $T_r = 450^\circ\text{C}$	84.2	47.0
Rice husk biochar produced at $T_r = 550^\circ\text{C}$	79.8	41.5
Rice husk biochar produced at $T_r = 700^\circ\text{C}$	74.1	77.4
Wheat, 2.6 mm $<D< 6.5$ mm	115.7	42.7
Wheat, 2.0 mm $<D< 2.6$ mm	111.5	42.7
Wheat, 1 mm $<D< 2$ mm	117.9	42.7
Wheat, 300 μm $<D< 1$ mm	97.6	42.7

Spontaneous ignition is possible for rock deposits of thickness between 10.7 m and 607 m for fine particles. These are all shale thickness sizes that can be found in natural geological deposits, present throughout the world, which are up to 600 m in thickness [44]. For the coarse particles in the same temperature range, the required thickness is between 30 km and 100,000 km, which is a range of sizes much greater than the natural geological deposits found on Earth. This work is presented in Chapter 2.

Having shown that particle size is an important parameter for shale, I then focused on quantifying the effect of particle size diameter on self-heating ignition for biomass

using isothermal oven experiments. This was carried out for wheat in four particle size distributions between 300 μm and 7 mm, corresponding to a range from dust to typical biomass pellet size. using four different particle size distributions. I show that for a given volume, the critical temperature for self-heating ignition decreases with particle size. In fact, particle size has a large effect on reactivity, with the finest particles in the size distribution between 300 μm and 1 mm being more reactive than coarse pellets of diameter between 2.6 mm and 6.5 mm and presenting a smaller effective activation energy of 97.6 kJ/mol compared to 115.7 kJ/mol. This was the first experimental quantification of the changing self-heating conditions for wheat biomass as a function of particle size, contributing to the understanding of fires in biomass storage and handling, which is an important problem especially for the energy industry. This work is presented in Chapter 6.

This thesis aimed to quantify the effect of inorganic content on self-heating ignition. This was done by carrying out bench-scale experiments to determine the self-ignition criteria for soil samples with different inorganic content (IC) values. The experiments predict and quantify the environmental temperature conditions necessary for the onset of smouldering fires in carbon-rich soil systems such as histosols or gelisols. Experimental results show that as the IC in the soil increases, the critical ambient temperature for self-ignition increases. Using the Frank-Kamenetskii theory, it is found that the effective activation energy for the soil increases from 105 kJ/mol to 133 kJ/mol as IC increases from 3% to 86%, indicating a significant reduction in reactivity and ignitability. I report a clear increase in the ambient temperature required for ignition as the IC increases. By upscaling the bench-scale experiments to natural ecosystem sizes, the minimum ambient temperature and soil layer thickness for self-heating ignition are predicted. For a 50 m thick soil layer, the minimum ambient temperature is estimated to be as low as 14 °C for IC=3%, but as high as 50 °C for IC=86%. The maximum IC possible for self-ignition at 40 °C for the maximum natural thickness of peat, 50 m, was estimated to be 68%. Wildfires in carbon-rich ecosystems are a hazard, and determining the ignition conditions is important. This chapter is the first in-depth experimental quantification of self-heating ignition of soil, showing that it is indeed possible that wildfires are initiated by self-heating of some soil types at the right conditions. This work is presented in Chapter 3.

The final area of focus in the thesis was the determination of the effect of pyrolysis reactor temperature used in the production of biochar on the propensity of the material to ignite because of self-heating. This was quantified by pyrolyzing softwood at seven different pyrolysis reactor temperatures and then basket experiments, thermogravimetric analysis and physical parameter measurements were carried out for each biochar product as well as the original softwood feedstock. This thesis shows that the reactivity of softwood torrefied biomass and biochar is not a monotonic function of pyrolysis reactor temperature. In fact, results show that biochar produced at a reactor temperature of 450 °C is the most prone to self-heating, and that the reactivity of the softwood increases

with reactor temperatures up to 450 °C but then significantly decreases and, for reactor temperatures above 550 °C, the softwood is less reactive than the feedstock. TGA data showed that for pyrolysis reactor temperatures below 450 °C the mass loss rate peaks occurred at different temperatures than for reactor temperatures above that temperature threshold. Furthermore, for reactor temperatures above 450 °C, the mass loss rate peaks are all located in the same temperature range around 500 °C, but with each peak decreasing in magnitude with increasing pyrolysis reactor temperature due to less carbon elements remaining in the solid phase. Thermal conductivity measurements of the different biochars also show that the least conductive of the softwoods is the one produced at a reactor temperature of 450 °C, while the feedstock softwood is the most thermally conductive. This work is presented in Chapter 4.

The quantification of pyrolysis reactor temperature was extended to other forms of biomass, and an experimental comparison of the self-heating ignition propensity of biomass and biochar products from softwood pellets, wheat pellets, and rice husk was carried out. The results show that the torrefied biomass produced at a reactor temperature of 450 °C is the most prone to self-heating ignition regardless of the natural feedstock source. However, different feedstock sources showed different proneness to self-heating ignition. For the experimental laboratory bench-scale studies, the fuel most prone to self-heating ignition was softwood, but softwood and wheat showed very similar characteristics. A few key differences found between the wheat and softwood biochars are that wheat biochar produced at 700 °C is much more prone to self-heating ignition than its softwood counterpart. The rice husk was shown to be overall less prone to self-heating ignition, with an upscaling analysis showing that, at typical temperature ranges found in areas like power plant storage, the required pile size of rice husk or one of its biochar products is well above what is found in standard domestic storage or open-top transport containers. This chapter gives the first in-depth experimental comparison of self-heating ignition of different biomasses and biochars as a function of both pyrolysis reactor temperature used for production and natural feedstock source. It highlights the differences between torrefied biomass produced from rice husk, wheat pellets, or softwood pellets, giving kinetic and thermal parameters that can be used to calculate safe sizes for transport and storage of softwood biomass and softwood biochars. The work shows that for fire safety and hazard assessment it is very important to know at what conditions biochar is produced in addition to its feedstock type, as its proneness to self-heating ignition varies dramatically with biochar production temperature, and that variation is dependent on the original biomass source, as the trends observed for a specific pyrolysis temperature change when analysing different feedstock sources. This work is presented in Chapters 5 and 6.

7.2 Future work

The work presented in this thesis uses experimental techniques to quantify kinetic and thermal properties that can be used to assess self-heating ignition tendencies of various reactive media, and extends these results to quantify self-heating ignition for typical ambient temperatures found in natural conditions. Future work can be carried out to utilise these kinetic and thermal properties to create a more generalised computational model that can be used to quantify effects of more complex scenarios like the effects of different convective cooling conditions and the effects of the reactive media being configured in more complex geometries.

7.2.1 Effects of moisture on self-heating ignition

Experimental techniques used for this thesis in the analysis of reactive porous media using basket experiments and Frank-Kamenetskii theory of ignition do not account for effects of moisture content. This is because in a laboratory-scale setting the sample volumes required to have self-heating ignition temperatures low enough to see the effect of moisture (i.e. below 100 °C) would be too large to conduct in a laboratory oven. However it has been shown in literature that for fuels such as coal, the effect of moisture content can be significant. Results from chapter 2 on shale ignition can be extended by studying the effects of moisture on large scale slabs. This would require a large amount of sample material. In chapter 3, the effect of inorganic content was reported for self-heating ignition, but literature shows there must be a limiting factor for moisture too, which was shown by Frandsen for external ignition [69, 70]. A setup can be constructed to test and quantify moisture effects. This would require sizes larger than what can be done on a laboratory scale (due to the volume requirement) and so could be carried out as field tests.

Moisture effect on biomass will vary depending on conditions, but has been studied and presented in literature for the combustion of biomass [112]. However, the effect of moisture on self-heating ignition has not been studied. Results from Chapters 4, 5 and 6 can be used to design larger scale experiments to study the effect of moisture content on self-heating ignition.

7.2.2 Self-heating modelling

Using Frank-Kamenetskii ignition theory, experimental results were used to predict critical ignition sizes for typical ambient temperatures found in power plants or the environment in regards to wildfire. However as already mentioned in the thesis, more complex analysis methods exist. Computational models with more complex kinetics, and which account for moisture content, have been developed for coal for example.

The first area of further work for modelling would be producing a computational model able to predict self-heating ignition of wildfires. Based on Chapter 3, a com-

putational model can be produced which can take into account more complex reaction schemes, for example, to include the effect of drying of the soil for temperatures below 100°C , the effect of different moisture conditions throughout the sample, and the fact that, in wildland areas, materials are not homogeneous and can therefore have different inorganic contents based on depth.

The experimental results in all chapters of this thesis rely on the fact that the samples effectively act as insulators, so ignition will occur at the centre of the sample. In reality boundary conditions will vary, and can be more complex, because porosity of the samples might not be homogeneous, there can be a temperature gradient within the studied thickness and, in the case of wildlands, there can be the effect of wind as a forced convection boundary condition. All of these effects can be studied using computational models, and can further advance the understanding of self-heating ignition.

7.2.3 Self-heating ignition delay time

Finally, the last main area I believe requires further study for self-heating ignition is the ignition delay, i.e. how long it will take for a system to reach ignition from self-heating. The main issue with utilising current experimental methodologies at the laboratory-scale to estimate self-heating ignition delay time is that the analysis carried out on results relies on assuming steady state conditions, which is the case in Semenov theory and Frank-Kamenetskii theory. In these methods, a single global reaction mechanism is assumed, and this works well when determining the critical temperature to critical size relationship. However, in practice, most of these materials have multiple reactions happening, from biological reactions to reactions associated with moisture, and the associated chemical reaction times are very important when trying to assess ignition delay [32, 35]. Further work is needed to present a methodology which can be effectively used to predict ignition delay time for large scale reactive materials.

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