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On the Piloted Ignition of Solid Fuels in Spacecraft Environments

By

Sonya M. Fereres-Rapoport

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering – Mechanical Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:
Professor A. Carlos Fernandez-Pello, Chair
Professor Robert W. Dibble
Professor Scott L. Stephens

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On the Piloted Ignition of Solid Fuels in Spacecraft Environments

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by

Sonya M. Fereres-Rapoport
Abstract

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Doctor of Philosophy in Engineering - Mechanical Engineering

University of California, Berkeley

Professor Carlos Fernandez-Pello, Chair

The effect of environmental variables on the ignition of solid combustible materials is explored through a combination of experimental, analytical and numerical analyses. This research stems from NASA’s design requirement to reduce the cabin internal pressure and increase the oxygen concentration in human space vehicles and in future lunar habitats of the Constellation Program. These new environmental conditions may result in an increased fire risk of combustible solid materials due to higher flame temperatures (attributed to enhanced oxygen) and reduced convective heat losses from heated surfaces (attributed to reduced pressure). In particular, the influence of low pressure on ignition is emphasized here because little is known concerning this topic.

A series of experiments conducted in a laboratory-scale combustion wind tunnel with externally irradiated samples of PMMA (polymethyl-methacrylate) showed that both the ignition delay time and the fuel mass flux at ignition decrease when the ambient pressure is lowered. An analytical model is used to identify the governing processes that lead to these results and then a numerical model is applied to quantify the influence of ambient variables (particularly pressure) on the piloted ignition of PMMA. The numerical model verifies the phenomenological explanations inferred from the experimental findings and the qualitative analytical results, and correctly simulates the thermo-physical mechanisms leading to ignition. It is concluded that reduced pressure environments result in: 1) smaller convective heat losses from the heated material to the surroundings due to a thickening of the thermal boundary layer next to the solid fuel surface, allowing for the material to heat more rapidly and pyrolyze faster; and, 2) a lower mass flux of volatiles required to reach the lean flammability limit of the gases at the pilot, leading to earlier ignition, due mainly to an enlarged boundary layer and a thicker fuel species profile under reduced pressures.
The findings from this research indicate that the flammability of combustible materials is enhanced at low ambient pressures and elevated oxygen concentrations, and may have significant consequences in the assessment of their fire risk in spacecraft and other environments where these conditions are encountered such as aircrafts and high altitude cities, among others.
To Daddy Rap
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NOMENCLATURE

Letters:
A Pre-exponential factor (1/s)
B Pre-exponential factor for gas phase (cm$^3$/mol-s)
C$\text{p}$ Specific heat at constant pressure (J/kgK)
D Diffusivity (m$^2$/s)
E Activation energy (kJ/mol)
Gr Grashof number
h Heat transfer coefficient (W/m$^2$K)
k Conductivity (W/mK)
$m''$ Mass flux (kg/m$^2$s)
M Molar mass (g/mol)
Nu Nusselt number
P Pressure (kPa)
Pr Prandtl number
Qc Heat of combustion (J/kg)
$q''$ Heat flux (W/m$^3$)
R Universal gas constant (J/kg K)
Re Reynolds number
Sc Schmidt number
T Temperature (K)
t$\text{ig}$ Ignition delay time (s)
u Velocity in x direction (m/s)
v Velocity in y direction (m/s)
x Distance (m)
X Mole fraction (-)
y Distance (m)
Y Mass fraction (-)
Greek symbols:

\( \alpha \) Thermal diffusivity \((m^2/s)\)

\( \delta \) Boundary layer thickness \((m)\)

\( \varepsilon \) Emissivity

\( \nu \) Kinematic viscosity \((m^2/s)\)

\( \rho \) Density \((kg/m^3)\)

\( \Delta H \) heat of reaction \((kJ/kg)\)

Subscripts:

a  Air

ad Adiabatic flame

c Concentration

F Fuel

g Gas

ig Ignition

\( \text{O}_2 \) oxygen

s Solid

T Thermal

0 Evaluated at \( y=0 \) (wall)

\( \infty \) Ambient flow
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CHAPTER 1 – INTRODUCTION AND BACKGROUND

1.1 An Overview of the Problem

The ignition of solid combustible materials plays a key role in the initiation of fires and is consequently of great importance in fire safety. Improving our understanding of ignition phenomena provides the necessary tools to prevent undesired fires and to inhibit fire growth.

In 2009 there were 1,348,500 fires reported in the United States (National Fire Protection Association, 2010) [1]. These fires caused 3,010 civilian fire deaths and 17,050 civilian fire injuries. Although the loss of life is disturbing to say the least, the number is a fraction of the 30,797 fatalities due to motor vehicle accidents that same year [2] and insignificant if compared to over 600,000 premature deaths a year due to heart disease [3]. However, those same fires caused a loss of $12.5 billion in property damage during 2009. To get an idea of the scale, this extraordinary amount is roughly twice the value of the deficit of the state of California for the 2009-2010 fiscal year [4]. Human life is priceless but the reality of the matter is that fires are also an enormous cause of property loss.

There is also another dimension to consider when this property loss is collective and it represents the forefront of human technological advances, such as space exploration vehicles. Human space travel represents a country’s technological leadership and is a source of national pride. Space tragedies such as the Apollo 1 (Saturn 204) fire which killed three astronauts in 1967 [5] affect the entire population. Even if there is no human loss involved, a sense of human vulnerability invades the general consciousness. A fire on board the International Space Station (ISS) would bring such pathos to our society that, without a doubt, it warrants fire prevention research.

At a time in which the direction of human space exploration is unclear but privatization is being encouraged, cost reduction plans will bring new concerns. It is imperative that the materials utilized in spacecraft are well characterized and their fire behavior is well understood. It is also important that the tests employed to determine the suitability of these materials are adapted to the worst possible conditions to be expected during operation.

The present research analyzes the ignition of solid combustibles under the environmental conditions that are present in the interior of human space exploration vehicles. The main aspect that is investigated is how a reduced ambient pressure may affect the flammability of materials and increase the ease of ignition. Like in many other areas where space research findings have transcended to daily situations, the results of this study can be extrapolated to fire prevention in different settings.
In addition to space facilities, the interior of other pressurized vehicles such as aircraft also have lower than sea level atmospheric pressure. Typically, aircraft cabin air is pressurized to an equivalent “cabin altitude” between 1500-2400 m (84-75 kPa) following FAA regulations [6] to enable passenger comfort while minimizing the fuselage structure fatigue. Fires in pressurized vehicles present the added disadvantage that it is extremely difficult to rapidly evacuate the passengers on board and these fires are not easy to detect. The disaster of Swissair Flight 111 in 1998 [7] is a dramatic example of how difficult it is to detect in-flight fires: the crew was unaware that there was a fire on board and an error in the instrumentation did not provide any warning. By the time the fire was detected, the fire had spread and the aircraft was uncontrollable. All 229 passengers died during the accident. The investigation became the longest and most expensive transport accident investigation in Canadian history, costing C$57 million (US$48.5 million) over five years. It was determined that the fire most likely started from an electrical arcing event that occurred above the ceiling near the cockpit rear wall. The electrical arcing acted as a heat source, igniting a nearby metalized thermoplastic resin used as insulation cover material. The legacy of this disaster was a renewed awareness of the importance of understanding material flammability in the environment where the material is used. Similarly, metropolitan areas at high altitude locations present atmospheric pressures below sea level on a constant basis and would also benefit from the findings of this research.

Fire is a concern for human safety, but also an enormous economical issue. Therefore it is much more reasonable and cost effective to invest in prevention, i.e. improving our understanding of how ignition processes occur.

1.2 Exploration Spacecraft Internal Atmospheres

The possibility of fires in space facilities and vehicles has been a concern for NASA since the beginning of the human space exploration program in the 1960s [8]. Internal fires in spacecraft are actually rare [9], but when they do occur they have such terrible consequences that fire hazards on board are taken very seriously. Considering the long duration of space missions and the large amount of combustible materials on board (electronic components, packing materials, paper, waste, etc.) on a long term basis the probability of a fire event on board is significant. Additionally, the enclosed nature of these facilities and limited egress makes it very difficult for the crew to escape.

However, the most important factor distinguishing spacecraft fire safety from terrestrial systems is the low-gravity environment that affects the characteristics of fire initiation, spread and suppression. The lack of natural convection in microgravity environments was initially thought to inhibit flame spread and to reduce material flammability. On the other hand material flammability in low-gravity is extremely sensitive to atmospheric flows (forced convection from ventilation flows) and composition (oxygen concentration) [9]. These particularities reveal that the typical mechanisms of ignition on
Earth might not be the same in non-buoyant flows found in space. Under some conditions such as low velocity flows, the flammability range of materials or the flame spread rate under microgravity might be larger than in normal gravity environments [10]. Therefore, the investigation of flammability and flame spread under worst case scenarios (which might not be the standard conditions found on Earth) is needed in order to ensure fire safety during human space travel.

In recent years the direction of the human spaceflight program has moved towards expanding space travel beyond Lower Earth Orbit. NASA’s Constellation Program (2004-2011) [11] had the main goal of developing the necessary technologies to extend human presence across the Solar System by gaining experience in operations and human support systems away from Earth’s environment. The Constellation Program included extended missions to the Moon and Mars in addition to present operation in the International Space Station. To enable extended extravehicular activities (EVAs) during these missions, Constellation’s space vehicles, habitats, and space suits were designed to have a series of internal atmospheres different from standard sea level conditions [12, 13]. These atmospheres were to mitigate the risks of fire, decompression sickness, and hypoxia (medical condition caused by insufficient oxygen supply), and enable frequent crew excursions on planetary surfaces. Both the Shuttle and the International Space Station (ISS) operate with a standard sea level internal atmosphere, i.e. 101.3 kPa and 21% oxygen concentration by volume. In contrast, Constellation’s Orion Crew Exploration Vehicle (CEV) that would transport the crew between the Shuttle and the ISS was to be designed to have a variable cabin total pressure between 101.3 and 70.3 kPa (14.7 and 10.2 psia). Other vehicles, such as the Altair Lunar Lander, Mars lander and future habitats on the Moon and Mars were designed to operate with an internal cabin total pressure of 55 kPa (8 psia) and 32% oxygen concentration. These reduced pressure and high oxygen concentration internal atmospheres present several advantages, such as lower internal vehicle pressures, reduced weight due to a smaller amount of inert gas, a reduced risk of decompression sickness during extra-vehicular activities and shorter pre-breathing times required for EVA preparation. NASA also took into consideration human physiological factors for possible operation.

However, the new environments proposed by NASA may increase material flammability due to higher flame temperatures (attributed to enhanced oxygen) and reduced convective heat losses from heated surfaces (attributed to reduced pressure). They may also affect gas phase processes related to material flammability such as time to reach a flammable mixture in the gas, and the gaseous mixture ignition induction time. These effects have potential consequences in the evaluation of the fire risk of materials under low pressure conditions and consequently call for further investigation.
The selection of the potential new exploration spacecraft internal atmospheres (Fig. 1.1) is a compromise between these characteristics briefly mentioned before: 1) reduced risk of decompression sickness for the crew to and from EVA, 2) material flammability requirements and 3) human physiological limits such as hypoxia or the lack of sufficient oxygen to breathe normally. The normoxic equivalent curve in Fig.1.1 corresponds to cabin total pressures and oxygen concentrations with a partial pressure of oxygen the same as at sea level standard conditions, i.e. \( \text{PO}_2 = 21 \text{ kPa} \). This curve is of great interest for future space habitats because the human lungs operate on an oxygen partial pressure basis. In other words, following the normoxic equivalent curve humans can breathe as effectively as they would at sea level conditions without the possibility of experiencing altitude sickness effects.

This work stems from the material fire safety and prevention requirements for the space exploration internal atmosphere selection in the Constellation Program. To this date there is a substantial understanding of how certain external variables affect material flammability in normal and microgravity conditions. The parameters previously investigated are primarily external heat flux, forced convection flow velocity and oxygen concentration [14-18]. Nevertheless, until the beginning of the Constellation Program there was very little information on how ambient pressure affected material flammability, or its combined effect.
with increased oxygen concentration. Based on human physiological concerns of altitude sickness the possibility of enriching the oxygen in room air at low pressures at high altitude installations such as mountain resorts [19] or astronomy observatories such as Mauna Kea, Hawaii [20] has been previously explored. These studies show that human mental and physical performance can improve drastically by increasing the oxygen partial pressure. However, these analyses address fundamentally medical aspects but deal superficially with flammability concerns. In particular West [21] suggests there is no additional fire hazard derived from increasing the oxygen concentration at high altitudes based on decreased burning rates at low pressures calculated following the National Fire Protection Association Standard for Hypobaric Facilities [22]. Flame spread and burn rates decrease in low pressure environments for a constant oxygen concentration by volume but fire initiation might be easier. The flammability of materials includes both fire initiation and growth. Ignition in these conditions has not been fully investigated.

In the past years there has been a renewed interest in understanding material flammability in low pressure environments directly related to the design requirements for NASA’s latest exploration vehicles [23-25] or associated with new experimental stations on Earth at high altitude locations [26], which demonstrates the need for a deeper understanding of how the total pressure affects the mechanisms that lead to the ignition of solid fuels.

Moreover, considering the economical advantages that low pressure environments represent for future commercial space travel (lower inert gas payload and reduced structural fatigue) and regardless of the cancellation of NASA’s Constellation program, the effect of reduced pressure on material flammability should be further investigated. Contrary to what intuitively is to be expected, if the total atmospheric pressure is reduced (because of a reduced quantity of oxidizer), lower pressure might actually enhance material flammability. This danger is thought to be due primarily to the reduction in convective heat losses of heated materials to their surroundings.

1.3 Forced Ignition and Spread Test (FIST)

The Forced Ignition and Spread Test (FIST) is a flammability assessment test developed at UC Berkeley in 1998 under NASA sponsorship [14]. Throughout the years FIST has evolved but the primary goal of this test still is to complement the NASA-STD-6001 Test 1 [27] in evaluating the flammability of materials in the conditions to be expected inside spacecraft vehicles. Those conditions are microgravity and low velocity flows and more recently low pressure and higher oxygen concentration. NASA-STD-6001 Test 1 is a pass/fail upward flame propagation test in which a sample is ignited at the bottom and the distance the flame propagates under natural convection determines whether a material is suitable for spacecraft use. As mentioned before, the absence of natural convection in microgravity alters the flammability characteristics of materials. In low gravity the main mechanism of
transport is diffusion unless there are low velocity flows such as those induced by air conditioning ventilation systems. It is extremely difficult to exactly reproduce microgravity flows in ground tests, where eliminating the naturally induced buoyant flows is impossible. Thus, studying the effects of forced flow conditions on ignition and flame spread can complement the existing natural convection based flammability tests to determine what conditions are the most conservative.

Some key findings from the FIST project to date are summarized in Table 1.1. The FIST project has primarily focused on analyzing the influence of environmental parameters on ignition and flame spread. The effect of 1) applied radiant heat flux, 2) forced flow velocity, 3) oxygen concentration and 4) total ambient pressure on ignition and on flame spread rates has been characterized throughout numerous years.

<table>
<thead>
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<th>Reference</th>
<th>Date</th>
<th>Type of Test</th>
<th>Key Finding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cordova et al. [14]</td>
<td>2000</td>
<td>Ignition</td>
<td>Critical solid gasification rate for ignition increases with the convective heat transfer coefficient</td>
</tr>
<tr>
<td>Cordova et al. [15]</td>
<td>2001</td>
<td>Ignition</td>
<td>Ignition delay, critical heat flux for ignition, and flame spread rate are functions of the free stream flow velocity. Tests under natural convection (e.g. LIFT) do not take into account oxidizer forced flow velocity effects.</td>
</tr>
<tr>
<td>Rolson et al. [16]</td>
<td>2001</td>
<td>Microgravity Ignition (KC-135)</td>
<td>Ignition delay times are reduced in low velocity flows (0.02-0.25 m/s) in microgravity conditions due to the absence of buoyant flows. The critical heat flux for ignition in microgravity can be up to half of value in normal gravity.</td>
</tr>
<tr>
<td>Rich et al. [28]</td>
<td>2006</td>
<td>Microgravity Flame Spread (KC-135)</td>
<td>Flame spread at microgravity can exceed normal gravity value under certain conditions.</td>
</tr>
<tr>
<td>McAllister et al. [23, 24]</td>
<td>2008-2010</td>
<td>Ignition</td>
<td>Ignition delay time decreases with low pressure and increased oxygen concentration.</td>
</tr>
</tbody>
</table>
The major difference between FIST and other flammability tests such as 1) Lateral Ignition and Flame-spread Test (LIFT- ASTM E 1321-93, 1996) [29], 2) the Cone Calorimeter [30] or even 3) NASA-STD-6001 Test 1, is that FIST includes a forced flow during the ignition or flame spread tests. This forced flow is superposed to natural convection flows during the ground-based tests, resulting in mixed flow conditions (if the oxidizer velocities are not large enough to overcome buoyancy induced flows). However, during the FIST microgravity tests performed with NASA’s KC-135 aircraft [16, 28] the oxidizer forced flows are intended to exactly reproduce the low velocity flows created by ventilation systems on spacecraft. Inside space facilities air conditioning systems typically induce low velocity flows on the order of 0.1 m/s. These low velocity flows distribute and spread the oxidizer in an environment where mixing would be otherwise entirely diffusion controlled. By analyzing the effect of oxidizer flow velocity, the FIST project was one of the first test methods to establish that non-quiescent microgravity environments can represent a larger fire hazard than normal gravity conditions.

The research carried out with the FIST Project has also emphasized the importance of analyzing the physical mechanisms responsible for the ignition of solid combustible materials. Rich et al. [18] showed how the “critical mass flux at ignition” is a more physically correct parameter than the semi-empirical “critical surface temperature” to evaluate the ignition of solid fuels. A material’s ignition temperature varies with the fuel and environmental conditions, and must be measured experimentally. However, the critical mass flux of pyrolysis gases is directly related to the physical process of a solid gasifying when exposed to a heat flux. Theoretically this critical mass flux criteria can be incorporated into numerical models in order to predict ignition delay times based solely on material properties and environmental conditions.

The most recent FIST research [23, 24] measured the ignition delay time in NASA’s Constellation proposed space exploration internal atmosphere (58.6 kPa and 32% oxygen concentration by volume) and found it to be 27% lower than ignition in standard conditions (101.3 kPa and 21% oxygen). In contrast to these FIST results, other different studies carried out in a NASA Zero Gravity Research Facility drop vehicle [31] show that when the applied radiant heat flux is extremely high, ignition under these conditions might be slower than at standard sea level atmosphere. These novel findings suggest that the effect of pressure is not entirely understood. The combination of low pressure and high oxygen concentration seems to have an intricate effect on ignition, depending on the dominating heat transfer mechanisms.
1.4 The Current Contribution

In order to improve the current understanding of the physical mechanisms controlling the ignition of solid fuels under low pressure in air and in oxygen-enriched air, the FIST experimental apparatus was used to explicitly measure the critical mass flux at ignition under varied environmental conditions. The current contribution is a natural consequence of the previous work in space exploration internal atmospheres reported by in 2009 McAllister et al. [23, 24] but aiming to measure the effect of those environmental conditions (low pressure, high oxygen concentration) on the critical mass flux at ignition. The experimental, analytical and numerical work presented here on the mass flux at ignition attempts to answer some of the questions that arose from the initial space exploration research with FIST. These previous ignition delay results in low pressure and air or oxygen-enriched air provide an indication of how a material will behave in a given set of environmental conditions but it does not explain the underlying physics responsible for ignition. A thorough analysis of the mass flux at ignition will be presented in this work with the intention of clarifying the determining processes involved.

Chapter 2 is a review of the literature on ignition of solid combustible materials and on the effects of environmental parameters on the flammability of materials. This review provides the necessary background on ignition criteria and critical mass loss rate at ignition to contextualize the experiments and numerical modeling presented in this work.

Chapter 3 presents experimental results of the ignition delay and mass flux at ignition of polymethyl-methacrylate (PMMA) samples exposed to an external radiant heat flux at ambient pressures lower than sea level standard conditions (1 atm) and elevated oxygen concentrations. These experiments confirm the findings of McAllister et al. [23, 24], i.e. that a solid fuel exposed to low external heat fluxes shows a decrease in ignition delay time if the ambient pressure is reduced. In addition to the ignition delay time the experiments measured the solid mass loss rate prior to ignition. This is the first time the mass flux at ignition has been measured at a range of sub-atmospheric pressures. The experiments will show that the critical mass flux at ignition also decreases with ambient pressure. Therefore, the critical mass flux at ignition cannot be a single value for a given material. The findings suggest that the typical exponential dependency of the mass flux with sample surface temperature does not completely agree with the experimental findings. Consequently, the gasification rate prior to ignition is not directly related to surface temperature or energy input. The reduction in ignition delay time with ambient pressure is explained primarily through a reduction in the convective heat transfer coefficient. Experiments with 30% O$_2$ by volume at a range of pressures below 1 atm are also presented and compared to normal air (21% O$_2$) results.

Chapter 4 describes a simplified analytical model based on a boundary layer integral model used to explain the mechanisms responsible for the observed ignition delay time trends with varied ambient pressure. Under low pressures the boundary layer thickness is increased which results in a lower heat transfer coefficient. Thicker boundary layers also
lead to lower species concentration gradients at the solid surface. A reduction of the fuel concentration gradient at the surface implies a reduction of the mass flux at the surface and therefore a reduction of the fuel mass flux at ignition. The results with this simplified model show qualitatively the same trends as the experiments presented in Chapter 3. A “B-number” theoretical analysis is also presented and compared to this simplified boundary layer analysis.

Chapter 5 presents a two-dimensional numerical model of the ignition of PMMA under different environmental conditions. This model was developed with the widely used Fire Dynamics Simulator (FDS) code [32]. FDS is a computational fluid dynamics (CFD) model developed by the National Institute of Standards and Technology (NIST) that provides a transient solution to low Mach number, buoyant, reactive Navier Stokes equations. The gas phase kinetics are modeled with a finite-rate single-step combustion model. The solid phase decomposition is modeled using a single-step Arrhenius non-charring reaction. Oxidative pyrolysis is not considered and the in-depth formed pyrolyzate is assumed to flow unrestricted through the PMMA. The calculated ignition times, surface temperatures and mass loss rates prior to the material ignition are compared to those measured experimentally and presented in Chapter 3. It is shown that the model qualitatively describes the mechanisms controlling piloted ignition of solid fuels, and that with appropriate kinetic parameters the model qualitatively agrees with the experimental data.

Chapter 6 summarizes the main conclusions of the experimental results and the analytical and numerical models presented in this investigation. Future lines of research are also suggested.
1.5 References


CHAPTER 2 – LITERATURE REVIEW

2.1 Ignition of Solid Fuels

Ignition occurs when a mixture of fuel and oxygen are in a flammable ratio and at a high enough temperature for a runaway chemical reaction to take place, leading to a sustained gas-phase diffusion flame. Regardless of the fuel’s state, whether it is gaseous, liquid or solid, the ignition event takes place in the gas phase. Thus, prior to the ignition of solid or liquid fuels there must be a phase change process to produce a gasified fuel. More specifically a solid fuel must be heated, gasified, and mixed with the oxidizer in the heated layer above the solid surface before it can react and ignite.

The gasification of a solid is generally more complicated than the evaporation of a liquid. Solid fuels gasify through a thermo-chemical decomposition or pyrolysis process, releasing gaseous fuel products and maybe producing a solid residue (char) depending on the type of fuel. Hence, combustible solids can be classified based on their behavior when exposed to high temperatures into those that “melt” and those that “char”. Most commonly used polymers do not char; they “melt” during the thermal decomposition producing fuel gaseous products. Wood is a typical example of the second category of materials (charring). The decomposition process or pyrolysis to produce a rate of gaseous fuel is typically idealized as an Arrhenius reaction of the form [1]:

\[ \dot{m}_{\text{fuel}} = \rho A_s e^{-E_s/RT} \]  

(2.1)

\( A_s \) and \( E_s \) are solid fuel properties, \( R \) is the universal gas constant and \( T \) is the solid surface temperature. Equation (2.1) shows that pyrolysis is a very nonlinear function of the solid temperature.

The ignition of solid fuels exposed to an external heat source can be classified as spontaneous (autoignition) or piloted (forced) ignition, depending on whether the ignition is assisted by a hot energy source (pilot) or not [1]. Typical pilots could be electrical sparks, hot wires, small flames or even flying embers. Analyzing piloted ignition is of greater relevance from the fire safety perspective because it occurs at lower temperature thresholds, with a lower surface temperature and depicts fires in a more realistic way because in general it is impossible to avoid all external heat sources [2].

This work focuses on the piloted ignition of polymethyl-methacryclate (PMMA), a very well characterized non-charring thermoplastic. PMMA has been widely used in the flammability literature because when it pyrolyses it decomposes fundamentally into its elementary monomer methyl-methacrylate (MMA). This simplifies the task of modeling and
understanding decomposition processes with PMMA in comparison to other thermoplastics that decompose into a wide range of different gaseous products. As mentioned before, several heat and mass transport processes take place in the piloted ignition of a solid combustible material including the heating and subsequent gasification of the solid fuel, followed by the transport and mixing of the gasified fuel in an oxidizer boundary layer flow. If the volatile gaseous products of the solid decomposition are produced at a sufficient rate and the rate of heat loss to the surroundings is less than the rate at which heat is generated by the reaction, ignition will occur. It is fundamentally a combustion problem, but it emphasizes the mass and heat transport processes that occur prior to ignition rather than the chemistry that eventually leads to the ignition. This is because with the presence of the pilot, ignition occurs as soon as a flammable gaseous mixture is formed near the ignition source.

The piloted ignition of a solid fuel can be summarized through a series of fundamental steps [3-5]:

1. Heat is transported to the solid fuel from the external radiant heat source by radiation and convection and it induces the thermal decomposition or pyrolysis of the fuel.
2. The gaseous products of the pyrolysis are diffused and convected through the oxidizer flow.
3. Once the mixture of oxidizer and vapor fuel reach flammable conditions at the heat source or pilot, a premixed flame appears at the source of ignition.
4. If a sufficient amount of pyrolysate vapors is generated, this premixed flame at the pilot can propagate upstream and a diffusion flame will anchor on the solid surface. This is identified as sustained burning.

Based on these steps, the time to ignition is generally simplified as the superposition of the time scales associated with these processes, namely solid heating and thermal decomposition, gaseous fuel transport and mixing with oxidizer, and gas-phase chemical induction:

\[
t_{\text{ig}} = t_{\text{heating}} + t_{\text{transport/mixing}} + t_{\text{chem.induction}}
\]  

(2.2)

Depending on the relative importance of each of these terms there will be different effects on the ignition delay time of an externally irradiated solid fuel. It should be noted that the addition in Eq. (2.2) should be understood loosely: these terms represent consecutive processes that are partially simultaneous. In other words, the mixing process will not occur until gaseous fuel is produced from the solid heating process, but once it has initiated, both processes will coexist.

The first term in Eq. (2.2) is primarily dominated by the heat transfer and therefore controlled by the method used to ignite (type of pilot) and the heat flux applied. In relation to their thermal behavior during the heating process, solid fuels are usually classified in two
distinct groups: thermally thick and thermally thin, depending if the thermal wave penetrates the solid during the heating process through its entire thickness or not. For thermally thin solids, heating times are inversely proportional to the applied heat flux, $t \sim 1/q''$ [1]. For thermally thick solids, the heating times can be estimated by pure conduction times yielding a quadratic dependency, $t \sim 1/q''^2$. In both cases (thermally thin and thick) high external heat flux values will lead to shorter heating times than lower heat flux levels. There is a critical heat flux (CHF) below which ignition will not occur. This CHF is commonly determined for thermally thick solids by plotting $1/t_{ig}^{1/2}$ vs. the external heat flux $q''$ and extrapolating the data linearly for $t_{ig} \to \infty$. The heating time is typically significantly larger than the transport/mixing time or the chemical induction time, therefore many simplified analytical models for solid ignition assume the ignition time is approximately equal to the heating time [1, 6].

The second term in Eq. (2.2) includes both convective and diffusive transport and mixing. For high flow velocities this time scale will be primarily controlled by convection. Diffusion will become more important when there are low oxidizer flow velocities. As a matter of fact, diffusion is the key mechanism determining mixing in low buoyancy flows such as those encountered in quiescent microgravity conditions.

The third term in Eq. (2.2) represents the induction time for the gas-phase chemical reaction. Due to the presence of a hot temperature pilot, ignition is induced at the igniter the moment there is a flammable mixture as determined by the lean flammability limit (LFL) of the fuel. If the oxidizer flow velocity is high or the oxygen concentration is high this induction time could be significant [3], but generally it is on the order of milliseconds. Since typical heating times can be on the order of 100 seconds and the transport/mixing times an order of magnitude below, it is common to neglect the effect of the chemical induction time. Situations where the chemical induction term might be comparable to the other two terms in Eq. (2.2) include ignition processes under extremely high heat fluxes because they reduce the heating times considerably. Only experiments with extremely high radiative heat fluxes on the order of 1000 kW/m$^2$ locally [7] can separate the influence of the chemical induction time from the other time scales in Eq. (2.2). The gas-phase chemistry is difficult to model due to the large number of chemical reactions involved and their coupling to the transport equations. Nevertheless a frequent simplification is to assume a single one-step overall reaction with an Arrhenius type reaction rate of the form [2, 3]:

$$\dot{\omega} = A_g \rho_g^2 Y_F Y_{O2} e^{-E_g/RT}$$  \hspace{1cm} (2.3)

Where $A_g$, $E_g$ are gas-phase material properties, $\rho_g$ the gas phase density, and $Y_F$ and $Y_{O2}$ the fuel and oxygen mass fractions respectively. The chemical induction time is inversely proportional to the reaction rate from Eq. (2.3). This large simplification does not address the chemistry in detail, but is very useful to understand the parameters involved in the problem and their overall effect on the induction time.
The decomposition of the time to ignite in these three consecutive processes establishes a framework to analyze and explain the influence of different environmental variables on the ease of ignition. This framework will be used throughout this work to discuss the findings and provide more insight into the processes taking place during the piloted ignition of solid fuels.

2.2 Ignition Criteria

There is no general consensus on what criterion is the best to characterize the ignition of solid combustible materials. Typical ignition criteria are based on the attainment of a critical or limiting value of a particular parameter assumed to be related to the ignition process such as a critical surface temperature at ignition [8], a critical flame temperature [9], a critical char depth, a critical heat flux for ignition (CHF)[10], a thermal response parameter (TPR) [11], a critical fuel mass flux [4, 12] or a critical heat release rate [13].

Traditionally and most frequently among fire safety engineers the ignition temperature has been used as an ignition criterion. By ignition temperature most authors [1, 2, 6, 8] refer to a critical surface temperature of the specimen just prior to ignition. The concept of an ignition temperature stems directly from comparison of solid fuel ignition with gas-phase autoignition temperatures or liquid fuels flashpoints [10]. This criterion can be easily related to the solid pyrolysis process. As Eq.(2.1) shows, pyrolysis has a strong temperature dependence (an exponential behavior through the Arrhenius form). Therefore ignition is assumed to have a temperature threshold, i.e. it doesn’t occur below a critical surface temperature. The ignition criterion is developed then as the time it takes a solid to reach a critical surface ignition temperature.

There are large databases of measured ignition temperatures for a wide range of materials. Although in the past the ignition temperature has been successfully correlated to piloted ignition experiments under fixed oxidizer and convective conditions, the extension of this concept to other environmental conditions is unclear [4]. One of the main issues with using a surface temperature as an ignition criterion is that an ignition temperature does not take into account the time scale of the problem, i.e. how fast a material might ignite. Also a large amount of combustible solids have similar ignition temperatures but they present diverse behavior at ignition [6]. This can be explained because the time dependency of the problem is neglected and should be introduced by a parameter such as the thermal inertia (or kpc: multiplication of thermal conductivity, density and heat capacity) which can differ substantially among dissimilar materials. Additionally the ignition temperature of solid combustibles is difficult to measure accurately and some external variables can have an effect on its value. Moreover, for thermally thin materials the concept of a surface temperature is not adequate, since there are no temperature variations throughout the
solid. However, the main deterrent for using this criterion is that the ignition temperature is empirically determined and cannot be calculated based on the fuel’s fundamental properties or as a function of environmental conditions.

Some other ignition criteria present similar inadequacies to predict solid fuel ignition. A critical flame temperature is also very difficult to measure accurately and it seems to be more suitable to describe extinction events rather than ignition [14]. A critical char depth is not valid for non-charring solids such as the thermoplastics analyzed here. The critical heat flux for ignition is very useful in certain circumstances, but it is highly dependent on the convective heat transfer conditions as determined by the flow velocity, geometry and orientation of the specimen during the experiments [5]. Tewarson’s thermal response parameter [11] is calculated based on the ignition temperature and the thermal inertia (kρc), so it has many of the issues associated with using a surface temperature at ignition as an ignition predictor.

Of all these criteria it is generally acknowledged that the most physically correct one is the critical mass flux at ignition [4, 6, 9] since it takes into account the decomposition of the solid fuel. Due to the interest of finding a more phenomenological explanation for the ease of ignition of solid fuels under different environmental conditions, the concept of mass flux at ignition was further explored for this work.

### 2.2.1 Critical Mass Flux at Ignition

The critical mass flux or mass loss rate of fuel vapors has been measured before for a range of solid fuels. Bamford et al. [15] seem to be the first to suggest the importance of this parameter. It was not until the late 1980s [9, 12] that this concept was measured in detail for a variety of materials and successfully employed as an ignition criterion. More recently Rich et al. [4] used the critical mass flux at ignition criterion to explain experimentally and analytically the effect of oxygen concentration, forced air flow and radiant external heat flux on ignition of two different materials, PMMA and a polypropylene-glass fiber composite.

There is interest in using this criterion because it attempts to predict ignition in a physical way by including the decomposition process of the condensed phase. A solid fuel such as PMMA decomposes when it is exposed to an externally applied heat flux and to a forced oxidizer flow. The decomposition can be due to a high temperature and also to the presence of an oxidizer, which further enhances the pyrolysis. This pyrolysis or decomposition extends throughout the specimen as far as the thermal wave penetration depth. The thermo-chemical decomposition breaks the polymer chains in the condensed phase, softening the polymer forming a polymer melt and releasing volatile monomer components that form bubbles of fuel vapor in the pyrolysis zone. The fuel vapor bubbles
grow, coalesce and migrate through the molten polymer until they are released to the surface [16].

As explained above, the fuel vapors are mixed with the oxidizer flow (natural or forced) right above the solid surface until a flammable mixture is formed. In piloted ignition firstly a premixed flame will form at the pilot location when the LFL is reached and propagate through the flammable mixture toward the solid fuel surface. In the fire community this is commonly referred to as the “flash point” by analogy with liquid fuel ignition. The fuel vapor mass flux required to reach the LFL at the pilot will correspond to these “flashing” conditions. Only if the fuel vapor is continued to be produced at a sufficient rate and the heat balance at the boundary layer adjacent to the solid surface is positive, a sustained diffusion flame will anchor at the solid surface. Sustained burning conditions are referred to as the “fire point” [5].

Simplified analyses at the flashpoint are usually based on attainment of flammable conditions (LFL) at the pilot. For a thermally thin material, since it has a uniform temperature, it is common to assume a single-step zero order Arrhenius kinetics, similar to the expression in Eq. (2.1). Thus, an exponential dependency with sample temperature can be assumed as a first order approximation to calculate the mass flux at ignition.

For sustained burning (fire point) most analyses are related to Spalding’s mass transfer number, B [17]. Rashbash [18] was the first to suggest the use of Spalding’s B number to calculate a critical mass flux at ignition. The B number was originally developed to explain the vaporization and burning of liquid fuel droplets, but when applied to solid fuels it provides a link between the critical mass flux of fuel volatiles at fire point and the stability of the combustion process in the flame. The general expression for the relationship between a critical mass flux at ignition and a critical B number is the following:

$$\dot{m}_{cr} = \frac{h}{C_p} \ln(1 + B_{cr})$$

(2.4)

where \( h \) is the convective heat transfer coefficient between the flame and the solid surface, \( C_p \) is the heat capacity of the oxidizer (usually air), and \( B_{cr} \) is the critical B number. The way to calculate the \( B_{cr} \) varies depending on the analysis. The B number theory has been modified several times in order to account for different processes such as the heat radiated to the environment from the flame or surface reradiation loss [19]. Essentially B is calculated as:

$$B = \frac{C_p(T_{flame} - T_s)}{\Delta H}$$

(2.5)

\( \Delta H \) is the heat of solid pyrolysis, \( T_{flame} \) is the flame temperature and \( T_s \) corresponds to the solid surface temperature. The various “modified” B number theories [4, 18, 19] and the classical theory differ on the effects that are taken into account in the calculation of the flame temperature and of the heat of solid pyrolysis. The most interesting conclusion of this
approach is that the critical mass flux at ignition can be estimated by a heat transfer balance between the flame and the solid surface. It generally presents good agreement with experimental results [4].

The critical mass loss can be measured experimentally by monitoring the weight of a sample material when exposed to a constant radiant heat flux and a pilot to induce piloted ignition. Measuring the mass loss rate at ignition accurately is not an easy task mainly due to the small mass changes to be measured. High resolution load cells must be used to provide sufficient sensitivity but also increase the likelihood of external noise and interferences affecting the measurements. Substantially different values have been reported in the literature for the critical mass flux at ignition. For example, Tewarson [20] reported values that were approximately double those of Drysdale and Thomson [12]. Although this shows that there is some inconsistency within the literature values of measured critical mass flux at ignition, there are clear trends. Drysdale and Thomson [12] found that hydrocarbon polymers such as polyethylene, polypropylene, and polystyrene presented roughly half the critical mass flux at ignition in comparison to oxygenated polymers such as PMMA. This is qualitatively consistent with the lower heats of combustion of the oxygenated polymers [5]. In other words, oxygenated polymers will have a higher fuel stoichiometric concentration (by mass) of the pyrolysis products in air than the common hydrocarbon polymers, leading to a higher mass flux ratio when both types of polymers are compared.

The use of Spalding’s B mass transfer number indicates a direct proportionality between the heat transfer coefficient and the critical mass flux at ignition (Eq. 2.4). It suggests that any air movement above the specimen surface which modifies the immediately adjacent boundary layer changes the effective heat transfer coefficient and therefore modifies the critical mass flux at ignition. This suggests that values measured under natural convection conditions might be lower than those with forced flow. It also indicates that mass flux measurements are extremely sensitive to convective conditions and it might account for the inconsistencies in the reported values mentioned above.

The phenomenological nature of the concept of a critical mass flux of fuel volatiles has made it a desirable ignition criterion to use, despite the difficulties in obtaining accurate measurements or its sensitivity to the convective environment surrounding the solid fuel. It provides insight on the heat and mass transfer processes involved in the complicated process of solid fuel ignition.
2.3 Effect of Environmental Variables on Ignition

There is a wide range of variables that can affect the piloted ignition of polymeric materials. These variables can be classified into environmental variables such as external heat flux applied, oxidizer flow velocity, moisture content, oxygen concentration and ambient pressure, and variables related to the experimental set-up such as pilot type, pilot location, or sample orientation. The second group is mainly apparatus dependent and therefore not of much interest. In contrast, the influence of external environmental variables on ignition can provide much insight into the physical mechanisms controlling the ignition event and is therefore studied with great interest.

The effect of environmental variables on piloted ignition of combustible solids can be explained through an analysis of their influence on each of the time scales in Eq. (2.2) and on the different ignition criteria (ignition temperature or mass flux at ignition) as presented above. The state of the art of the effect of several of these environmental parameters is summarized below.

2.3.1 Heat Flux

Due to the importance of the heat transfer processes in the ignition of solid fuels, one of the main variables to investigate is the applied radiant heat flux. The thermal behavior depends on the type of specimen analyzed, whether it is thermally thick, thermally thin or an intermediate behavior between the two. In any case it has been found that the time to ignition decreases with increasing external heat flux [21, 22]. This parameter mainly affects the heating time: as the applied heat flux is increased, the solid will heat up faster, leading to an overall shorter ignition delay time. Interestingly enough, the trend is not followed by the surface temperature at ignition. A substantial number of polymers present an ignition temperature that is relatively insensitive to the external heat flux for values away from the critical heat flux (q”>17 kW/m²) [6, 12, 21].

The applied heat flux has other effects in addition to reducing the solid heating time. Drysdale and Thomson [12] and Rich et al. [4] both found the critical mass flux at ignition to decrease with the applied radiant heat flux even though the analysis they used for the critical mass flux (B-number theory) suggests there should be no dependency with external flux as per Eqs.2.4-2.5. They suggested this finding was due to increased oxidative pyrolysis present at higher heat fluxes. At higher heat fluxes the pyrolysis reaction within the solid is confined to a thinner layer near the solid surface which facilitates oxygen penetration, hence enhancing the oxidative pyrolysis process. Increased thermal oxidation leads to a higher proportion of oxygenated compounds being released from the decomposition process at higher heat fluxes. Higher oxygenated compounds reduce the effective heat of combustion, requiring a larger mass flux of fuel vapor in order to ignite.
A similar explanation for the effect of heat flux on the fuel mass flux can be found in Kashiwagi and Ohlemiller [23]. At higher heat fluxes the polymer degradation happens in a thinner thermal layer with shorter exposure times (since the solid heats up faster). The fuel vapor bubbles formed during this type of process are smaller and are released to the surface more frequently than at lower heat fluxes. The high heat flux increases the polymer surface temperature leading to a decrease in the degrading polymer's viscosity. The fuel bubbles find less resistance to move in a lower viscosity zone and reach the surface where they are released in a quicker manner. This process explains why higher mass fluxes of fuel vapor are to be expected if the samples are exposed to higher heat fluxes. To tie it to the critical heat flux at ignition, it was suggested that in a high fuel mass flux zone the diffusion and mixing of the oxidizer with the fuel vapor is more difficult, therefore needing a larger mass flux at ignition to reach flammable conditions.

2.3.2 Oxidizer Flow Velocity

The effect of air flow velocity on ignition can be easily analyzed from a heat transfer perspective. Increased air flow velocities enhance the effective convective heat transfer and therefore lead to larger convective heat losses from the heated material to its surroundings. With larger heat losses, it will take more time to heat the solid to pyrolysis temperatures. This agrees with the results from Cordova et al. [21] and McAllister et al. [22] which presented ignition delay time results with PMMA exposed to a constant heat flux at various air forced flow velocities, at standard pressure and at pressures below one atmosphere respectively. This last reference also shows how increased oxidizer flow velocity can produce rise in the estimated value of the CHF of 30% approximately.

Additionally, the critical mass flux at ignition is also dependent on the convective heat transfer coefficient, \( h \). Spalding’s B number theory (Eq. 2.4) suggests that the critical mass flux at ignition will increase with larger forced flow velocities, since they increase \( h \). This explanation is in agreement with the experiments and analytical results of Rich et al. [4].

2.3.3 Microgravity

The acceleration of gravity (or lack of) seems to have a minor effect on the LFL of materials [24]. However, under microgravity the heat and mass transport mechanisms are very different from those experienced in normal gravity conditions. The lack of buoyant flows reduces the convective heat transfer, generating transport and mixing times that are typically dominated by diffusion (at least in quiescent conditions). Hence, reaching a flammable mixture might take more time in low gravity but materials will heat up more
quickly. In microgravity overheating electrical components which are designed to be cooled under normal gravity represent a common and more frequent ignition threat [25]. Other unusual events that might take place in absence of a downward gravitational force include the ejection of hot particles by burning plastics, which could represent new ignition sources [26]. As these examples show, the mechanisms that initiate ignition could be very different and more frequent in low gravity.

For low-gravity environments with forced flows such as those induced by the currents of air conditioning systems, the critical heat flux for ignition could be up to half of the value in normal gravity [27]. Ignition delay times also have been reported to decrease under microgravity low-flow velocity conditions. There are not many experiments in this area, but enough to affirm that low-velocity flows in microgravity conditions increase the ease of ignition.

\subsection{2.3.4 Oxygen Concentration}

Theoretically oxygen should not affect tremendously the gas-phase processes in piloted ignition. Per Eq. (2.3) a higher oxygen concentration leads to a faster reaction rate. However, the piloted ignition is associated with reaching flammable conditions at the pilot. Since the lean flammability limit is not affected by varying the oxygen concentration, this is not expected to be an important variable in the process [28].

On the other hand, oxygen can affect the solid phase processes associated with ignition. It has been shown that if the solid presents oxidative degradation in addition to thermal degradation, the volatile production rate will increase [4, 6, 23]. Thermogravimetry studies of the decomposition of PMMA in both air and a pure N\textsubscript{2} atmosphere [29] suggested that oxygen has two effects on the pyrolysis of PMMA: it has a stabilizing effect at low temperatures (which increases the initial decomposition temperature with respect to inert atmospheres) but at high temperatures the polymers decompose more quickly with significantly lower activation energies describing the decomposition processes. The overall effect of these two competing effects is a pyrolysis rate that increases with O\textsubscript{2} concentration. Oxidative thermal degradation is known to be both a more complex and faster process than purely thermal degradation once the solid has reached decomposition temperatures.

Several authors [28] have shown analytically and experimentally that there is a limiting oxygen concentration below which ignition will not occur. This value depends on the experimental configuration but it is suggested to be in the vicinity of 15\% O\textsubscript{2}. Ignition delay times from experiments [30] with plywood at a range of heat fluxes and oxygen concentrations below or at 21\% O\textsubscript{2} by volume increased so slightly with decreasing oxygen concentration, that it was suggested that there was no relationship between both as long as
conditions were above the LFL. Cordova et al. [21] saw a slight decrease in ignition delay time when the oxygen concentration was increased from 21% to 25% by volume but noticed no significant change when the oxygen concentration was further increased. It has been suggested that the unclear trends with oxygen are subjected to differences depending on the external heat flux level applied. Recent work [22] that compared ignition delay tests with PMMA at 21% and 32% $O_2$ showed a slight reduction of the time for ignition with higher oxygen concentrations. This seems to be in agreement with the results of Ref. [21], but showed a larger reduction probably since the experiments in [22] are at lower heat flux levels and near the CHF. In summary, the effect of oxygen concentration on ignition delay time varies somewhat in the literature, but there is consensus on ignition delay time slightly decreasing when the oxygen concentration is increased from 21% to 25-32% $O_2$ by volume.

The effect of oxygen concentration on the critical mass flux at ignition was analyzed by Rashbash et al. [9] and later by Rich et al. [4]. These authors reported a large decrease in the critical mass flux at ignition ("fire point") when oxygen was increased from 18% to 21% by volume, but the trend was unclear for oxygen concentrations above 21%. However the mass flux at the "flash point" was found to be insensitive to oxygen concentrations for the whole range tested (15-28% $O_2$), confirming that the LFL conditions should not be greatly affected by oxygen.

2.3.5 Pressure

Most of the literature on the effects of pressure on ignition is oriented towards the engine community and therefore focus on total ambient pressures substantially above one atmosphere. There are limited studies of the effect of sub-atmospheric pressure on the ignition of solid fuels.

Total ambient pressure can affect the ignition of solid fuels indirectly through its effect on the LFL. However, for a wide range of materials and pressures the LFL does not change significantly with pressures [6]. Pressure can affect both the gas phase processes (through its influence on the convective heat transfer or its influence on the chemical reaction rates) and the solid phase process. If pyrolysis is assumed to follow an Arrhenius type behavior (Eq. 2.1) then theoretically it should not be affected by changes in the total pressure. This is in agreement with the results from Koptelov and Karyazov [31]. They found the thermal decomposition of PMMA to be insensitive to pressure during thermogravimetry and calorimetry tests in different inert gases at pressures ranging from 1.3 kPa to 13 MPa. However, the pyrolysis rate of PMMA is very sensitive to oxygen concentration [29] so it is unclear if the trends would remain if the previous analysis were performed in air. Additionally, pressure can affect the distribution of decomposition gases formed [32], which could affect the ignition process depending on the igniter location.
Pressure effects on ignition have been investigated at high elevations conditions. Experiments performed in a Tibetan experimental station [33] have shown that autoignition of wood occurs earlier with faster decomposition rates at high altitudes than at sea level pressure conditions. Piloted ignition experiments that also compare results in Tibet with sea level measurements [34] show a decrease in ignition delay time with increasing altitude.

Piloted ignition results from McAllister et al. [22, 35] with thick slabs of PMMA show similar trends: ignition delay time decreases with total pressure. This decrease in ignition times was attributed primarily to the reduction in convective heat losses from the heated material to its surroundings in lower pressure environments. Reduced heat losses lead to a solid fuel heating more quickly and therefore reducing the ignition time. These authors reported a “U-shape” dependency of the ignition delay time with total pressure: at a certain point if the pressure was too low, it began to affect the chemical kinetics by slowing down the reaction rate. For those very low values of total ambient pressure (around 13-27 kPa) the ignition delay time increased with decreasing pressure. The critical mass flux at ignition was not measured in this work but it was hypothesized that perhaps a lower critical mass flux at ignition was needed at lower pressures.

In contrast to McAllister et al. [22, 35], Olson [7] reported experimental results of piloted ignition of a thermally thin fuel (cellulose) with the opposite trends: ignition delay time increased at lower total pressures. This is attributed to the very high heat flux levels used in these experiments. For thin fuels exposed to very high heat fluxes, the heating times are comparable to the chemical induction times and mixing times. Since the reaction rate decreases with reduced pressure, and the induction time is inversely proportional to the reaction rate, it is not surprising to find that low pressure increased the chemical induction time and the overall ignition delay time. If the chemistry is the dominant effect such as in Olson et al. [7] or at the very low pressures presented by McAllister et al. [35], one should expect the ignition delay time to grow as the pressure is reduced.

The effect of pressure seems to be somewhat related to the oxygen concentration. Additional studies performed with aerospace materials [36] determined the flammability pressure thresholds, i.e. maximum pressure in which the sample would self extinguish in 99.8% O₂ environments to be between 2.7 and 6.2 kPa. This means that materials might be flammable in oxygen in pressures as low as 2.7 kPa, a much lower value than is generally to be expected. The mechanisms responsible for the trends found with combined oxygen and low pressures conditions are complex and not entirely well understood. The work presented below will try to shed some light into the determining processes involved.
2.4 References


CHAPTER 3 - EXPERIMENTAL RESULTS

3.1 Introduction

Fires can occur in lower than standard atmospheric pressure either in natural high altitude environments or inside pressurized vehicles such as aircraft and spacecraft. Ambient pressures at high altitude locations such as Lhasa, a city in Qinghai-Tibet Plateau at approximately 3650 m above sea level are about 67 kPa, which is 34% lower than standard sea level atmospheric conditions. Although the majority of the world population lives within 500 m of sea level conditions, there are approximately 0.4 billion persons living at elevations above 1500 m [1], with typical ambient pressures around 85 kPa or 15% lower than standard sea level.

Air composition and pressure are not constant throughout Earth’s atmosphere. Standard sea level conditions are 101.325 kPa (or 1 atm) and 15°C. However, these conditions vary significantly with elevation. The International Standard Atmosphere (ISA) accounts for the differences in air properties with altitude through a linear temperature distribution. Other properties such as pressure are derived based on physical relations such as ideal gas law. In the troposphere air temperature is assumed to decrease with altitude at a rate of a=6.5 °C/km. Using this linear temperature distribution \(T = T_0 - az\), and ideal gas law \(\rho = P/RT\) combined with the expression for hydrostatic pressure variation with height \(dP/dz = -\rho g\), one can integrate to determine an approximate relation between pressure and altitude, \(z\):

\[
P = P_0 \left(\frac{T_0}{T_0 - az}\right)^{\gamma/aR}
\]

Figure 3.1 shows the variation of pressure with altitude using the expression in Eq. 3.1 with the data from Ref. [1], About 7% of the world population lives above 1500 m. Fires are a concern at high elevation metropolitan areas just as much as they are at sea level locations, but the main issue is that flammability behavior in hypobaric (low pressure) environments is not well understood. Additionally most of the fire safety material certification is performed at sea level conditions and there is limited research on how to extrapolate results for low altitudes. Nonetheless experiments conducted in Lhasa on the spontaneous ignition of wood [2] have shown a considerable reduction in ignition delay time when compared to similar experiments at standard atmosphere. This indicates that perhaps material flammability testing is not being conducted at the most conservative environmental conditions.

Moreover, the concern for fire hazard intensifies if high elevation is combined with increased oxygen concentration. Air typically contains 21% by volume oxygen, but as the pressure is lowered the partial pressure of oxygen also decreases. The human body needs...
an oxygen partial pressure near sea level values in order to breathe comfortably. Lower partial pressures of oxygen lead to hypoxia or altitude sickness. For example, in order to reduce the effects of altitude sickness of their guests a hotel in Cuzco, Peru is evaluating an oxygen enrichment system for its facilities. Recent large scale experiments in Peru [3] show that fire behavior in those conditions differs substantially from that at standard sea level and needs to be better characterized.

![Figure 3.1: Variation of atmospheric pressure with altitude](image)

Hypobaric environments can be also found inside pressurized vehicles. Typically aircraft cabin air is pressurized to an equivalent “cabin altitude” between 1500-2400 m (84-75 kPa) following FAA regulations [4]. Lower inside cabin pressure reduces the aircraft structure fatigue risks by minimizing the pressure differential exerted on the aircraft fuselage. The cabin inner pressure varies depending on the flight segment, altitude level and route, but the general rule is to keep the equivalent altitude as close to sea level as practical for passenger comfort, without exceeding a cabin-to-outside pressure differential of 59 kPa (8.6 psi). In-flight fire safety is one of the industry’s major concerns, yet again there is limited information on how the reduction in pressure affects ignition inside a vehicle full with thermoplastics used for casings, coverings, and furniture.

Space exploration vehicles and Lunar/Mars stations can also have reduced pressure internal environments. As mentioned in Chapter 1, the cabin environment of NASA’s latest generation of spacecraft (Orion Crew Exploration Vehicle, Altair Lunar Lander) and future lunar habitats has lower pressures and increased oxygen concentrations (55-70 kPa, 27-32% $O_2$) than standard atmosphere [5]. These new environment conditions present several advantages, such as lower internal vehicle pressures, a reduced risk of decompression
sickness during extra-vehicular activities (EVA) and shorter pre-breathing times required for EVA preparation. However, they may increase material flammability due to higher flame temperatures (attributed to enhanced oxygen) and reduced convective heat losses from heated surfaces (attributed to reduced pressure). They may also affect gas phase processes related to material flammability such as time to reach a flammable mixture in the gas, and the gaseous mixture ignition induction time. These effects may have potential consequences in the evaluation of the fire risk of materials under low pressure environmental conditions and consequently warrant attention.

Recent work by McAllister et al. [6, 7] on piloted ignition of thick samples of PMMA (Poly-methyl methacrylate) under external radiant heating shows that ignition delay times decrease with decreasing pressure and increasing oxygen concentration. In contrast, Olson [8] found the opposite trend with pressure for thin fuels: ignition delay times decrease with increasing pressure and increasing oxygen concentration for thin fuels exposed to very high heat fluxes and ignited by a hot wire energized in contact with the fuel sample. It should be noted that the ignition process in both types of experiments is dominated by very different modes of heat transfer. In the first type of experiments [6, 7] the primary mode of heat transfer is the applied radiant heat flux on the sample. Convection to the surrounding boundary layer also plays a key role. The heat flux levels used in [6, 7] are low and consequently the fuel heating times are long (on the order of 10 minutes), significantly larger than the mixing or chemical induction times. In the second type of experiments [8] the primary mode of heat transfer to the fuel is believed to be the conduction from the hot wire igniter, although radiation might be a factor too. The heating times in these experiments are extremely short (on the order of 0.1 seconds) to the point that the determining process seems to be the chemical induction time. The effect of reducing ambient pressure varies in these two processes, i.e. solid heating or chemical induction in the gas phase, and they each influence solid fuel ignition to different degree in each type of experiment. Solid heating is enhanced by reduced pressure whereas gas-phase chemical reactions are typically hindered in low pressure ambients. Therefore it is not surprising to find different trends with decreasing ambient pressure in McAllister et al. [6, 7] and Olson [8].

Additional studies performed with aerospace materials [9] determined the flammability pressure thresholds, i.e. maximum pressure in which the sample would self extinguish in 99.8% O₂ environments to be between 2.7 and 6.2 kPa. In other words, materials might be flammable in oxygen in pressures as low as 2.7 kPa, a much lower value than is generally to be expected. Thus, the mechanisms responsible for these trends with ambient pressure are not entirely understood but the heat transfer mode leading to ignition might play a fundamental role. Furthermore, the combination of low pressure with high oxygen concentration might be more complex than it seems at first glance.

However, since piloted ignition is associated with reaching a critical mass flux from the fuel surface [10-12], it has been hypothesized that the reduction in ignition time with decreasing pressure reported in Ref. [6, 7] is due to two effects: firstly, a decrease in the
heat transfer coefficient that reduces the heat losses from the solid fuel to its surroundings, leading to a faster solid heating process, and secondly, a decrease in the mass flux from the fuel surface necessary to generate a flammable mixture near the igniter.

Although the critical mass flux at ignition has been previously measured at ambient pressures for a range of oxygen concentrations and variable external heat fluxes [11, 12], no other experiments have been identified where mass loss rates at ignition are measured under reduced atmospheric pressure conditions. Therefore, the objective of the present work is to explicitly measure the fuel mass flux at ignition in reduced pressures to verify experimentally the mechanisms leading to the reduction of the piloted ignition delay with pressure.

3.2 Description of Experiments

Piloted ignition experiments were performed in a controlled-atmosphere version of the Forced-flow Ignition and flame Spread Test (FIST) apparatus developed at UC Berkeley under NASA sponsorship [13]. The approach followed for the experiments is analogous to that of Ref. [12] but in a similar set-up to that presented in Ref. [6, 7] for Space Exploration Atmospheres (SEA). Figure 3.2 shows a simplified schematic of the FIST apparatus. It consists of a small-scale combustion wind tunnel and supporting instrumentation that is mounted horizontally in a sealed pressure vessel (Fig. 3.3) that allows tests to be performed at a range of ambient conditions.

![Figure 3.2: Schematic of FIST tunnel.](image)

The wind tunnel is 39.2 cm long in the streamwise direction, 14.9 cm wide, and 8 cm high. A fan at the downstream end of the tunnel induces a forced-flow of oxidizer through the tunnel that recirculates inside the pressure vessel. Test samples (3 cm by 3 cm by 1 cm thick) positioned in the bottom wall of the flow tunnel are irradiated by an infrared radiant...
heater mounted directly above that produces a uniform heat flux over the sample surface. The material tested was commercially available black PMMA (Type G, Atoglas). The selection of black PMMA was made to have a material with an emissivity close to unity. Ignition is induced with a 3-mm diameter coiled Kanthal wire mounted 10 mm downstream of the sample and centered 5 mm above the tunnel wall.

The FIST-SEA apparatus [6, 7] was redesigned and retrofitted in order to conduct mass loss experiments. The hardware changes to the FIST-SEA apparatus included raising the wind tunnel inside the pressure chamber in order to incorporate a load cell underneath the sample. This load cell had to be located on a variable surface (or ‘elevator’) to permit sample loading and unloading between tests.

Figure 3.3: FIST tunnel and pressure chamber.
The surface of the wind tunnel was to have as little change as possible with previous configurations to facilitate the comparison with earlier FIST-SEA results [6, 7]. The main design requirements were that the fuel sample be positioned flush with the wind tunnel bottom surface and that the sample holder not be in direct contact with the tunnel walls, by simply resting on top the weigh cell to enable the measurement of mass. Figure 3.4 shows the design of the elevator mechanism that holds the weigh cell and polymer sample.

The solid fuel sample is placed inside an aluminum sample holder insulated with Cotronics ceramic paper (2 mm thick) on the sides and Cotronics insulating board (RESCOR-360H, 28 mm thick) on the bottom (inside the sample holder). The aluminum sample holder is inserted in an opening in the bottom of the wind tunnel. It is ensured that the holder is not touching any of the tunnel surfaces, because contact with the tunnel walls could invalidate the mass loss measurements due to friction. The aluminum sample holder rests on a slab of marinite insulating material (25 mm thick by 102 mm long by 46 mm wide) that is used to position the sample holder on the weigh cell. The marinite support has the objective of covering the weigh cell plate to avoid direct radiation from the infrared heater reaching it. Figure 3.5 (a) shows the aluminum sample holder and the marinite support.

The weight of the polymer sample is measured continuously with a Sartorius WZ214S data logging scale with 0.1 mg resolution that is positioned below the sample holder. Figure 3.5 (b) shows the sample holder placed on top of the weigh cell (data logging scale) inside the tunnel in the configuration used during the experiments. Because the mass loss rate is very small, the measurements are sensitive to external effects such as variations in the gas flow over the sample, room vibrations, etc. To reduce the potential error introduced by these effects at least four tests are conducted for each data point and the values averaged.
A photograph of the sample surface inside the wind tunnel is shown in Fig. 3.6. In this picture it can be seen that there is a small gap (1.5 mm approximately) between the sample holder and tunnel structure that enables the free movement of the sample and, therefore, allows mass loss measurements. Figure 3.6 also shows the igniter coiled wire that induces ignition in the gas phase. A K-type thermocouple is used to monitor the igniter temperature. Previous FIST work [12, 13] highlighted the importance of utilizing a repeatable igniter (position and intensity). It was determined that an igniter at a temperature above 1000 °C minimized variations in ignition delay times.

One K-type thermocouple was mounted on the top surface of the sample, as shown in Fig. 3.5. (a) and Fig.3.6. Although care was taken to ensure that the thermocouple bead was embedded flush with the sample surface, the measured temperature is only an approximation of the actual surface temperature due to potential movement of the thermocouple during heating of the material. However, these inaccuracies are not sufficiently large to affect the trends observed in the experiments presented below.
To perform a test, the fan is turned on and the flow is allowed to reach a steady state. The infrared radiant heater is then turned on in order to heat the sample, and the igniter is energized after the measured surface temperature reaches 280°C. The pyrolyzed vapors leave the surface of the solid fuel and convect and diffuse downstream toward the igniter, where the mixture may ignite if the conditions are appropriate.

The ignition time was measured as the elapsed time between initiation of the external heat flux and permanent attachment of a diffusion flame at the sample surface (burning). Time to ignition is judged visually and confirmed by inspection of surface thermocouple temperature traces and changes in the mass loss.

3.3 Atmospheric Pressure Results

Prior to conducting reduced ambient pressure experiments, several tests were performed with air as an oxidizer at sea level atmospheric pressure (100 kPa, 21% O\textsubscript{2} by volume) to ensure the proper operation of the experimental set-up. These tests are used as a baseline for comparison with future tests.

![Figure 3.7: Test at 100 kPa, air (21% O\textsubscript{2}), flow velocity = 0.4 m/s, q''=16 kW/m\textsuperscript{2}.](image-url)
A sample test at 100 kPa with air is shown in Figure 3.7. The external radiant heat flux applied is 16 kW/m² and the forced airflow velocity is 0.4 m/s. The data from the surface thermocouple and the load cell are used to obtain histories of surface temperature and sample mass loss, respectively. The top curve in Fig.3.7 corresponds to the sample mass loss and the bottom curve corresponds to the sample surface temperature. Sample surface temperature and sample mass were recorded until ignition was observed. Time zero corresponds to the application of the external heat flux and the sudden change in slope in both temperature and mass loss corresponds to the onset of ignition. The fuel mass flux at ignition (or mass loss rate at ignition) is calculated as the slope of the mass loss time history data during the 5 second window prior to the observed ignition.

3.3.1 Applied Radiant Heat Flux

The thermal conductive behavior of the solid has a marked effect on the solid pyrolysis. In relation to their thermal behavior during the heating process, solid fuels are usually classified in two distinct groups: thermally thin and thermally thick [14]. Thermally thin solids have no spatial internal temperature gradients and are typically on the order of 1 mm thick. Examples of thermally thin solids can be sheets of paper, plastic films, fabrics etc. Thermally thick solids in contrast have distinct temperature gradients through their thickness and the thermal wave penetrates the solid during the heating process but does not reach the back face of the solid. They behave as a semi-infinite medium since the back-face boundary condition has little effect on the solution of the problem.

Based on the sample thickness of the experiments presented in this work (10 mm) one is to expect thermally thick behavior. However, due to the long ignition times (~ 800 seconds at 100 kPa), the type of thermal behavior of the samples is questionable. Ignition times for thermally thin solids have a dependency on the external heat flux of $t_{ig} \sim 1/q''_{ext}$. Thermally thick solids show ignition delay times that vary with the external heat flux as $t_{ig} \sim 1/q''_{ext}^2$ [14]. Therefore, measuring the variation of ignition times with the external heat flux will determine the thermal behavior of the sample.
Figure 3.8 shows ignition delay time data for \( p = 1 \) atm and airflow velocity \( v = 0.3 \) m/s at a range of applied heat flux values. The curve presents the expected trends: higher applied radiant heat flux leads to shorter ignition times. Extrapolation of curves such as the one presented in Fig. 3.8 to infinitely long times (\( t_{\text{ig}} \rightarrow \infty \)) is typically used to determine the critical heat flux (CHF) for ignition or limiting value below which ignition will not occur [15].

To determine whether the data fits better to the thermally thin or thermally thick criterion, the physical thickness \( d = 10 \) mm is compared to the thermal penetration depth \( \delta_t = \sqrt{\alpha t} \), where \( \alpha \) is the thermal diffusivity (\( \alpha = k/\rho c \)) and \( t \) time. Using typical property values for PMMA such as \( k = 0.19 \) W/mK, \( c = 1400 \) J/kgK and \( \rho = 1190 \) kg/m\(^3\) [15] and the ignition times (\( t \)) presented in Fig.3.8 the thermal penetration depths for these tests are determined, yielding values between 8 and 11 mm. Hence, it can be confirmed that the thermal behavior of the samples in these tests is neither purely thermally thick (\( d \gg \delta_t \)) nor purely thermally thin (\( d \ll \delta_t \)). It seems that the ignition times are long enough that the thermal wave penetrates a substantial part of the 10 mm sample thickness, resulting in thermally “intermediate” behavior. This information will be useful when designing a numerical model (Chapter 5) that describes the solid fuel ignition experiments presented below.

3.3.2 Air Flow Velocity

A series of experiments at a range of airflow velocities (0.2- 0.6 m/s measured at the fan inlet) were conducted with air at 100 kPa and a constant external heat flux of 16 kW/m\(^2\). The objective was mainly to determine if the trends observed were comparable to previous
literature results and to discover any possible anomalies with the test apparatus retrofit. Figure 3.9 shows that ignition delay time increases with oxidizer flow velocity. This is explained by the cooling effect of the forced flow, i.e. higher velocity flows enhance the sample surface cooling, increasing the convective heat losses of the heated material to its surroundings. Therefore a critical sample surface temperature such as the ignition temperature will be attained later on. This is consistent with results from [6], where ignition delay results were presented for a range of airflow velocities and external heat flux values.

Figure 3.9: Ignition delay time vs. airflow velocity for $P=100$ kPa, $q^\infty=16$ kW/m$^2$. Data points are the average of four tests, vertical bars correspond to standard error.

Figure 3.10 shows the raw data from four representative experiments at different airflow velocities at a constant radiant heat flux of 16 kW/m$^2$. Ignition occurs when the sample surface temperature trace presents an abrupt change in slope. The comparison of the four surface temperature traces in Fig.3.10 indicates not only that ignition occurs significantly earlier at lower airflow velocities but also that the polymer samples are heating at a faster rate at low velocities. Reduced airflow velocities decrease the effective convective heat transfer coefficient. The reduction in the heat transfer coefficient leads to a decrease in convective heat losses from the solid to its surroundings, heating up more quickly. It is also interesting to note that the surface temperature at ignition does not vary notably for this range of airflow velocities (values are around $316-322^\circ$C for the data in Fig. 3.10) while the ignition time can be more than double the value when the airflow velocity is increased from 0.2 m/s to 0.5 m/s.
It should be noted that buoyancy induces vertical flow velocities on the order of 0.3 m/s. The experiments performed to determine the effect of pressure and oxygen concentration that will be presented below were conducted at a constant flow velocity of 0.4 m/s. Therefore, it is to be expected to find mixed forced flow and natural convection conditions during the experiments. This buoyant induced flow is due to the density difference between the cold and the hot gases immersed in a gravitational field. When the total pressure is reduced, the cold flow will have a lower density and therefore, the density difference that drives the buoyant flow will be reduced. Consequently, the buoyant flow will become less important and the resulting mixed flow will not have the same exact characteristics throughout the range of pressures presented below.

3.3.3 Comparison of Mass Loss Rate at Ignition with Literature

Measuring the mass flux at ignition with accuracy is notoriously difficult [15] primarily because the mass change is small, it is very sensitive to external vibrations. Additionally the experimental determination of the mass flux at ignition has been approached in different ways in the past. The variations reside in how the derivative (or mass flux) is calculated from the mass loss data obtained experimentally.

Figure 3.10: Surface temperature vs. time for four representative experiments at 100 kPa at a range of airflow velocities
Drysdale and Thomson [10] calculated the mass flux at ignition by fitting a cubic expression to the mass loss curve up to the point of ignition, differentiating it and solving for t= time of ignition. Rich et al. [12] determined the mass flux at ignition by a finite difference method applied to the 10-14 second period around the point of ignition. Rashbash, Drysdale and Deepak [11] calculated the mass flux as the limiting slope of the mass loss curve at the moment a flame established. The approach followed here was similar to [11]: the mass flux at ignition was calculated using the slope of the mass loss time history curves in the 5 second window prior to observed ignition and divided by the front surface area of the sample (9 cm$^2$).

Figure 3.11 shows the mass flux at ignition results measured at 100 kPa for a range of air flow velocities. This data corresponds to the mass flux measurements of the same experiments presented in Fig. 3.9 where the ignition delay results were presented. Figure 3.11 compares the results of this work obtained in the FIST pressure chamber experimental set-up with previous literature results, also performed in the FIST apparatus [12]. The concept is the same in both apparatus, however the tunnel from Ref. [12] has a longer length and it is exposed to the laboratory environment at sea level atmospheric conditions.
The value for mass flux at ignition for PMMA varies substantially throughout the literature, but it is generally between 1.9 – 3.2 g/m^2s [16]. Table 3.1 presents a summary of the literature values for the critical mass flux at ignition also referred to as “fire point” for PMMA. The polymer manufacturer and fabrication method also seem to affect the measured values. Considering the variability of mass flux results presented in general in the literature, the agreement between both sets of data in Fig.3.11 is remarkable.

**Table 3.1: Mass flux at ignition literature values**

<table>
<thead>
<tr>
<th>Source</th>
<th>Convective Conditions</th>
<th>Heat Flux (kW/m^2)</th>
<th>Mass Flux at Ignition (g/m^2s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drysdale &amp; Thomson</td>
<td>Natural convection</td>
<td>13</td>
<td>1.80-2.05</td>
</tr>
<tr>
<td>1989 [8]</td>
<td></td>
<td>19</td>
<td>1.85-2.05</td>
</tr>
<tr>
<td>Rich [12]</td>
<td>Forced flow, 1 m/s</td>
<td>18</td>
<td>1.8</td>
</tr>
<tr>
<td>Tewarson [17]</td>
<td>Natural and mild co-flow convection</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>Kashiwagi [18]</td>
<td>Natural convection</td>
<td>9-30</td>
<td>0.6-0.9</td>
</tr>
</tbody>
</table>

### 3.4 Low Pressure Results

Piloted ignition tests were performed with an applied radiant heat flux of 16 kW/m^2 and a forced air flow of 0.4 m/s, for ambient pressures ranging from 7 - 100 kPa to determine the effect of total pressure on ignition times and mass flux at ignition.

#### 3.4.1 Visual Observations

Visual observation of the fuel sample surface and flame characteristics give a first indication of the significant influence that ambient pressure has on the mechanisms leading to the ignition of the PMMA and on the characteristics of gas above the sample surface. Figure 3.12 shows photographs of two tests, one at 21 kPa (a) and one at 83 kPa (b). The images in Figure 3.12 (top row) were taken during the heating process, approximately at one minute before ignition. The surface behavior changed significantly depending on the ambient pressure. At lower pressures the bubble formation that takes place during the pyrolysis of the PMMA occurred earlier, the size of the bubbles was considerably smaller and the bursting of the bubbles occurred in a less violent manner. Prior to sustained burning conditions, most of the ignition events were accompanied by visible flashes. These flashes were more noticeable and frequent at lower pressures. The characteristics of the
flame that is established over the solid surface after ignition is also notable different (Figure 3.12 – bottom row). At low pressure the flame is bluer, of rounder shape and more separated from the solid surface than at standard pressure. These visual observations indicate that the effect of pressure on the ignition of solid combustibles may be complex, affecting the heating of the solid, its pyrolysis or gasification process, and the characteristics of the gas above the solid surface.

![Visual Observations at Different Pressures](a) 21 kPa (b) 83 kPa

Figure 3.12: Visual Observations at Different Pressures (a) 21 kPa and (b) 83 kPa. Pictures above were taken 1 min before ignition, while those below correspond to sustained burning of the solid fuel.

### 3.4.2 Experimental Results

The data from the surface thermocouple and the load cell are used to obtain histories of surface temperature and sample mass loss, respectively. Figure 3.13 compares measured surface temperature and mass loss for four representative experiments performed at ambient pressures of 21, 55, 83 and 100 kPa. The top curves correspond to the sample mass loss and the lower curves to surface temperatures. Time zero corresponds to the application of the external heat flux and the sudden change in slope in both temperature and mass loss corresponds to the onset of ignition. It can be seen that the
ignition time decreases considerably as ambient pressure is reduced, which confirms previous results in complementary work by Ref. [6, 7]. These four tests show a clear difference in the surface temperature and mass loss histories with pressure. As the pressure is reduced, the surface temperature and mass loss increase faster. The differences in the traces reveal the influence of pressure on the sample heating. The fluctuations in the measured surface temperature appear to be the result of movements of the thermocouple bead due to the PMMA melting and the bubbling during pyrolysis that as indicated above is more intense at increased pressure. The surface temperature at ignition is slightly higher at lower pressures. The mass loss traces show that the cumulative mass loss prior to ignition decreases as pressure is reduced. This is a novel observation that may have notable implications in material flammability issues. Data similar to that presented in Fig. 3.13 are used to calculate the variation with pressure of the time to ignition, the total mass lost at ignition, and the mass flux at ignition.

Figure 3.14 shows the measured variation of the ignition delay time \( t_{ig} \) with pressure. For the range of pressures tested the ignition time decreases linearly with ambient pressure as: \( t_{ig}=4.57\cdot P + 358.51 \) (\( t_{ig} \) in s and P in kPa). Ignition was not attained for pressures below 10 kPa. For the range of pressures considered by NASA for the latest space
exploration vehicles (58.6 - 68.6 kPa), the ignition delay time is reduced by 18-24% when compared to sea level conditions. In the present experiments the boundary between ignition and no ignition at low pressure is sharper than that observed in the work of Ref. [6]. This may be due to differences in the air flow pattern between the two experimental set-ups in part created by flow perturbations caused by the air gap surrounding the isolated sample holder needed for mass loss measurements and by the a reconfiguration of the tunnel ceiling.

**Figure 3.14:** Ignition delay time vs. pressure. Data points are the average of four tests and vertical lines represent the standard error.

\[
t_{ig} = 4.57 \cdot P + 358.51
\]

\[R^2 = 0.98\]

Figure 3.15 shows the average total mass loss for the tests performed at different pressures. The total mass loss is calculated as the sample initial mass minus the sample mass at ignition. On average, samples show lower mass loss for ignition under reduced ambient pressure. Although this is not a typically measured quantity, it provides an indication that the total amount of fuel volatiles required for ignition is smaller at lower pressures.
Figure 3.16 depicts the measurements of the fuel mass flux at ignition with pressure. This is an important parameter in the fire science literature because it describes the process leading to the ignition of a solid combustible material in a more physically correct manner than other ignition criteria, such as a critical surface temperature [11, 12]. It is related to the attainment of a flammable mixture near the ignition source (pilot) and often referred to as the critical mass flux, critical mass loss rate, or critical volatile flow rate at ignition [19]. It is seen that the fuel mass flux at ignition also decreases linearly with pressure, although the pressure dependence is weaker than that of the ignition delay time, as shown by the gentle slope of the regression line: $\dot{\omega} = 0.005 \cdot P + 1.48$ (P in kPa and $\dot{\omega}$ in g/m$^2$s). The mass flux at ignition varies by 8-11% for the range of pressures considered by NASA (58.6 - 68.6 kPa) when compared to 101 kPa. The mass flux at ignition obtained at sea level conditions (Fig. 3.16, approximately 2.1 g/m$^2$s for 100 kPa and an incident heat flux of 16 kW/m$^2$) is in good agreement with previously reported values (Table 3.1).
3.4.3 Analysis of the Results

The piloted ignition of a thermally irradiated combustible solid can be described as a sequence of three events [14, 20]: the solid is heated and pyrolyzed; the pyrolyzate are transported and mixed with the oxidizer to form a combustible mixture; and finally this mixture is ignited by the pilot. As a result, the ignition delay time can be viewed as the sum of three characteristic times: heating time, mixing or transport time and chemical induction time. Depending on the ignition process and ambient conditions, the relative importance of each of these steps might vary. For ignition under low external heat fluxes, such as those presented in this paper, the solid heating time is of the order of hundreds of seconds which is significantly larger than the transport/mixing time and the thermal induction time, which are on the order of seconds to milliseconds. Since changes in ambient pressure influence the heating time, they consequently will have a first order effect on the ignition delay time.

3.4.3.1 Solid Heating

For solid heating from an external radiant flux, pressure affects the solid heating time directly through the convective heat losses from the solid surface to the oxidizer flow. For forced flow over a flat plate, the thickness of the thermal boundary layer ($\delta_t$) depends on the problem parameters in the form $\delta_t \sim x/(Re^{1/2} Pr^{1/3})$. The Prandtl number is not a
function of pressure, but the Reynolds number is directly proportional to pressure through the density (Re=ρUx/μ), resulting in a pressure dependence of δt~1/P^{1/2}. Consequently as pressure is reduced, the thickness of the thermal boundary layer increases and the temperature gradients at the solid surface are reduced, resulting in decreased heat losses from the solid to the surrounding gas.

An analogous result can be reached by analyzing the effect of pressure on the convection heat transfer coefficient. For forced laminar flow the heat transfer coefficient is of the form h~Nu_F ~ Re^{1/2} Pr^{1/3} [21], resulting in h~P^{1/2}. Similarly, for pure natural convective flow the heat transfer coefficient varies as h~Nu_N ~ Gr^{1/4} Pr^{1/4}. If the oxidizer is assumed to behave as an ideal gas, the Grashof number is proportional to the pressure squared, resulting in h~P^{1/2}. For mixed forced and free flow over a flat plate the heat transfer coefficient can be approximated as a combination of the forced and natural convection correlations of the form: Nu_{mixed}^{n} = Nu_{F}^{n} + Nu_{N}^{n}, where n is typically a value between 3 and 4. For horizontal flows n~4 seems to correlate better to experimental data [21]. This approximation with the Nusselt numbers described before leads to an expression of the form h ~ Re^{1/2} Pr^{1/3} (1+GrPr^2/Re^2)^{1/4}, which also has a pressure dependence of h~P^{1/2}. Thus, regardless of the flow type (buoyant or forced), simple arguments suggest h~P^{1/2}. Consequently, if pressure is reduced then convective heat losses from the solid fuel to its surroundings will also be reduced, which in turn will result in the solid heating more rapidly and earlier fuel pyrolysis. This effect can be clearly seen in the sample surface temperature histories from Fig. 3.13, where the traces corresponding to lower ambient pressure show higher temperatures resulting from faster heating rates of the PMMA prior to ignition.

Since convective heat losses from the solid to the gas decrease as pressure is reduced, the effect of reduced pressure could be interpreted as an effective increase of the net applied external heat flux. Previous work [11] shows that the surface temperature at ignition increases with the external radiant heat flux, which seems to corroborate the results presented in Fig. 3.17. This figure shows that the ignition temperature is approximately constant for pressures above 55 kPa, with values around 324-330ºC and it slightly increases with decreasing pressure for pressures below 55 kPa, reaching values around 345ºC. Alternatively the increase in surface temperature at ignition with decreasing pressure could also be due to the more frequent flashing that occurs at lower pressures. More frequent flashes in the gas phase can cause an increase in energy input to the sample and subsequently increase the surface temperature prior to sustained ignition [18]. Overall, the surface temperature values at ignition for pressures around 80-100 kPa seem reasonable considering the wide range of ignition temperatures reported in the literature for piloted ignition of PMMA (310ºC in Ref. [10], 265ºC in Ref.[11], and 374ºC in Ref. [14]).
3.4.3.2 Solid Thermal Decomposition

The thermal decomposition of a polymer is strongly temperature dependent. Pyrolysis of PMMA is generally described as an unzipping process of the polymeric chain. The rate of unzipping, or pyrolysis, can be described by the Arrhenius reaction of the type:

\[ m^n = A \rho \int_{0}^{d} e^{-\frac{E_s}{RT}} dx \]  

(3.2)

where \( A \) is the pre-exponential factor, \( \rho \) the solid density, \( E_s \) the activation energy for the solid decomposition reaction, \( T \) is the solid temperature and \( d \) is the solid depth. Because the activation energy for PMMA pyrolysis is large, the first order dependency of solid pyrolysis is on the solid temperature near the surface. Since the surface temperature is higher at lower pressure it can be inferred that the pyrolysis rate would also be higher as pressure is decreased. On the other hand, the thickness of the solid thermal layer decreases as the pressure is decreased because ignition occurs sooner. It appears that the former effect is dominant since the experiments of Fig.3.13 show an increase in mass loss as the pressure is reduced. Another aspect of the PMMA thermal decomposition process that should be considered is the bubble dynamics that affect the in-depth pyrolysis of the PMMA and the movement of pyrolyzate through the softened condensed phase [22, 23]. As the PMMA is heated by external thermal radiation, it undergoes a glass transition around 100°C. As its temperature is increased further, the amorphous component of the polymer continues to soften, the molecules inside the polymer become increasingly mobile, and

\[ y = 0.003x^2 - 0.569x + 353.02 \]

\[ R^2 = 0.95 \]

Figure 3.17: Surface temperature at ignition vs. pressure. Data points are the average of four tests and vertical lines represent the standard error.
eventually they depolymerize (unzip), forming gaseous compounds (primarily MMA) which nucleate as bubbles in the softened condensed phase. The resultant gas bubbles diffuse throughout the softened polymer, eventually reaching the surface where they burst, exposing subsurface layers of the polymer to surrounding oxygen. Previous work on the bubble dynamics of PMMA under variable external heat flux and oxygen concentration [22] shows that the mass transfer of pyrolyzate is not only diffusive but bubble induced, and that consequently the gasification rate cannot be simply proportional to surface temperature or to energy input. The results of the present work seem to confirm the previous statement.

Plots of mass loss (g) and mass flux (g/m²s) as a function of surface temperature for different ambient pressures as those of Figs. 3.18 and 3.19 show that they are not function of surface temperature only, at least for pressures lower than 28 kPa. The mass flux data in Fig.3.19 was smoothed using a moving average during 40 second intervals. If there was no pressure effect on the mass loss rate then the curves in Figs. 3.18-3.19 at different ambient pressures should all overlap; but the differences we see seem to be beyond experimental variability. This suggests that other processes may participate in the thermal decomposition of the PMMA. In Ref. [22] it is also reported that smaller bubbles occur with increased oxygen concentration and increased radiant flux. The present observation that smaller pyrolyzate bubbles appear at lower pressures is similar to the results of Ref. [20], since decreasing pressure can be thought of as analogous to an increase of the net heat flux into the solid. Furthermore the bubbles add complexity since they alter the optical properties of the polymer sample and consequently its reflectivity and in-depth radiation [22]. These effects are complex and their study beyond the scope of this work.

![Figure 3.18: Mass loss vs. surface temperature.](image)

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3.4.3.3 Mass Flux at Ignition

The observed reduction in the mass flux at ignition with pressure (Fig. 3.16) is attributed primarily to the attainment of a flammable mixture conditions near the igniter sooner. This can be explained phenomenologically by the simple fact that as the total pressure is reduced, the oxygen concentration is also reduced, therefore less fuel vapor is needed to reach the lower flammability limit at the pilot. Though the oxidizer flow velocity is the same in all the tests, the oxidizer mass flow rate decreases with pressure because the density is reduced. For Lewis number close to unity the thermal and concentration boundary layers are equivalent, thus the concentration boundary layer thickness has a pressure dependence proportional to $1/P^{1/2}$. As a result, a reduction in pressure leads to a thicker species boundary layer profile which results in lower species gradients at the solid fuel surface. A reduction of the species concentration gradient at the surface implies a reduction of the mass flux at the surface and therefore a reduction of the fuel mass flux at ignition as observed experimentally in Fig.3.16. Consequently, the lower flammable limit at the igniter is achieved at lower fuel mass fluxes as the ambient pressure is reduced. This conclusion will be explained in Chapter 4 [24], where a simple integral boundary layer analysis is used to demonstrate that as the pressure is reduced, a lower fuel mass flux is necessary to reach the lower flammable limit at the igniter. It appears that this is the dominant effect that is responsible for reduction of the critical mass flux at ignition with pressure.

Figure 3.19: Mass flux vs. surface temperature.
3.5 High Oxygen Concentration Results

The combined effect of reduced total pressure and increased oxygen concentration was also measured with the FIST experimental test. It is well known that an increase in oxygen concentration reduces the ignition delay time [15, 25, 26]. The necessary condition for ignition in the gas phase at the pilot is that the gases in the pilot vicinity reach the lean flammability limit. The lean flammability limit is normally unaffected by an increase in ambient oxygen composition since there is already excess oxygen. Thus, an increase in oxygen concentration is not expected to be an important variable affecting the piloted ignition of solids. However, ignition seems to be easier in high oxygen concentration environments primarily due to different solid surface oxidation, decomposition and gasification processes [15].

The magnitude of the reduction in ignition time with oxygen concentration depends on the externally applied heat flux level [6, 25, 27]. Experiments from [25] and [27] that compared various oxygen compositions present a greater difference in ignition delay times at higher heat flux levels. For instance, in Cordova et al. [25] an increase in the oxygen concentration from 21% to 25% by volume produced a reduction in ignition delay time between 15% and 40%, with the highest increase corresponding to the higher heat flux levels. McAllister et al. [6] presented the combined effect of oxygen concentration and reduced pressure on ignition delay time. However the data from [6] showed that when the oxygen level is increased from 21% to 32% by volume at 59 kPa, the largest reduction in ignition delay time corresponds to lower heat flux levels in contrast to [25, 27]. This is most likely because the heat flux levels in [6] are very close to the critical heat flux, CHF (between 8-14 kW/m$^2$), whereas those in [25, 27] are much larger (approximately 20 – 50 kW/m$^2$). It is usual to find greater deviation in ignition delay times in general for experiments conducted near the CHF. In any case, it seems clear that there is a decreasing effect of ignition delay time with higher oxygen concentrations.

If reduced pressure is viewed as an effective increase of the net heat flux on the sample surface, it can be expected that the combined effect of reduced pressure and increased oxygen concentration on ignition delay would be similar to that of higher external heat flux and oxygen concentration. In order to prove this hypothesis, the ignition delay time for PMMA at 30% oxygen content by volume was measured for pressures between 40-101 kPa. The results of these experiments are presented below.

3.5.1 Visual Observations

Kashiwagi and Ohlemiller [22] showed that gas phase oxygen deeply affects the surface reactions that take place during the solid decomposition. In the presence of oxygen, the surface bubbles are smaller, appear more frequently and they burst in a less violent fashion when compared to experiments with only nitrogen. During the experiments
reported here a similar change in surface behavior was noticed. Figure 3.20 shows pictures at taken one minute before ignition at 69 kPa comparing 21% (a) and 30% O\textsubscript{2} (b). Tests at 30% O\textsubscript{2} presented a slightly smaller bubble size and a more uniform size distribution than tests at 21% O\textsubscript{2}. At standard air (Fig.3.20 a) there was a higher bubble size distribution and the bubbles seemed to coalesce forming larger bubbles that caused more violent explosions when they burst.

![Figure 3.20: Visual observations at 69 kPa at different oxygen concentrations (a) 21% O\textsubscript{2} and (b) 30% O\textsubscript{2}. Pictures were taken 1 min before ignition](image)

3.5.2 Experimental Results

Figure 3.21 shows the measured ignition delay at a range of pressures (40-101 kPa) for 30% O\textsubscript{2} compared to those previously reported for 21% oxygen content. Due to equipment failure, only one experiment was performed at 40 kPa; the other two points at 101 and 69 kPa represent the average of three tests each. It can be seen that the ignition delay time is reduced as the oxygen concentration is increased. The reduction in ignition delay time with increased gas phase oxygen is larger at higher ambient pressures, as can be seen by the difference in slopes of the two regression lines in Fig. 3.21.

The results for the measured mass flux at ignition at 30% O\textsubscript{2} for the same range of pressures are shown in Fig. 3.22. Comparison with the previous results from Fig.3.16 shows that the mass flux at ignition is only about 1-2% higher at 30% O\textsubscript{2} compared to standard air conditions (21% O\textsubscript{2}). This confirms that mass flux at ignition is to some extent insensitive to oxygen concentration if compared to its variation with total ambient pressure.
Figure 3.21: Ignition delay time vs. ambient pressure at different oxygen concentrations. Vertical lines represent the standard error.

\[ t_{ig} = 4.57P + 358.51 \]
\[ t_{ig} = 2.43P + 421.90 \]

Figure 3.22: Mass flux vs. ambient pressure at different oxygen concentrations. Vertical lines represent the standard error.

\[ m'' = 0.005P + 1.49 \]
\[ m'' = 0.005P + 1.48 \]
3.5.3 Analysis of the Results

The effect of oxygen on mass flux at ignition has been investigated before. Trends are not uniform over a wide range of oxygen concentrations. Rashbash et al. [11] showed how the mass flux at ignition decreases rapidly for oxygen concentrations below 21% by volume, but that it did not vary significantly for concentrations above 21%. The trends reported for oxygen concentrations around 21-50% suggest that there is not a great influence of oxygen concentration on the mass flux at ignition above 21% oxygen. The results presented in Fig. 3.22 seem to confirm this observation. Mass flux is greatly affected by the external heat flux applied and slightly influenced by the surface decomposition process [15]. Again, if lower pressure is interpreted as an increased effective net flux on the sample, a greater effect on the mass flux at ignition is to be expected with decreasing pressure when compared to increasing oxygen concentration, just as Fig.3.22 shows.

Kashiwagi and Ohlemiller in [22] showed that the differences in the near-surface behavior between inert atmospheres (N\textsubscript{2}) and oxidative environments (40% O\textsubscript{2}, 60% N\textsubscript{2}) were more pronounced at lower heat fluxes (17 kW/m\textsuperscript{2}) than at higher heat fluxes (40 kW/m\textsuperscript{2}). If low pressure is similar to a higher net or effective heat flux, this would explain the difference in slopes in the regression lines in Fig. 3.21. McAllister et al. [7] also found similar trends for pressures above 40 kPa, where the greatest reduction in ignition delay time when O\textsubscript{2} was increased from 21 to 32% by volume seems to be at standard sea level conditions.

The effect of gas phase oxygen on sample surface temperature at ignition is shown in Fig. 3.23. Surface temperature at ignition is found to decrease when the oxygen concentration was increased to 30%. This is comparable to Kashiwagi and Ohlemiller’s [22] decreasing trend of surface temperature with increasing oxygen concentrations during the thermal and oxidative decomposition of PMMA. Considering the relationship between surface temperature and mass flux at ignition, the comparison of Figs. 3.21 and 3.23 again illustrates how the mass flux at ignition cannot be computed as a single Arrhenius function of surface temperature. Since there is a great difference between the surface temperatures at ignition in Fig.3.23 one would expect larger differences in the mass flux at ignition in Fig.3.22 if the relationship between both quantities was simply exponential. Consequently, the gasification rate cannot be simply proportional to surface temperature or to energy input.
3.6 Conclusions

The ignition delay time, mass flux at ignition and surface temperature at ignition were measured for a range of ambient pressures and for two different oxygen concentrations. It was found that ignition delay time decreases with reduced ambient pressure and oxygen concentration, similar to what previous authors have reported [7]. These results indicate that solid combustible materials are easier to ignite in low pressure environments such as those found at high altitude locations or inside under-pressurized compartments such as aircraft and spacecraft. This may represent a higher fire hazard, which may be even more significant if the environment also includes an elevated oxygen concentration.

The mass flux at ignition was found to also decrease with ambient pressure and seemed to be relatively insensitive to oxygen concentration. The findings from these experiments suggest that:

1. The mass flux at ignition should not be considered a single value for a given material, since it varies with ambient variables such as pressure.

2. The relationship between surface temperature and mass flux is more complicated than a simple Arrhenius type dependency, since the gasification rate prior to

![Figure 3.23: Surface temperature at ignition vs. ambient pressure at different oxygen concentrations. Vertical lines represent the standard error.](image-url)
ignition is not merely directly related to surface temperature or energy input. Surface behavior differences at various pressures confirm this statement.

3. To a certain extent a decrease in ambient pressure can be viewed as an effective increase of the net heat flux applied. In both cases ignition delay time is decreased and sample surface temperature at ignition is increased. Solid phase surface behavior and bubble dynamics at high heat flux and low pressure also show some similarities. However, the mass flux at ignition increases for higher heat fluxes but it decreases with reduced pressure. This indicates that a reduction in ambient pressure cannot be simply described as an increase in applied heat flux or a reduction in convective heat loses.

4. Reduced pressure reduces both the heat transfer coefficient (leading to faster heating of the solid) and the fuel mass flux necessary to reach the lower flammable limit at the igniter (leading to ignition at a lower fuel mass flux). An analytical model presented in the following chapter will clarify the latter.
3.7 References


CHAPTER 4 – ANALYTICAL MODEL

4.1 Introduction

Based on the experimental results presented in Chapter 3, a simplified theoretical explanation for the variation with ambient pressure of ignition times and the mass flux at ignition is investigated. The objective is to develop an analytical model that is sufficiently simple yet phenomenologically correct to describe the most important processes taking place and to understand the effects of pressure on the ignition of solid fuels.

The ignition of a solid fuel is a complex problem to analyze. Most solid ignition theoretical models focus on describing the solid phase process, i.e. the solid heating, thermal decomposition and subsequent gasification. The condensed phase processes are inherently transient and solid phase quasi-steady solutions do not depict the physics correctly. For example, Kindelan and Williams [1] used asymptotic expansions to obtain a transient solution to the gasification of a semi-infinite solid whose surface is subject to a constant heat flux. The products of the gasification are assumed to lead to ignition through a gas-phase reaction, but the gaseous phase was not analyzed. Quintiere and Iqbal [2] used an integral model approach to also solve the one-dimensional unsteady heating and gasification of a semi-infinite solid. A quadratic temperature profile that satisfied the heat transfer boundary conditions of the problem was used. Again, these authors focused on analyzing in great detail the solid heating and decomposition from a heat transfer perspective but they did not analyze gas phase processes. These models have been subjected to successive modifications and improvements [3, 4 among others] and have been shown to adequately predict burning rates of various thermoplastics. Many simplified theoretical models exist that successfully describe the solid heating, decomposition and gasification required for ignition. Nevertheless, because these models strictly address the solid phase processes, they offer little insight on how environmental variables such as air flow velocity, oxygen concentration or pressure affect the gas phase transport, mixing and chemical reactions needed for the ignition of a pyrolyzed solid fuel.

The current study presents a simplified model of piloted ignition of solid fuels that analyzes the physical processes occurring in the gas-phase prior to ignition. Following the flame spread model approach from Ref. [5] a steady boundary layer integral method is developed to qualitatively analyze the gas phase above the transient gasification of a solid fuel. The analysis is aimed to provide a better understanding of the processes that lead to the attainment of flammable conditions when a non-charring solid fuel is exposed to a constant heat flux in a boundary layer flow. Similarly to most flash point analyses in the literature [6], this study is based on the concept of reaching the lean flammability limit at the pilot location. While the analysis is not as detailed as the references mentioned above, it provides a sufficient description of the gas-phase transport processes to extract
behavioral trends. The variation of gas properties and boundary layer shape with ambient pressure provides insight on some of the effects this parameter has on the processes that lead to the ignition of a pyrolyzed solid. The qualitative trends of this analysis are compared to the experimental results from Chapter 3.

The effect of other environmental variables such as the oxygen concentration on the critical mass flux at ignition has been investigated in the past by other authors through a mass transfer B-number analysis at the fire point [7, 8]. This B-number analysis has some shortcomings that will be explored below. For instance, it uses empirical quantities such as the fuel’s critical flame temperature to determine the mass flux at fire point. However, it has shown good agreement with previous experimental studies. Therefore, this approach is also analyzed and compared to both the experimental results from Chapter 3 and to the flashpoint analysis developed with the integral boundary layer approximate method.

4.2 Boundary Layer Integral Method

An integral boundary layer model was developed to provide insight on the physical phenomena occurring in the gas phase adjacent to a pyrolysing fuel. Although a numerical method is more precise, an analytical approach may be appropriate to capture qualitative trends. The integral method can be used to calculate the effect of pressure on the temperature and species distributions, and through them calculate the resulting effect on the heat losses from the solid and mass flux at the surface (through the corresponding gradients). Specifically, it can be used to estimate the mass loss rate at which a flammable concentration (lower flammable limit, LFL) is obtained at the pilot through the analysis of the fuel concentration profile. Attaining the LFL at the igniter is a necessary but not sufficient condition for piloted ignition (fire point). Consequently, the boundary layer analysis presented below provides an indication of the mass loss rate at the flash point, but it does not address whether conditions are favorable for establishment of an anchored diffusion flame (fire point).

![Figure 4.1: Simplified schematic of FIST tunnel showing different boundary layers.](image)
The boundary layer integral method is an approximate approach to solve the boundary layer equations introduced by von Karman and developed by Pohlhausen [9]. It assumes certain velocity (U), temperature (T) and species (Y_i) profiles that are functions of the non-dimensional variable y/\delta(x), where “y” is the distance from the wall and \delta(x) the boundary layer thickness. The most typical case is to assume polynomial profiles for U, T and Y_i. The profiles are used to integrate the boundary layer equations in the transversal y-direction in order to obtain explicit expressions for the boundary layer thicknesses (hydrodynamic \delta, thermal \delta_T or concentration \delta_c) as a function of the longitudinal coordinate “x” and fluid properties. The expressions for \delta(x), \delta_T(x) or \delta_c(x) are then introduced in the previously assumed profiles to obtain U=U(x,y), T=T(x,y) or Y_i= Y_i(x, y) respectively.

Although the pyrolysis of a solid is inherently a transient process, the gas phase above the solid surface can be assumed to behave in a quasi-steady manner for a first order approximation. This is appropriate if the characteristic time for the development of a thermal boundary layer is much shorter than the characteristic time for the solid to achieve steady state. This can be proven by comparing the characteristic diffusion times in the solid and in the gas. The thermal diffusivity in the solid PMMA can be estimated with the following property values from [10] k= 0.21 W/m-K, \rho=1190 kg/m^3, c=1460 J/kg-K, which yield \alpha_{PMMA}=k/\rho c=1.2\times10^{-7} m^2/s. The thermal diffusivity of air at standard temperature is approximately \alpha_{air}=2\times10^{-5} m^2/s. Characteristic diffusion times can be estimated as t~ l^2/\alpha. If the characteristic length is taken as 10 mm for example, then it can be seen that the characteristic diffusion times are very different: t_{air}~ 5 s and t_{solid}~ 833 s. This quick calculation suggests that the quasi-steady state approximation for the gas phase is adequate.

The boundary layer equations for steady, incompressible, two-dimensional, laminar parallel flow over a flat plate (no longitudinal external pressure gradient, based on the coordinates in Fig. 4.1) and constant properties for a binary non reacting mixture are:

Continuity:
\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{4.1}
\]

x-Momentum:
\[
u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = v \frac{\partial^2 u}{\partial y^2} \tag{4.2}
\]
Energy:

\[
 u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2}
\]  \hspace{1cm} (4.3)

Fuel mass fraction:

\[
 u \frac{\partial Y_F}{\partial x} + v \frac{\partial Y_F}{\partial y} = D \frac{\partial^2 Y_F}{\partial y^2}
\]  \hspace{1cm} (4.4)

The Prandtl number and Schmidt number are assumed to be unity (\(\alpha = \nu = D\)), and changes in gas density throughout the boundary layer attributed to temperature differences are neglected. In keeping with the qualitative nature of the model, buoyancy is neglected to simplify the problem. The boundary conditions are as follows:

\(y=0:\) \hspace{1cm} u = v = 0, \quad T = T_0, \quad Y_F = Y_{FO} \hspace{1cm} (4.5)

\(y=\delta, \delta_T \) or \(\delta_c:\) \hspace{1cm} u = U_\infty, \quad T = T_\infty \quad Y_F = Y_{FO} = 0 \hspace{1cm} (4.6)

where the boundary conditions at \(y \rightarrow \infty\) have been replaced by boundary conditions at the edge of the hydrodynamic (\(y=\delta\)), thermal (\(y=\delta_T\)) or concentration (\(y=\delta_c\)) boundary layers. With this approximation \(\partial u/\partial y\) becomes zero if \(y > \delta\). Similarly, the derivative of the temperature and mass fraction is zero if \(y > \delta_T\) or \(y > \delta_c\) respectively. Forcing the derivatives of \(u, T\) and \(Y_F\) with respect to \(y\) to be continuous in the vicinity of \(y=\delta, \delta_T \) or \(\delta_c\), the following boundary conditions are obtained:

\[ \frac{\partial u}{\partial y} = 0 \]

\(y=\delta, \delta_T \) or \(\delta_c:\) \hspace{1cm} \frac{\partial T}{\partial y} = 0 \quad \frac{\partial Y_F}{\partial y} = 0 \hspace{1cm} (4.7)
Inserting these boundary conditions in Eqs. 4.2-4.4, the following conditions are obtained:

$$y=0: \quad \frac{\partial^2 u}{\partial y^2} = 0, \quad \frac{\partial^2 T}{\partial y^2} = 0, \quad \frac{\partial^2 Y_F}{\partial y^2} = 0$$

(4.8)

Within the boundary layers the velocity, temperature and fuel mass fraction profiles are approximated by third order polynomials that satisfy the boundary conditions in Eqs. 4.5-4.8:

$$\frac{u}{U_\infty} = \frac{3 y}{2 \delta} - \frac{1}{2} \left( \frac{y}{\delta} \right)^3$$

(4.9)

$$\frac{T - T_0}{T_\infty - T_0} = \frac{3 y}{2 \delta_T} - \frac{1}{2} \left( \frac{y}{\delta_T} \right)^3$$

(4.10)

$$\frac{Y_F - Y_{F0}}{Y_{F\infty} - Y_{F0}} = \frac{3 y}{2 \delta_c} - \frac{1}{2} \left( \frac{y}{\delta_c} \right)^3$$

(4.11)

Integrating the momentum equation (Eq. 4.2) with respect to $y$, and combining it with the integration of continuity (Eq.4.1), the momentum integral equation for steady incompressible boundary layer is obtained [11, 12]:

$$\frac{d}{dx} \int_0^\delta (U_\infty - u) dy + \frac{d U_\infty}{dx} \int_0^\delta (U_\infty - u) dy = \nu \left( \frac{\partial u}{\partial y} \right)_{y=0}$$

(4.12)

Integrating Eq. 4.12 with the use of the velocity profile from Eq. 4.9, yields the following differential equation for $\delta(x)$:

$$\delta \frac{d \delta}{dx} = \frac{140}{13} \frac{\nu}{U_\infty}$$

(4.13)

The integration of Eq. 4.13 with the condition that $\delta=0$ at $x=0$ provides an expression for the hydrodynamic boundary layer thickness:

$$\delta = \sqrt{\frac{280 \nu x}{13 U_\infty}} \approx 4.64 \sqrt{\frac{\nu x}{U_\infty}} \approx 4.64 \frac{x}{\sqrt{Re_x}}$$

(4.14)
4.2.1 Thermal Boundary Layer

The same procedure is followed with the thermal boundary layer, i.e. integrating the energy equation (Eq. 4.3) to obtain the energy integral equation (Eq. 4.15), inserting the temperature profile to determine a differential equation for $\delta T$ (Eqs. 4.16, 4.17).

$$\frac{d}{dx} \int_0^{\delta T} (T_\infty - T) u dy = \alpha \left. \left( \frac{\partial T}{\partial y} \right) \right|_{y=0} = \frac{1}{\rho C_p} q_w^* \tag{4.15}$$

$$\frac{d}{dx} \left( \delta T (T_0 - T_\infty) \left[ \frac{3}{20} \frac{\delta T}{\delta} - \frac{3}{280} \left( \frac{\delta T}{\delta} \right)^3 \right] \right) = \frac{1}{\rho C_p U_\infty} q_w^* \tag{4.16}$$

Due to the unheated starting length $\delta T \ll \delta$ and the second term inside the brackets in Eq. 4.16 can be neglected in comparison to the first term. Also, note that the thermal problem corresponds to a constant heat flux at the wall with an unheated starting length and that $q_w'' = -k \left. \left( \frac{\partial T}{\partial y} \right) \right|_{y=0} = 3k \frac{(T_0 - T_\infty)}{2\delta T}$. The latter provides a relationship to replace $(T_0 - T_\infty)$ by a function of $\delta T$ and $q_w''$ (constant for $x > x_T$) to aid the integration of Eq.4.16 into a much simpler differential equation:

$$\frac{d}{dx} \left( \frac{\delta T}{\delta} \right)^3 = \frac{10k}{\rho C_p U_\infty} \tag{4.17}$$

Finally, the solution of Eq. 4.17 provides an expression for the thermal boundary thickness:

$$\delta_T = \left[ \frac{10ax \delta}{U_\infty} \left( 1 - \frac{x_T}{x} \right) \right]^{1/3} \tag{4.18}$$

4.2.2 Concentration Boundary Layer

To determine the concentration profile, the species equation (Eq.4.4) is integrated to give Eq. 4.19. The concentration problem corresponds to a constant wall mass fraction (equivalent to a constant wall temperature thermal case).
Another differential equation results from evaluating Eq. 4.19 with the same type of assumptions as with the thermal problem ($\delta_c \ll \delta$), although it is not as straightforward to solve:

$$\frac{d}{dx} \left( \frac{\delta_c^2}{\delta} \right) = \frac{10D}{U_\infty \delta_c}$$

(4.20)

The integration of Eq. 4.20 yields the expression for the concentration boundary thickness shown in Eq. 4.21:

$$\delta_c = \delta \left( \frac{13D}{14 \nu} \left[ 1 - \left( \frac{x_c}{x} \right)^{3/4} \right] \right)^{1/3}$$

(4.21)

Note that the thermal boundary layer thickness (Eq. 4.18) and the concentration boundary layer thickness (Eq. 4.21) do not coincide because the starting lengths and boundary conditions are different. The thermal starting length is $x_T = 101$ mm while the species starting length is $x_c = 181$ mm (see Fig. 4.1), and the boundary condition for the thermal case corresponds to a constant wall heat flux whereas the mass transfer problem has a constant fuel mass fraction at the wall.

### 4.2.3 Pressure Effects on Boundary Layers

Equations 4.14, 4.18 and 4.21 are explicit expressions to determine the different boundary layer thicknesses as a function of the longitudinal coordinate $x$ and the fluid properties. Figure 4.2 illustrates the relative position of the hydrodynamic, thermal and concentration boundary layer thicknesses calculated with these expressions. By evaluating these equations with properties at different pressures (100 kPa and 55 kPa) one can see how the boundary layer thicknesses grow as the ambient pressure is reduced.
As mentioned before, equations for the velocity, the temperature and the fuel mass fraction at any given spatial coordinate, i.e. \( U=U(x,y) \), \( T=T(x,y) \) and \( Y_i=Y_i(x,y) \) can be determined by inserting the expressions for the boundary layer thicknesses \( \delta(x) \), \( \delta_t(x) \) and \( \delta_C(x) \) from Eqs. 4.14, 4.18 and 4.21 (shown in Fig. 4.2) into the assumed polynomial profiles described in Eqs. 4.9-4.11. Figure 4.3 shows the non-dimensional temperature (a) and species (b) profiles at the igniter location \( x_{ig} \) as a function of the vertical distance from the wall \( y \) for a range of different pressures in order to gain insight of how ambient pressure affects the shape of these profiles. A reduction in pressure from 100 kPa to 41 kPa leads to a significantly “thicker” species profile which results in lower temperature and species gradients at the solid fuel surface. Consequently, the heat losses from the solid surface to the gas are reduced as pressure is decreased. Also, a particular concentration for a flammable mixture, as determined by the LFL for Methyl-methacrylate or MMA, would be achieved at the igniter sooner for lower ambient pressures.
4.2.3.1 **Heat Transfer Coefficient**

The heat transfer coefficient can be estimated by $h_c = k/\delta_T$. The results for a range of ambient pressures are shown in Fig. 4.4. The unheated starting length ($x < x_T$) is also taken into consideration when plotting the results. Inspection of Eqs. 4.14 and 4.18 provides $\delta_T \sim x/Re_x^{0.5}$. Thus, the convective heat transfer coefficient varies like $h_c \sim k/\delta_T \sim k \cdot Re_x^{0.5}/x$. Since the Reynolds number ($Re_x = \rho U \infty x/\mu$) has a linear dependence with pressure through the density, it follows that $h_c \sim P^{0.5}$. As a result, when the ambient pressure is decreased, the convective heat transfer coefficient also decreases as seen in Fig. 4.4. A reduction in the convective heat losses will lead a solid fuel to heat up more quickly under radiant heating, reducing the overall ignition delay time. At the leading edge of the solid sample ($x_c = 181$ mm) the heat transfer coefficient decreases by approximately 26% when the pressure is reduced 45% from 100 kPa to 55kPa (Fig. 4.4).
4.2.3.2 Mass Flux

The mass flux at any location can be determined from:

\[ \dot{m}'' = \rho v Y_F - \rho D \frac{\partial Y_F}{\partial y} \]  

(4.22)

For this analysis only mass transfer in the y-direction is considered. Additionally it is assumed that there is a low mass transfer rate at the wall and that consequently the mass transfer is dominated by diffusion rather than convection (\(v_{wall} \ll \frac{\partial Y_F}{\partial y}\)). Simplifying Eq.4.22 for \(v=0\) (diffusion-dominated mass transfer) and substituting Eq. 4.11 for the rate of change of \(Y_F\), the mass flux, \(\dot{m}''\) is given as:

\[ \dot{m}'' \approx -\rho D \left( \frac{\partial Y_F}{\partial y} \right)_y = \frac{3}{2\delta_c} \rho D Y_{F0} \left( 1 - \left( \frac{y}{\delta_c} \right)^2 \right) \]  

(4.23)

Setting \(y=0\) in Eq. 4.23, the fuel mass fraction at the wall \(Y_{F0}\) is calculated as a function of the mass loss rate at the wall \(\dot{m}_0\) for each ambient pressure with the following expression:
Knowing $Y_{F0}$, the polynomial profile from Eq. 4.11 is then used to calculate the fuel mass fraction as a function of distance above the wall ($y$). Because the LFL is often given in terms of mole fraction, the fuel mass fraction is converted into mole fraction with:

\[
X_F = \frac{Y_F \bar{M}}{M_F} = \frac{Y_F}{M_F[Y_F/M_F + (1 - Y_F)/M_a]}
\] (4.25)

The variation of the fuel (MMA) mass mole fraction at the igniter location ($x_{ig}=221\text{mm}$, $y_{ig}=5\text{mm}$) for different surface mass loss rates is given in Fig. 4.5. To generate Fig. 4.5, the mass loss rate at the wall $\dot{m}_0^*$ is varied from 0 to 2 g/m$^2$s and used to calculate the corresponding $Y_{F0}$ through Eq.4.24. This value is used to determine $Y_F$ through the profile from Eq.4.11, which is converted into mole fraction with Eq. 4.25. Ignition is considered to occur when the mole fraction of fuel at the igniter is equal to the LFL of the fuel.

Since the critical adiabatic flame temperature at the LFL is approximately 1600 K +/- 150 K for a variety of fuels [13], the LFL of MMA in air can be estimated by determining the fuel concentration necessary to give an adiabatic flame temperature of approximately 1600 K. The fuel mass fraction at the LFL is calculated as:

\[
Y_{F,LFL} = \frac{C_p(T_{ad} - T_\infty)}{Q_c}
\] (4.26)

Considering an adiabatic flame temperature $T_{ad}=1600K$, $T_\infty = 300K$, $C_p= 1100 \text{ J/kgK}$ and $Q_c= 25\text{MJ/kg}$, Eq. 4.26, yields $Y_{F,LFL}=0.057$ or (corresponding to $X_{F,LFL}=0.017$ through Eq. 4.25). This calculated mole fraction for the LFL of MMA is in agreement with typical values from the literature. For instance, both Yaws’ Handbook [14] and Babrauskas’ Ignition Handbook [10] indicate a LFL =2.1% by volume for MMA. Since pressure has little effect on the LFL for pressures below atmospheric [6, 10] this analysis considers a $Y_{F,LFL}$ constant value equal to that calculated with Eq. 4.26 for the entire range of pressures studied. The intersection of the curves in Figure 4.5 with the horizontal line corresponding to $X_{F,LFL}=0.017$ indicates the mass flux required to reach the fuel LFL. Consequently, Fig.4.5 shows that the fuel mass loss rate at the solid surface required to achieve a given fuel mole fraction, such as the LFL for MMA vapor, is lower at lower ambient pressures. Specifically, the calculated mass loss rate corresponding to $X_{F,LFL}=0.017$ at the igniter (flash point) is roughly three times higher at 100 kPa than at 55 kPa.
4.2.3 Comparison with Experiments

The results from Fig. 4.5 for the variation of the mass flux at ignition with pressure are plotted in Fig. 4.6 for comparison purposes with the experimental results from Chapter 3. Both the results of the simplified analysis mass flux at the LFL and the experimental measurements of mass flux at ignition decrease with ambient pressure, although the analysis is more sensitive to pressure. The calculated mass flux at ignition is roughly half the experimental mass flux for the range of pressure analyzed.

This simplified analysis indicates that the observed reduction in ignition delay time with pressure is the result of both a reduction in the heat transfer coefficient and a lower required fuel mass flux at ignition. The reduction in the heat transfer coefficient is due to the increase in the thermal boundary layer thickness which leads to lower temperature gradients at the solid surface with decreasing pressure. The reduction in the required fuel mass flux at ignition is due to the lean flammability limit being reached earlier at lower pressure (Fig. 4.5). However it should be noted that the analysis is not intended to provide quantitative data but information about the controlling mechanisms of the effect of pressure on ignition. Furthermore the results are consistent with the fact that the analysis provides the minimum conditions for ignition (flashing) while the experiments indicate ignition leading to burning of the solid fuel [7], which generally takes longer than flashing.

Figure 4.5: Integral model results: fuel mole fraction vs. mass flux at igniter location, $x_{ig}=221$mm.
4.3 Modified B-number Theory

As previously stated, reaching flammable conditions (flash point) at the pilot are necessary but not sufficient conditions for sustained burning (fire point) to occur. Rasbash [7] developed a “fire point theory” by proposing a link between the critical mass flux at ignition and attainment of a critical value of Spalding’s B number [15]. The mass transfer number or B-number was originally developed to explain the vaporization and burning of liquid fuel droplets, but when applied to solid fuels it provides a link between the critical mass flux of fuel volatiles at fire point and the stability of the combustion process in the flame. This approach has been used before to describe the effect of the free stream oxygen content on the critical mass flux at fire point of solid fuels presenting good agreement with experimental results [8].

The general expression for the relationship between a critical mass flux at ignition and a critical B number is the following [7, 8]:

![Figure 4.6: Mass flux at ignition vs. ambient pressure. Experimental results correspond to burning conditions; the boundary layer analysis is at the flash point. Experiments are the average of four tests; vertical lines represent the standard error.](image-url)
\[
\dot{m}_F^* = \frac{h_c}{c_p} \ln \left(1 + B_{cr}\right) \tag{4.27}
\]

where \(h_c\) is the convective heat transfer coefficient between the flame and the solid surface, \(C_p\) is the specific heat capacity of the oxidizer (typically air), and \(B_{cr}\) is the critical Spalding B-number. Equation 4.27 is appropriate for small scale burning dominated by convective heat transfer to the surface.

The way to calculate the \(B_{cr}\) varies throughout the literature. The B number theory has been modified several times in order to account for different processes such as the heat radiated to the environment from the flame or surface reradiation loss. Following Rich et al. [8] and Torero et al. [16] a modified critical B number is used that incorporates the heat radiated from the flame to its surroundings through the radiative fraction \(\chi\), and a modified heat of reaction of the solid pyrolysis \(\Delta H^*\):

\[
B_{cr} = \frac{Y_{O_2}^\infty(1 - \chi)(\Delta H_c/r) - C_p(T_s - T_{\infty})}{\Delta H^*} \tag{4.28}
\]

where \(Y_{O_2}^\infty\) is the oxygen mass fraction far from the solid surface (0.23 for air), \(\chi\) the radiosity, \(\Delta H_c\) the fuel heat of combustion, \(r\) the stoichiometric oxygen to fuel mass ratio, and \(T_s\) and \(T_{\infty}\) the temperatures at the solid surface and at the free-stream respectively. The mass transfer B-number is essentially a ratio of the energy released by the combustion (numerator) and a modified heat of the pyrolysis reaction (denominator) where both terms account for various types of losses. The energy released by the combustion is calculated as a modified heat of combustion that accounts for the loss due to flame radiation (left-hand term in numerator of Eq. 4.28) and the energy necessary to heat the air from the free-stream temperature \(T_{\infty}\) to the solid surface temperature \(T_s\) (right-hand term in numerator of Eq. 4.28). Substitution of the critical B-number expression (Eq.4.28) into Eq.4.27 yields the following expression that is to be determined:

\[
\dot{m}_F^* = \frac{h_c}{c_p} \ln \left(1 + \frac{Y_{O_2}^\infty(1 - \chi)(\Delta H_c/r) - C_p(T_s - T_{\infty})}{\Delta H^*}\right) \tag{4.29}
\]

The modified heat of pyrolysis \(\Delta H^*\) is a not an easy term to evaluate. As Rich et al. [8] suggest it should include the following terms to account for losses at the solid surface:

\[
\Delta H^* = \Delta H_{vol} + \frac{q''_{cond} + q''_{rerad} - q''_{flamerad} - q''_{external}}{\dot{m}_F^*} \tag{4.30}
\]

where \(\Delta H_{vol}\) is the heat of volatilization or of the pyrolysis reaction, \(q''_{cond}\) is the conductive heat flux from the solid surface toward its interior, \(q''_{rerad}\) is the surface reradiation loss, \(q''_{flamerad}\) accounts for the radiative heat transfer from the flame to the solid surface,
q"_{\text{external}} is the external radiative heat flux (constant and equal to 16 kW/m² in the experimental results from Chapter 3). In spite of this detailed breakdown of the terms that should be included to evaluate the modified heat of pyrolysis (Eq. 30), it does not provide a practical method to calculate this value. Roberts and Quince [17] developed an expression to calculate the theoretical temperature of a diffusion flame established over a liquid surface. This expression is related to the modified heat of pyrolysis as follows:

$$C_p(T_{f,cr} - T_\infty) = \frac{(Y_{O_2}^{\infty}/r)(1 - \chi_r)\Delta H_c - \Delta H^*}{1 + (Y_{O_2}^{\infty}/r)} - C_p(T_s - T_\infty)$$

(4.31)

where $T_{f,cr}$ is the critical flame temperature. Manipulation of Eq. 31 yields an explicit expression to calculate the heat of pyrolysis $\Delta H^*$:

$$\Delta H^* = (1 - \chi_r)\Delta H_c - \left(\frac{C_p}{Y_{O_2}^{\infty}}\frac{r}{T_s - T_\infty + (T_{f,cr} - T_\infty)}\left(1 + \frac{r}{Y_{O_2}^{\infty}}\right)\right)$$

(4.32)

If the fire point corresponds to the attainment of a critical flame temperature, then the critical mass flux at the fire point can be calculated by substituting the term $\Delta H^*$ in the critical mass flux expression in Eq. 4.29. This relationship determines the critical mass flux at fire point as a function of the heat transfer coefficient $h_c$, fuel properties (heat of combustion $\Delta H_c$ and stoichiometric oxygen to fuel mass ratio $r$), oxidizer properties (specific heat $C_p$ and oxygen mass fraction $Y_{O_2}$), radiative fraction $\chi_r$, and temperatures for the solid surface ($T_s$), free-stream ($T_\infty$) and critical flame temperature ($T_{f,cr}$):

$$\dot{m}_F^* = h_c\ln\left(1 + \frac{Y_{O_2}^{\infty}(1 - \chi_r)(\Delta H_c/r) - C_p(T_s - T_\infty)}{(1 - \chi_r)\Delta H_c - \left(\frac{C_p}{Y_{O_2}^{\infty}}\frac{r}{T_s - T_\infty + (T_{f,cr} - T_\infty)}\left(1 + \frac{r}{Y_{O_2}^{\infty}}\right)\right)}\right)$$

(4.33)

As it was explained in Chapter 2, the concept of a critical flame or ignition temperature has many shortcomings in characterizing solid fuel ignition. The most important of these limitations is that it is an empirical quantity which cannot be determined from fundamental fuel properties or as a function of environmental conditions [8]. However, it has been shown to be useful in analyses such as this one, where the objective is to determine qualitative effects of environmental variables on the mass flux at ignition.

Another term in Eq. 4.33 that is challenging to evaluate is the radiative fraction $\chi_r$. It corresponds to the fraction of the total energy released by the flame that is radiated to the environment and is a function only of the emissivity of the flame. In practice $\chi_r$ is not easy to determine. Values reported in the literature span from $\chi_r = 0.1$ to $\chi_r = 0.35$ [16]. This value also varies with ambient pressure since the buoyant characteristics of the flow affect the flame shape and its radiative properties. This was confirmed by comparison of flame images at different pressures presented in Chapter 3, Fig.3.12. However, in keeping with the qualitative nature of this analysis, the radiative fraction is maintained constant in the results presented below.
Equation 4.33 is evaluated for a range of ambient pressures and compared to the experimental results from Chapter 3 in Fig. 4.7. The pressure dependence is not explicitly shown in Eq.4.33. The main term that varies significantly with pressure is the heat transfer coefficient. The heat transfer coefficient calculated in the boundary layer analysis (forced flow conditions) could be used for this exercise. Alternatively a mixed forced and natural convection flow can also be used as it is shown below. For mixed forced and free flow over a flat plate the heat transfer coefficient can be approximated as a combination of the forced and natural convection correlations of the form: \( \text{Nu}_{\text{mixed}} = \text{Nu}_f^n + \text{Nu}_N^n \), where \( n \) is typically a value between 3 and 4. For this calculation \( n=3 \) is used. The Nusselt number correlation suggests that the effective heat transfer coefficient can be calculated as \( h_{c,\text{mix}} = h_{c,f}^3 + h_{c,N}^3 \).

For forced flow over a flat plate with an unheated starting length \( \xi \) (\( x_T = 101 \text{ mm} \) in Fig. 4.1) the following correlation is used [11]:

\[
h_{c,F} = \frac{0.332 \ Pr^{1/3} \ Re_x^{1/2} k}{x} \left[ 1 - \left( \frac{\xi}{x} \right)^{3/4} \right]^{-1/3}
\]

where \( x \) is the distance from the tunnel inlet, \( k \) the conductivity, \( Pr \) the Prandtl number and the Reynolds number based on the tunnel longitudinal distance \( Re_x = U_{\infty} \frac{x}{\nu} \). The Reynolds pressure dependency leads to a forced flow heat transfer coefficient that varies as \( h_{c,f} \sim P^{1/2} \).

For natural convective conditions, defining \( L \) as the ratio between the heated area and the perimeter of the heated area, the heat transfer coefficient can be calculated as:

\[
h_{c,N} = 0.54 \ Gr^{1/4} Pr^{-1/4} \frac{k}{L}
\]

If the oxidizer is assumed to behave as an ideal gas, the Grashof number is calculated as \( Gr_x = g \Delta T x^3 \rho^2 / (T \mu^2) \). Thus, \( h_{c,N} \) varies with pressure as \( h_{c,N} \sim P^{1/2} \). The effective heat transfer coefficient for mixed flow conditions is then calculated with Eqs. 4.34-4.35 as \( h_{c,\text{mix}} = (h_{c,f}^3 + h_{c,N}^3)^{1/3} \).

### 4.3.1 Comparison with Experiments

An estimation of the mass flux at fire point calculated with Eq. 4.33 is shown an compared to the experimental results in Fig.4.7. The following property values were used: \( C_{p,\text{air}} = 1100 \text{ J/kg}, k_{\text{air}} = 0.04 \text{ W/m K}, T_{\infty} = 20^\circ \text{C}, T_s = 330^\circ \text{C}, T_{f,cr} = 1300^\circ \text{C}, X_r = 0.1 \), and for PMMA \( \Delta H_c = 24.9 \text{ MJ/kg} \) and \( r = 1.92 \).
Figure 4.7 shows that a modified B-number theory presents the same trend as the experiments: as ambient pressure is reduced the critical mass flux at ignition also decreases. The modified B number analysis at fire point seems to match reasonably well to the experimental results. The difference between the experiments and B-number analysis results grows as pressure is decreased.

This decrease in mass flux at ignition is due only to the change with pressure of the heat transfer coefficient, as Eq. 4.33 shows. Further possible variations with pressure of other variables that were neglected and kept constant in this analysis such as $\chi_r$ or the critical flame temperature $T_f$ would not substantially affect the results presented in Fig.4.7 since they have a secondary effect on the mass flux at ignition. Nevertheless, additional tweaking of the property values used for this calculation could provide an even better agreement between the analysis and the experiments, but they would not provide any further insight on the physical processes taking place. Simplifying the effect of pressure on ignition to merely an influence in the convective heat transfer coefficient is an important limitation of this analysis.
4.4 Conclusions

In Chapter 3 it was found that the ignition delay time and the fuel mass flux at ignition decreased with ambient pressure through a series of experiments. It was hypothesized that this behavior was due to two main effects: 1) the decrease in the effective heat transfer coefficient with reduced pressure that lead to faster solid heating and 2) a reduction in the fuel gradients at the solid surface under low pressures that enable reaching the LFL with a lower fuel mass flux.

An integral method boundary layer analysis was developed to show how the shape of the hydrodynamic, thermal and species boundary layers change with pressure. The analysis of the thermal boundary layer described how the heat transfer coefficient decreases with pressure (Fig.4.4) due to a “thicker” thermal boundary layer and reduced temperature gradients at the solid surface. The analysis of the concentration boundary layer described how reduced pressure also leads to “thicker” fuel concentration boundary layer and consequently would produce a decrease in the fuel mass fraction gradients at the solid surface. Thus, a lower fuel mass flux is required to achieve a given concentration such as the LFL for MMA vapor at lower ambient pressures (Fig.4.5). Although the boundary layer analysis is an approximate solution, it describes clearly the physical processes taking place in a boundary layer flow adjacent to a pyrolyzing solid fuel. This analysis confirms that the reduction in convective heat losses to the surroundings is not the only responsible for the mass flux decreasing trends with pressure. Most importantly, it confirms that in order to reach flammable conditions a lower mass flux of pyrolysate gases is required at low ambient pressures.

Following previous literature analyses, a modified B-number theory was also explored to understand the trends in the mass flux at ignition. The results of this analysis show a better quantitative agreement with the experiments from Chapter 3 than the simplified boundary layer integral method, as can be seen by comparison of Figs. 4.6 and 4.7. However it fails to provide insight on the physics of the problem other than the reduction in convective heat losses (or heat transfer coefficient) with decreasing pressure.

Additionally it should be noted that both the B-number theory analysis and the experiments correspond to the fire point or sustained burning conditions. The boundary layer analysis corresponds to the flash point which is a necessary but not a sufficient condition for sustained burning to occur. Therefore and considering the large number of simplifications taken into account in the boundary layer analysis, it is not surprising that the results are roughly half of the experimental values.
4.5 References


CHAPTER 5 – NUMERICAL MODEL

5.1 Introduction

The objective of the present study is to model the effect of ambient variables such as pressure on the piloted ignition of a solid fuel exposed to an external radiant heat flux and an oxidizer forced convective flow. Chapter 3 presented a series of ignition experiments under reduced pressure environments and the trends of those experiments were explained through phenomenological arguments. Chapter 4 contained a simplified model that further described the effect of pressure on ignition in a qualitative manner. In this chapter a numerical model is developed to present a more detailed investigation of the physical processes underlying the piloted ignition of a solid fuel. The numerical model will help substantiate the phenomenological concepts and extrapolate the trends to conditions not experimentally tested.

Understanding the influence of environmental variables on ignition from the standpoint of fire initiation and prevention is essential. Moreover, predicting fire initiation and growth under realistic conditions is still a very challenging task. As it has been explained throughout the previous chapters, the physical mechanism of a piloted ignition event is quite complex. An externally irradiated solid fuel will thermally decompose, producing fuel vapor. Due to the presence of the pilot, gas phase thermal runaway occurs as soon as a flammable gaseous mixture forms near the ignition source. If the external heating of the solid produces pyrolyzate vapors at a sufficient rate and the heat losses to the surface are overcome, the premixed flame at the pilot propagates towards the solid fuel and a diffusion flame is established on its surface. The establishment of a diffusion flame is referred to as sustained ignition. Thus, for ignition to occur, certain conditions must be attained in both the gas and condensed phase. Accordingly, a complete model of the piloted ignition process should include a transient analysis of all these processes: 1) the solid phase heating and decomposition, 2) the mixing of the fuel vapor and oxygen, 3) a premixed flame originating at the pilot, 4) intermittent propagation of this premixed flame through the mixture due to depletion of the fuel and heat losses to the surface (flashes), and 5) eventual establishment of a diffusion (non-premixed) flame on the solid surface [1].

There are numerous numerical studies in the literature describing the piloted ignition of solid fuels. Theoretical and numerical analysis of piloted ignition are usually grouped into two categories: 1) those that focus only on the solid phase and adopt a criterion to determine ignition and 2) those that simultaneously solve both the solid phase and gas phase governing equations. In the first category, common simplified criteria used to characterize ignition are a critical surface temperature [2], a critical pyrolyzate mass flux at ignition [3, 4] or a critical heat release rate [5]. In the second category, i.e. models that couple gas phase and solid phase processes, the numerical complexities of solving the
governing equations in both phases simultaneously have led many investigators to focus on particular phenomena in order to simplify the problem [6, 7].

In spite of the complexity involved there are many numerical models for the piloted ignition of PMMA that analyze the coupled gas phase and solid phase problem. For example, Chandrasekaran et al. [8] developed a three-dimensional model for pilot ignition of PMMA in a cone calorimeter, i.e. under natural convection conditions, that calculated the solid phase decomposition with a zero-order Arrhenius reaction and the gas phase with a global single step reaction. Some improvements of the numerical analysis have focused on including in-depth pyrolysis and radiation absorption through the solid fuel, but have had to simplify the models in other ways. For example, Esfahani et al. [9] included in-depth radiation absorption in a one-dimensional model for the decomposition and ignition of PMMA, which also modeled both solid and gas phases.

The influence of an external radiant heat flux, the oxygen concentration and the oxidizer forced flow velocity on the piloted ignition of a solid fuel has been studied in the past by Zhou et al. [10]. They used a first-order Arrhenius solid phase decomposition model and included reactive boundary layer equations to model the transport phenomena occurring in the gas phase. However, one of the shortcomings this model had was that upstream flame propagation could not be modeled due to the parabolic nature of the governing equations. Therefore ignition was determined by thermal runaway at the pilot, but the upstream establishment of the diffusion flame on the solid surface was not evaluated.

In an effort to apply elliptic equations that would permit upstream flame propagation and consequently describe the establishment of a diffusion flame, Lautenberger et al. [11] combined the solid phase model from Zhou et al. 2002 [10] with the Fire Dynamics Simulator (FDS) code [12, 13] for the gas phase processes. FDS is a computational fluid dynamics (CFD) model developed by the National Institute of Standards and Technology (NIST) that provides a transient solution to low Mach number, buoyant, reactive Navier Stokes equations. In their investigation of piloted ignition of composite materials, Lautenberger et al. [11] also analyzed the influence of the external radiant heat flux, the forced flow velocity and microgravity conditions on ignition.

This analysis presents a similar approach to that of Lautenberger et al. [11] but it utilizes FDS for all processes, in both the solid and the gas phases. By customizing an existing CFD code, a numerical model is developed to evaluate the effect of pressure and other environmental variables on the piloted ignition of PMMA. The model’s ability to describe the different steps involved in piloted ignition of solid fuels is analyzed. The results of this model are also compared with the experiments presented in Chapter 3, Ref. [14].
5.2 Numerical Model Description

The numerical model is a 2-dimensional simulation of the piloted ignition experiments carried out in the Forced Ignition and Spread Test (FIST) apparatus described in Chapter 3 [14]. It is performed with Fire Dynamics Simulator (FDS), [12] version 5.5.3. FDS is a computational fluid dynamics program for applications of fire-driven flows developed by the National Institute of Standards and Technology (NIST). The FDS software numerically solves a form of the Navier-Stokes equations appropriate for low-speed, thermally-driven flow, with an emphasis on smoke and heat transport from fires. The core algorithm is a finite difference explicit predictor-corrector scheme that is second order accurate in space and time. The model developed with FDS for this study simultaneously considers processes in the solid and in the gas phase. The default pyrolysis model from FDS is used for the solid phase decomposition with a single-step global Arrhenius reaction rate. Oxidative pyrolysis is not considered and the in-depth formed pyrolyzate is assumed to flow unrestricted through the solid combustible. A finite rate reaction model is used to model the gas-phase kinetics with a single-step first order Arrhenius reaction rate.

The model presented in this work has two main differences with the mainstream treatment of FDS simulations. FDS is typically used with Large Eddy Simulation (LES) to model large scale fires. However, the convective heat transfer calculations with LES in FDS are determined based on a combination of natural and forced convection correlations. For the present problem it is important to calculate the convective heat transfer in the gas phase directly through temperature gradients, thus it is necessary to use the Direct Numerical Simulation (DNS) option of FDS. DNS computes the dissipative terms directly although it is much more costly in terms of computational time. It is unclear whether LES is able to reproduce the piloted ignition process from the experiments presented in Chapter 3, [14] correctly, but DNS has successfully been used in the past for similar piloted ignition models of composite materials [11]. There are also other examples where FDS in DNS form has been used to effectively model flame spread and compare to experimental results which are suggested as verification for this use of FDS [13].

The other major characteristic of the present research is that a finite rate chemical reaction is used instead of the FDS default mixture fraction combustion model. A finite rate reaction model is necessary if one is to predict accurately the ignition process for the piloted ignition of a solid fuel, otherwise the reaction would simply take place once a flammable mixture is generated over the solid. Since the attainment of a flammable mixture at the pilot is a necessary but not sufficient condition for sustained burning to occur, using a finite rate combustion model is necessary.
5.2.1 Computational Domain

Figure 5.1 is a schematic of the problem under consideration and the selected computational domain. The computational domain includes the entire heating length in the FIST tunnel [14]: 152 mm in the streamwise, x-direction, 120 mm in the cross-stream y-direction. This represents only a fraction of the complete wind tunnel length (392 mm). A sensitivity analysis to quantify the variations of including the complete length of the domain is also performed below.

From similar numerical models of the FIST experiment it is noticed that a relatively small cell size is required for grid insensitivity. Lautenberger et al. [11] used 1.1 mm in the x-direction and 0.6 mm in the y-direction for a two-dimensional domain that was 28 cm long by 7.6 cm high. As a compromise between grid size and computational time, a uniform cell size of 2 mm in the x-direction and 1 mm in the y-direction is used here throughout the entire domain as a baseline case. This is achieved by dividing the domain into a uniform rectilinear computational mesh of 76 cells in the x-direction by 120 cells in the y-direction. A grid sensitivity analysis is presented below to assess the adequacy of the grid size selection.

5.2.2 Boundary Conditions

An outlet boundary condition on the -x of the domain induces a prescribed velocity suction flow to simulate the forced flow in the experiment. The +x domain (inlet) is kept as an “open” boundary condition. The inlet flow has prescribed temperature, pressure and oxygen concentration. An open vent condition in FDS is a passive opening to the outside and it implies that the fluid entering the domain is inviscid, incompressible and steady (Bernoulli conditions). Also, in terms of radiative behavior, open boundaries are treated as black walls.
The infrared heater that irradiates the solid fuel sample is modeled as a surface at a constant temperature that radiates the desired heat flux onto the sample surface. For the experiments in Chapter 3, [14] the external heat flux is constant and equal to 16 kW/m$^2$. This heat flux value is obtained by iterating on the heater surface temperature and measuring the radiative heat flux on the sample surface with a radiometer device. For the baseline grid a heater temperature of 538°C provides q"=16 kW/m$^2$ on the center of the sample surface.

The sample holder is simply modeled as an insulated surface at the unexposed side of the fuel sample. The tunnel floor is modeled as a 6 mm thick surface surrounding the sample with material properties of mica mimicking the actual tunnel composition.

The igniter location and shape are known to have a substantial effect on the ignition delay times. For this study it is fixed as a single grid (2 mm wide by 1 mm high) obstacle at 1350°C located 10 mm downstream from the sample trailing edge and 3 mm above the tunnel floor. The emissivity of the igniter is kept at 0.01 to minimize its influence on radiatively heating the trailing edge of the sample.

![Figure 5.2: Two-dimensional computational domain with boundary conditions](image)

The initial conditions are air at 20°C and at a particular pressure (varied for each different simulation). The air temperature in FDS is assumed to be constant with height and air density and pressure decrease with height.
5.2.3 Hydrodynamic Model

Conservation of mass, conservation of momentum and conservation of energy are used in FDS version 5 [12] in an appropriate form for low speed thermally driven flow. The low Mach speed assumption filters acoustic waves while permitting large variations in temperature and density throughout the flow field. The Navier-Stokes equations in this form are elliptic, which is typical for low speed convective thermal flows. This entails that the pressure \( p = p(x,y) \) is not directly resolved, but a “background” or average pressure is used instead. The pressure is solved as the superposition of the background pressure \( \bar{p}(y,t) \) and a flow-induced perturbation \( p'(x,y,t) \). The low Mach assumption also implies that the ideal gas equation of state can be evaluated with this background pressure \( \bar{p}(y,t) \).

It should be noted that the flow that we are trying to reproduce is essentially laminar, therefore using DNS can be understood as merely an artifact to disable the default LES in the FDS model. The thermal conductivity, the viscosity and diffusivity are calculated directly from kinetic theory of gases in order to include a temperature variation of these properties.

5.2.4 Energy Transport

Energy transport is modeled through conduction, convection and radiation. Radiation is evaluated with a grey-gas radiation model. Details can be found in Ref. [12].

Convection in the gas phase is determined through the conservation equations. Because DNS is used, the convective heat flux to a solid surface is calculated as the temperature gradient at the boundary:

\[
q_{\text{conv}} = -k \frac{\partial T}{\partial n} = -k \frac{T_{\text{wall}} - T_{\text{gas}}}{\delta n/2}
\]  

where \( k \) is the gas thermal conductivity, \( n \) the normal direction pointing into the solid, \( T_{\text{wall}} \) the solid surface temperature and \( T_{\text{gas}} \) the temperature in the center of the first adjacent gas phase cell. This differs from the default LES calculation, where the convective heat transfer is determined through a combination of forced flow and natural convection correlations.

Inside the solid, only one-dimensional heat conduction is considered, i.e. conduction only occurs in the direction normal to the surface. The solid phase temperature distribution, namely \( T_s = T_s(y,t) \), is calculated through a one-dimensional heat conduction equation:
\[
\rho_s c_s \frac{\partial T_s}{\partial t} = \frac{\partial}{\partial y}\left(k_s \frac{\partial T_s}{\partial y}\right) + \dot{q}_s'''
\]  
(5.2)

where \( \rho_s, c_s, k_s \) are solid properties and the source term \( \dot{q}_s''' \) includes pyrolysis reactions and radiative absorption.

Boundary conditions at the solid fuel are the following:

Front (\( y=0 \)):
\[
-k_s \frac{\partial T_s}{\partial y} (0, t) = \dot{q}_\text{conv}'' + \dot{q}_\text{rad}''
\]  
(5.3)

Backside (\( y=-0.01\text{m} \)):
\[
k_s \frac{\partial T_s}{\partial y} = 0
\]  
(5.4)

5.2.5 Pyrolysis Model

The solid phase pyrolysis reactions are included in the chemical source term inside the solid heat conduction equation (Eq.5.2). Black PMMA (Polymethylmethacrylate) is the solid fuel used in the present analysis. PMMA is a non-charring polymer and the pyrolysis product is assumed to be 100% monomer with no significant residue yield. This is very close to literature values which report a MMA monomer yield of 91-98\% by weight for the thermal decomposition of PMMA [15].

The assumptions used in this model include: 1) instantaneous release of volatiles from solid to the gas phase, 2) local thermal equilibrium between the solid and the volatiles, 3) no condensation of gaseous products, and 4) no porosity effects. A first order Arrhenius reaction is used to calculate the condensed phase decomposition, namely:

\[
r = \left(\frac{\rho(t)}{\rho_0}\right) A_{\text{solid}} \exp\left(\frac{-E_{\text{solid}}}{RT_s}\right)
\]  
(5.5)

where \( \rho \) is the fuel density, \( A_{\text{solid}} \) the pre-exponential factor, \( E_{\text{solid}} \) the activation energy for the pyrolysis reaction, \( R \) the universal gas constant and \( T_s \) the solid temperature.

5.2.6 Combustion Model

The FDS model uses a DNS calculation to model the diffusion of the chemical species (fuel, oxygen and combustion products) directly and a finite rate reaction to model the
chemical kinetics. A global single-step Arrhenius reaction rate is used to model the chemical kinetics following the expression:

$$\frac{d[C_xH_y]}{dt} = -B_{of}[C_xH_y]^a[O_2]^b \exp\left(\frac{-E_{gas}}{RT}\right)$$

where $B_{of}$ (mol/cm$^3$s) is the pre-exponential factor, $E_{gas}$ (kJ/mol) the activation energy the gas phase reaction, $R$ the universal gas constant, $[C_xH_y]$ and $[O_2]$ fuel and oxygen concentrations respectively. In this case $a=b=1$. It should be noted that it is not universally accepted that such a simple mechanism can correctly represent the chemistry in a combustion reaction, but it has proven useful for first order approximations.

5.3 Material Properties

When simulating ignition problems one of the major challenges is to choose the most appropriate material properties to characterize practical combustibles. “Material properties” refers to the model input parameters and therefore includes the reaction kinetics parameters as well as the thermo-physical properties.

5.3.1 PMMA Material Properties in the Literature

The physical properties for PMMA are well known and similar values are used in different references. Table 5.1. shows values from research on polymer pyrolysis and numerical simulations of both ignition and flame spread. The references are organized based on the numerical model approach, i.e. if both the solid and gas phases were solved or if just the solid decomposition was modeled. The larger discrepancies in property values correspond to differences in the reference temperature chosen. For example, the thermal conductivity of PMMA is 0.19 W/m-K at room temperature and it is approximately 0.23 W/m-K at temperatures around 100 ºC. To address this issue Ref. [5] directly presents temperature dependent thermo-physical properties. For black PMMA an emissivity between 0.9 and 1 seems to be used in previously reported models.
Table 5.1: PMMA properties in the literature

<table>
<thead>
<tr>
<th></th>
<th>Ignition (Gas &amp; solid phase)</th>
<th>Ignition (Solid phase)</th>
<th>Flame spread (Gas &amp; solid phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bhattacharjee 2004 [19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Di Blasi 1989 [20]</td>
</tr>
<tr>
<td>$k$ (W/mK)</td>
<td>0.19</td>
<td>0.188</td>
<td>0.185</td>
</tr>
<tr>
<td>$\rho$ (kg/m$^3$)</td>
<td>1190</td>
<td>1200</td>
<td>1170</td>
</tr>
<tr>
<td>$c$ (J/kgK)</td>
<td>1420</td>
<td>1500</td>
<td>1220</td>
</tr>
<tr>
<td>$\varepsilon$ (-)</td>
<td>-</td>
<td>0.9</td>
<td>-</td>
</tr>
</tbody>
</table>

The solid phase reaction kinetic parameters vary significantly in the literature (Table 5.2). Models that only resolve the solid phase decomposition such as Ref. [4, 5] have higher activation energies for the pyrolysis reaction than models that account for both the gas phase and solid phases. There is a known relationship between the activation energy $E_{\text{solid}}$ and the pre-exponential factor $A_{\text{solid}}$ called ‘compensation effect’ [21] of the form $\ln(A_{\text{solid}})=a+bE_{\text{solid}}$. Therefore it is expected that models with higher activation energies also present higher pre-exponential factors. This is can be seen in Table 5.2. where the models in Ref. [4, 5] with higher activation energies have pre-exponential factors orders of magnitude above the values in the other references.

The heat of the PMMA pyrolysis reaction in the literature varies from 800-2000 kJ/kg. In general the heat of pyrolysis is in the lower limits (800-1300 kJ/kg); only Ref. [4] presents $\Delta H_{\text{vol}}=2000$ kJ/kg. The values from Ref. [4] come from a numerical analysis to fit cone calorimeter data by Rhodes and Quintiere [22] which is known to have found substantially higher property values than other investigations.

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Table 5.2: PMMA solid phase decomposition kinetics in the literature

<table>
<thead>
<tr>
<th>Ignition</th>
<th>Ignition (Gas &amp; solid phase)</th>
<th>Flame spread (Gas &amp; solid phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zhou 2001 [10, 17]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lintiris 2010 [4]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stoliarov 2009 [5]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{\text{solid}}$ (s$^{-1}$)</td>
<td>2.82E9</td>
<td>8.50E12</td>
</tr>
<tr>
<td>$E_{\text{solid}}$ (kJ/mol)</td>
<td>130</td>
<td>128</td>
</tr>
<tr>
<td>$\Delta H_{\text{vol}}$ (kJ/kg)</td>
<td>1160</td>
<td>800</td>
</tr>
</tbody>
</table>

Previously reported gas phase kinetic parameters are shown in Table 5.3. Most of the values are based on the findings of Seshadri and William [23] or Williams [24]. The heat of combustion is roughly 26 MJ/kg, the gas phase activation energy $E_{\text{gas}}$ is between 156-180 kJ/mol but the pre-exponential factor $B_{\text{of}}$ has a larger range of possible values.

Table 5.3: PMMA gas phase kinetics in the literature

<table>
<thead>
<tr>
<th></th>
<th>Ignition (Gas &amp; solid phase)</th>
<th>Diffusion Flame Experiments</th>
<th>Flame spread (Gas &amp; solid phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zhou 2001 [10, 17]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Seshadri &amp; Williams 1978 [23]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{\text{of}}$ (cm$^3$/mol-s)</td>
<td>2E15</td>
<td>2.3E16</td>
<td>8.93E12</td>
</tr>
<tr>
<td>$E_{\text{gas}}$ (kJ/mol)</td>
<td>156</td>
<td>179.9</td>
<td>88.9</td>
</tr>
<tr>
<td>$\Delta H_{\text{comb}}$ (MJ/kg)</td>
<td>26.82</td>
<td>26</td>
<td>25.2</td>
</tr>
</tbody>
</table>
5.3.2 Selection of Baseline Properties

Following the PMMA material properties as well as the gas phase and solid phase kinetic parameters found in the literature a rough parametric study was conducted to choose the optimal (“baseline”) properties. The properties selected for the baseline case are shown in Table 5.4. Essentially the values selected are similar to those in Ref. [16] due to the similarities in both models (Ref. [16] also uses FDS), except that the solid phase kinetics selected for this research have a higher activation energy and a higher heat of reaction ($\Delta H_{\text{vol}}$), which are closer to the values used for the solid decomposition in [10, 17].

Table 5.4: Baseline Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (W/m-K)</td>
<td>0.19</td>
</tr>
<tr>
<td>$\Delta H_{\text{vol}}$ (kJ/kg)</td>
<td>1100</td>
</tr>
<tr>
<td>$\rho$ (kg/m$^3$)</td>
<td>1190</td>
</tr>
<tr>
<td>$A_{\text{solid}}$ (s$^{-1}$)</td>
<td>$4.0 \cdot 10^9$</td>
</tr>
<tr>
<td>$c$ (J/kg-K)</td>
<td>1400</td>
</tr>
<tr>
<td>$E_{\text{solid}}$ (kJ/mol)</td>
<td>142</td>
</tr>
<tr>
<td>$\varepsilon$ (-)</td>
<td>0.9</td>
</tr>
<tr>
<td>$B_{of}$ (cm$^3$/mole-s)</td>
<td>$1.2 \cdot 10^{16}$</td>
</tr>
<tr>
<td>$\Delta H_{\text{comb}}$ (MJ/kg)</td>
<td>25.2</td>
</tr>
<tr>
<td>$E_{\text{gas}}$ (kJ/mol)</td>
<td>165</td>
</tr>
</tbody>
</table>

5.4 Baseline Case Results

The baseline case consists of the property values and kinetic parameters described in Table 5.4, the domain and grid resolution described in section 5.2.1 and the boundary conditions in section 5.2.2, i.e., an external radiant heat flux of 16 kW/m$^2$, air (21% O$_2$), an oxidizer forced flow velocity of 0.4 m/s and an ambient pressure of 100 kPa. These boundary conditions (forced flow velocity, ambient pressure and oxygen concentration) will be then modified to analyze the effects of environmental variables on ignition.

The model represents qualitatively well the process of piloted ignition. Figures 5.3-5.6 show snapshots of the numerical results at four representative instants during the simulation. Figure 5.3 shows the heat release rate (HRR) per unit volume, which is proportional to the reaction rate. The HRR plots show how a gas phase reaction appears first at the pilot location (Fig.5.3.a), grows (Fig.5.3.b), until it ‘jumps’ upstream onto the solid surface (Fig.5.3.c), and finally a diffusion flame establishes and travels on the solid surface (Fig.5.3.d). It should be noted that because the flow velocity is low buoyancy takes an important role once the flame is established over the PMMA surface. The temperature distribution in the gas phase for the same instants in time can be seen in Fig.5.4.
Figure 5.5 shows the fuel mass fraction distribution during the simulation. It can be seen that amount of fuel volatiles (products of the pyrolysis) increases with time and temperature (compare Figs. 5.5.a and 5.5.b). Additionally the fuel is being consumed behind the igniter in a premixed type flame (Fig.5.5.b) until a diffusion flame establishes on the solid surface with clear delimited fuel rich areas and fuel lean areas (Fig.5.5.c).

Figure 5.3: Heat release rate results.

Figure 5.4: Gas phase temperature results.

Figure 5.5: Fuel mass fraction.
The production of CO\(_2\) can give a good indication of the distribution of the products of combustion (Fig. 5.6). CO\(_2\) starts forming at the igniter where the reaction is taking place (Fig.5.6.a) and increases with the growth of the reaction area. Figure 5.6.b shows a significant amount of CO\(_2\) being produced in the reaction zone, which is a premixed type flame. In contrast, Fig. 5.6.d shows that in the diffusion flame the products of combustion are being formed at the upper edge of the reaction area and not over the whole reaction area as with a premixed flame (Fig.5.6.b). Furthermore, comparison of Figs. 5.5.c and 5.6.c (fuel and CO\(_2\) all at 646.5 s) show that the fuel and CO\(_2\) production are both essentially in the same area, above the sample surface and downstream. However, Figs. 5.5.d and 5.6.d (both at 648 s) show the fuel production is spatially separated from the formation of CO\(_2\) (products of combustion). These comments suggest that a non-premixed (diffusion) flame has appeared.

The temperature distribution inside the condensed phase (PMMA) is shown in Fig.5.7. The solid initial temperature is 20ºC. The applied radiant heat flux causes the solid fuel to heat up and thermally decompose. The pyrolysis temperature is approximately 300ºC for PMMA. Figure 5.7.a corresponds to a time when a gas phase reaction appears at the igniter location, downstream from the solid sample which has started to pyrolyze (temperatures on the surface above 300ºC). Ignition occurs at 646.5 s (Fig. 5.7.c.) and sustained burning conditions correspond to Fig.5.7.d. The asymmetry in the solid heating can be due to additional heating from the gas phase reaction at the igniter and also to reduced heat losses due to a thicker thermal boundary layer on the left hand side of the sample (downstream).

Inspection of the solid temperature distribution in Fig. 5.7 confirms that the sample’s thermal behavior is neither thermally thin (which would have a constant temperature through the depth) nor thermally thick (which would have the back-side of the solid unaffected by the heating). As it was suggested from the measurements presented in
Chapter 3, the solid fuel has a thermally ‘intermediate’ behavior between thin and thick and the thermal wave penetrates the depth of the sample.

5.5 Effect of Environmental Conditions

The effect on ignition of ambient variables such as air flow velocity, pressure, oxygen concentration and microgravity conditions is investigated in the following section. The material properties, kinetic parameters and grid size from the baseline case are kept constant while each ambient variable is changed accordingly to study its influence.

5.5.1 Air Flow Velocity

The effect of the oxidizer flow velocity was analyzed and compared to experimental results from the FIST experiment (Chapter 3) for an external heat flux of 16 kW/m² with air as the oxidizer. The model predicts well the experimental trends of ignition delay time increasing with forced air flow velocity (Figs.5.8-5.11). The model results with the kinetic parameters and properties from the baseline case present less change in ignition delay with forced air flow velocity than the experiments, over-predicting ignition times for lower air flow velocity values and under-predicting results for higher air flow velocity values.

Figure 5.7: Solid phase temperature distribution.
Figure 5.8: Model predictions and experimental data comparison: Ignition delay time vs. air flow velocity. Experimental values represent the average of three tests and vertical lines represent the standard error.

Figure 5.9 compares the sample surface temperature time history predictions with the model and the raw data of three representative experiments. Fig.5.10 is a closer look at the sample surface temperature time histories from the numerical model only that includes the three tests in Fig.5.9 in addition to other flow velocity values. Although the ignition times in the model vary with airflow velocity, it does not show significantly different surface temperatures for each velocity analyzed. This can be seen in the overlap of the model temperature history data (Fig.5.9 -5.10). However, as the air flow velocity is increased a larger amount of fuel needs to be produced for ignition (as shown by the fuel mass flux in Fig. 5.11). Therefore, higher surface temperatures must be reached to attain a larger fuel volatile mass flux with increased forced flow velocities and, consequently, ignition is delayed.
For the applied heat flux value (16 kW/m²), the model does not present ignition for air flow velocities above v=0.6 m/s. This can be seen in Figs. 5.10-5.11. Flashing conditions appear (Fig.5.10, irregularities in the v=0.6 m/s surface temperature trace around 600 s), but the cooling effect of a higher air flow velocity prevents a diffusion flame from establishing on the sample surface.

Figure 5.9: Model predictions and experimental data comparison: surface temperature traces at various air flow velocities.

For the applied heat flux value (16 kW/m²), the model does not present ignition for air flow velocities above v=0.6 m/s. This can be seen in Figs. 5.10-5.11. Flashing conditions appear (Fig.5.10, irregularities in the v=0.6 m/s surface temperature trace around 600 s), but the cooling effect of a higher air flow velocity prevents a diffusion flame from establishing on the sample surface.

Figure 5.10: Model results: surface temperature at a range of air flow velocities.
5.5.2 Pressure

The effect of pressure on the ignition delay time, surface temperature and mass flux at ignition for the baseline case is explored in the following figures. The surface temperature history data is presented in Fig.5.12 for a range of pressures. The abrupt change in slope corresponds to the ignition event. The surface temperature plots show that: 1) ignition occurs earlier at lower pressures, 2) the solid heats up more quickly when the pressure is reduced, and 3) for $P>14$ kPa, the surface temperature at ignition grows with pressure. The temperature curve at 10 kPa presents a change in behavior, showing a slight increase in the temperature at ignition.

In Chapter 3 it was suggested that the reduction in ignition delay time with pressure was primarily due to a reduction of the convective heat transfer coefficient. This reduction in the convective heat transfer coefficient translated into diminished heat losses from the solid surface to its surroundings when the ambient pressure is decreased. In order to confirm this assumption, the calculated convective heat flux at the center of the solid surface is shown for a range of pressures in Fig. 5.13. The sudden change in trend shows when ignition occurs: $q''_{\text{conv}} < 0$ means the solid is losing heat to the surroundings whereas $q''_{\text{conv}} > 0$ indicates that the environment is hotter than the solid. The reversal in slope may be due to the onset of weak flashing.
Figure 5.14 shows the mass flux for the same simulations shown in Fig.5.12-5.13. Similarly to the temperature curves, the mass flux presents a sudden change in slope when ignition occurs. The curves in Fig.5.14 show that as pressure decreases, ignition takes place earlier and with a lower mass flux of pyrolysate products. Once again the simulation at p=10 kPa presents dissimilar trends to the rest of the pressure values analyzed: the mass flux at ignition is slightly larger than the value at p=14 kPa, and there seems to be a two distinct mass loss rate trends (as opposed to only an instantaneous vertical line $\dot{m} \rightarrow \infty$).
The boundary layer integral model in Chapter 4 suggested that as pressure decreases the fuel concentration boundary layer becomes thicker, leading to lower gradients at the fuel surface. Figure 5.15 shows the vertical distribution of the fuel mole fraction at the center of the sample surface at two instants during the simulation for a range of ambient pressures. As time increases the fuel concentration grows due to the progress of the pyrolysis reaction. Low pressures present a thicker fuel mole fraction profile (Fig. 5.15 a, b).

Figure 5.14: Mass flux vs. time for a range of pressures.

Figure 5.15: Fuel mole fraction vs. vertical distance at sample surface at two instants for a range of ambient pressures.
Additionally it was suggested in Chapter 4 that a lower mass flux of fuel volatiles was required to reach flammable conditions. This statement is explored in the following figures. The time evolution of the fuel mole fraction 1 mm above the igniter is shown in Fig. 5.16. The appearance of the gas phase reaction at the igniter (marked by a decrease of fuel concentration) takes place earlier at lower ambient pressures. In addition, the gas phase reaction occurs at lower fuel concentrations at reduced pressures. The vertical slopes in Fig. 5.16 correspond to the appearance of a diffusion flame anchored at the solid surface, i.e. sustained ignition. Note that the time lapse between the appearance of a gas phase reaction and the establishment of a diffusion flame also decreases with pressure.

Figure 5.16: Time evolution of fuel mole fraction at the igniter. Local maxima correspond to a gas-phase reaction (R) appearing at the igniter; vertical slopes correspond to sustained ignition (I).

The time dependency can be eliminated in Fig. 5.16 in order to show the relationship between the fuel concentration at the igniter and the fuel mass flux at the center of sample surface (Fig. 5.17). The same qualitative trends that were calculated with the analytical model in Chapter 4 (Fig. 4.5) are obtained with the model. As Fig. 5.17 shows, a lower mass flux of fuel volatiles is required for flammable conditions at lower pressures (Fig.5.17).
The ignition delay times corresponding to Figs. 5.10-5.17 are compared to the experimental results from Chapter 3, Ref. [14] in Fig. 5.18. As in the experiments, the ignition delay time is reduced as the total ambient pressure decreases. Because the slopes of the experimental and numerical results are similar, the model captures the relative effect of pressure observed in the experiments. However, the absolute value of the predicted ignition delay at a given ambient pressure is less than that observed in the experiments. Note that in the experiments no ignition was found at pressures below P<13 kPa, but in the model there seems to be an apparent ignition at 10 kPa. This reaction is substantially different from the other model results although it is uncertain whether sustained burning is achieved at 10 kPa.

The predicted surface temperatures at ignition are compared to the experimental results in Fig.5.18. While the quantitative values are similar over rather wide pressure ranges, the trends predicted by the model do not match the experimental trends. Figure 5.19 shows the mass loss at ignition as a function of ambient pressure. Because the mass flux at ignition is highly dependent on the surface temperature, some disagreement is to be expected between the experimental and model mass flux results since the predicted and measured temperatures are not identical. Nevertheless, the model shows a decrease of mass flux at ignition with reduced pressure as observed in the experiment. The mass flux dependence on pressure is weaker in the experiments from [14] than the model prediction.
Figure 5.18: Ignition delay time vs. pressure. Comparison of numerical model with experiments (average of four tests; standard error bars represented)

\[ t_{ig} = 4.6P + 358.5 \]

\[ t_{ig} = 4.6P + 170.3 \]

Figure 5.19: Surface temperature at ignition vs. pressure. Comparison of numerical model with experiments (average of four tests; standard error bars represented)
Figure 5.20: Mass flux at ignition vs. pressure. Comparison of numerical model with experiments (average of four tests; standard error bars represented)
5.5.3 Oxygen Concentration

The oxygen concentration was increased to 30% by volume in the model baseline case to compare to the experimental trends presented in Chapter 3, Section 3.5. The results are shown in Figs. 5.21-5.22. The model exhibits less sensitivity to oxygen concentration than the experiments probably because oxidative pyrolysis is not included in the model. It has been shown that thermal oxidation decomposes the polymer faster, with a lower activation energy than simple thermal degradation [25]. In other words, the same rate of decomposition can be achieved in oxygen rich environments at a lower surface temperature. Therefore, one would expect lower surface temperatures at ignition than the model predicts in Fig. 5.22 b.

![Figure 5.21: Ignition delay time vs. pressure: O\textsubscript{2} concentration comparison](image)

![Figure 5.22: Mass flux at ignition (a) and surface temperature at ignition (b) vs. pressure: O\textsubscript{2} concentration comparison](image)
5.5.4 Microgravity

Simulations of zero gravity conditions are shown in Figs. 5.23-5.27. Removing gravitational effects eliminates buoyancy and simplifies the problem by converting the surrounding oxidizer flow to pure forced flow. The Rayleigh-Taylor instability which appeared in the top of the images in Fig.5.4 disappears under zero gravity conditions. This can be seen in Fig.5.23 where the simulation images from Fig.5.4 under normal gravity ($g=9.8 \text{ m/s}^2$) are included in the top row for comparison to 0-g conditions (bottom row). The simulations shown in Fig. 5.23 correspond to the same pressure (100 kPa), air flow velocity (0.4 m/s) and incident radiant heat flux ($q''=16 \text{ kW/m}^2$), but ignition occurs earlier in 0-g than in 1-g. The flame in 0-g is not affected by buoyancy and shows a more uniform shape in the direction of the horizontal forced flow.

![Simulation images](image)

**Figure 5.23:** Gas phase temperatures around ignition at 100 kPa, air flow velocity 0.4 m/s and $q''=16 \text{ kW/m}^2$. Top row (a-c) corresponds to 1-g, bottom row (d-f) to 0-g.

The lack of buoyant flows in microgravity reduces the convective heat transfer, leading to solid fuels heating up more quickly in 0-g compared to 1-g. This can be seen in Fig. 5.24, where the convective heat flux and the temperature at the sample surface are shown for two simulations at 1-g and 0-g, with an ambient pressure equal to 100 kPa, air flow velocity of 0.4 m/s and a constant external radiant heat flux of 16 kW/m². In other words, although the external radiant heat flux applied on the solid surface is the same, since
the convective heat flux is reduced (Fig. 5.24 a), the net or effective heat flux on the solid is higher at 0-g, leading to a faster heating of the solid fuel (Fig. 5.24 b). However, unless there is an imposed forced flow, the transport processes in 0-g are dominated by diffusion. If the transport in microgravity is enhanced with an imposed oxidizer forced flow (as is the case with this model), then mixing will be more effective and a flammable mixture can be obtained earlier, leading to shorter ignition times. Additionally, since pyrolysis is an exponential function of temperature, the increased surface temperatures at 0-g lead to a quicker thermal decomposition. Figure 5.25 shows the fuel mass flux time evolution for the same tests compared in Fig. 5.24. At 0-g the fuel mass flux increases more quickly due to the increased effective heat flux on the sample, and ignition occurs earlier.

Figure 5.24: Convective heat flux (a) and temperature (b) at sample surface vs. time for 0-g and 1-g.

Figure 5.25: Fuel mass flux vs. time at 0-g and 1-g.
The results at 0-g for a range of ambient pressures are presented in Figs. 5.26-5.27 and compared to experiments and numerical results at 1-g. It is not surprising to find less discrepancy between the results at 1-g and 0-g at lower pressures, since reducing the ambient pressure also reduces the buoyancy effects.

**Figure 5.26:** Ignition delay time vs. pressure: gravity effects

**Figure 5.27:** Mass flux at ignition (a) and surface temperature at ignition (b) vs. pressure: gravity effects
5.6 Grid Sensitivity Analysis

A grid sensitivity study was conducted in order to evaluate the accuracy of the numerical solution. Different solutions were computed for a range of grid sizes, all with the same material properties and kinetic parameters as the baseline case.

It was found that the level of grid refinement necessary depends on the ambient pressure. One of the preferred methods to determine the optimal grid size of a DNS simulation is to estimate the Kolmogorov length scale \( \eta \sim (\nu^3/\varepsilon)^{1/4} \), where \( \nu \) is the kinematic viscosity, and \( \varepsilon \) the dissipation [26]. The Kolmogorov length scale \( \eta \) is typically the smallest scale that needs to be resolved. In reality, the smallest resolved scale can be on the order of \( \eta \) and still provide accurate results. If ambient pressure decreases, the kinematic viscosity \( \nu=\mu/\rho \) increases and consequently the Kolmogorov scale \( \eta \) also increases. Thus at lower pressures the smallest scale that needs to be resolved is larger than the scale required to fully resolve the problem at higher pressures. This explains why grid convergence on the ignition delay time in Fig. 5.28 is obtained at larger grid sizes at reduced ambient pressures than at elevated pressure.

The error values from this grid refinement analysis are presented in Figures 5.28-5.30 and Table 5.5. Figure 5.28 shows that the baseline grid size, grid 1 (\( \Delta x=2 \) mm, \( \Delta z=1 \) mm) for pressures \( P \leq 55 \) kPa is fully resolved, since the difference in ignition delay times for different grids is under 3%. For pressures \( 55 \) kPa\(< \) \( P \leq 83 \) kPa, grid 2 (\( \Delta x=1.6 \) mm, \( \Delta z=0.8 \) mm)
is needed to attain differences in ignition delay times below 5%. For results in the vicinity of 100kPa, a smaller grid size (Δx=1.1 mm, Δz=0.6mm) should be used. The trends in mass flux at ignition with grid size are shown in Fig. 5.29. Errors in surface temperature at ignition are below 3% for all the grid sizes analyzed (Fig.5.30, Table 5.5). Ideally the simulation should be run at the smallest grid size mentioned, but the computational cost especially at low pressures is prohibitive (> 5 weeks on a linux server running on a single core 3.12 Ghz x86 platform).

With the smallest grid size, the slope of the ignition delay time vs. pressure curve decreases slightly, but the surface temperature at ignition and the mass flux at ignition results show better agreement with the experimental measurements. More specifically, the linear dependency of the mass flux at ignition with pressure that was observed experimentally is attained with the smaller grid resolution (Fig.5.29).

![Figure 5.29: Grid sensitivity: mass flux at ignition vs. pressure.](image)
Table 5.5: Percentage error of data with respect to grid 3 (Δx=1.1mm, Δz=0.6mm)

<table>
<thead>
<tr>
<th>Grid</th>
<th>P (kPa)</th>
<th>Δt\text{ig}</th>
<th>ΔT_{\text{surf,ig}}</th>
<th>Δm_{\text{ig}}''</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Δx=2 mm Δz=1 mm</td>
<td>100.0</td>
<td>29%</td>
<td>3%</td>
<td>96%</td>
</tr>
<tr>
<td></td>
<td>82.7</td>
<td>19%</td>
<td>3%</td>
<td>76%</td>
</tr>
<tr>
<td></td>
<td>68.9</td>
<td>17%</td>
<td>1%</td>
<td>56%</td>
</tr>
<tr>
<td></td>
<td>55.2</td>
<td>5%</td>
<td>2%</td>
<td>31%</td>
</tr>
<tr>
<td></td>
<td>41.4</td>
<td>4%</td>
<td>1%</td>
<td>27%</td>
</tr>
<tr>
<td></td>
<td>27.6</td>
<td>1%</td>
<td>1%</td>
<td>16%</td>
</tr>
<tr>
<td></td>
<td>20.7</td>
<td>-1%</td>
<td>0%</td>
<td>5%</td>
</tr>
<tr>
<td>Grid 2 Δx=1.6 mm Δz=0.8 mm</td>
<td>100.0</td>
<td>13%</td>
<td>2%</td>
<td>68%</td>
</tr>
<tr>
<td></td>
<td>82.7</td>
<td>5%</td>
<td>1%</td>
<td>22%</td>
</tr>
<tr>
<td></td>
<td>68.9</td>
<td>3%</td>
<td>0%</td>
<td>14%</td>
</tr>
<tr>
<td></td>
<td>55.2</td>
<td>1%</td>
<td>1%</td>
<td>12%</td>
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<td>41.4</td>
<td>2%</td>
<td>1%</td>
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<td>0%</td>
<td>6%</td>
</tr>
<tr>
<td></td>
<td>20.7</td>
<td>-1%</td>
<td>0%</td>
<td>3%</td>
</tr>
</tbody>
</table>

Figure 5.30: Grid sensitivity: ignition delay time vs. pressure.
Another aspect to consider is that flame thickness changes with pressure. It has been shown that flame thickness \( l \) is inversely proportional to pressure, varying as \( l \sim 1/P^{1/2} \) [27]. As a result, the flame stabilization zone grows with decreasing pressure. This is yet another explanation of why a larger grid size can be used at low pressures to obtain the same resolution.

5.7 Domain Sensitivity Analysis

A sensitivity analysis was performed to determine the error that is being made by using the reduced size domain shown in Fig. 5.1. Both computational domains (complete and reduced domain) have the same height as the wind tunnel in the experimental apparatus. The only difference is in the x-direction: the reduced domain is 152 mm, and the complete domain is 392 mm.

The effects of increasing the domain are similar to those for a reduction in grid size. Similarly, the error in the results decreases with pressure. For the baseline grid size (\( \Delta x=2\text{mm}, \Delta z=1\text{mm} \)) the error in ignition delay time varied from 13% to 1%, the surface temperature at ignition varied from 2% to 0% and the mass flux at ignition varied from 28% to 5% when compared to the complete wind tunnel domain.

5.8 Parametric Study

In an effort to improve the agreement between the baseline case and the experiments presented in Chapter 3, Ref. [14], a parametric study was performed to examine the effects of pressure on the gas phase and solid phase kinetics. A further optimization of the baseline case is presented and discussed.

For the parametric study, the material properties \((k, \rho, c \text{ and } \varepsilon)\) as well as the heat of combustion \( \Delta H_{\text{comb}} \) were kept constant. The rest of the kinetic parameters were varied, resulting in diverse trends on ignition delay time \( t_{\text{ig}} \), mass flux at ignition \( m_{\text{ig}}'' \), and surface temperature at ignition \( T_{\text{ig}} \). The trends found are shown in Table 5.6. However, these trends were found not to hold for the entire range of ambient pressures analyzed. All cases were performed with a grid size of 2mm by 1mm (baseline case grid) for computational economy reasons.
5.8.1 Gas Phase Kinetics

Figures 5.31-5.32 show the effects of varying the gas phase activation energy ($E_{\text{gas}}$) on the ignition delay time, mass flux and surface temperature at ignition. Although increasing $E_{\text{gas}}$ provides a better match with experiments at pressures near 100 kPa, it does not significantly affect the results for lower pressures. The results are relatively insensitive to changes in $E_{\text{gas}}$ for $P < 60$ kPa, indicating another parameter dominates the reactions in the lower pressure range.

![Figure 5.31: Ignition delay vs. pressure: variable $E_{\text{gas}}$ (kJ/mol)](image-url)

**Figure 5.31: Ignition delay vs. pressure: variable $E_{\text{gas}}$ (kJ/mol)**
Figures 5.33-5.34 show the influence of the pre-exponential factor (B_{of}) of the gas phase reaction on the ignition delay time, mass flux at ignition and surface temperature at ignition. For variations near the baseline case, no substantial difference is found in the results. However, if B_{of} is decreased an order of magnitude, the pressure dependency becomes irregular. While this order magnitude decrease in the pre-exponential factor will fit the ignition delay experimental data better for pressures between 70 kPa and 100 kPa, it completely changes the shape of the pressure dependency (Fig. 5.33). The combination of a pre-exponential factor B_{of}=1.2 \cdot 10^{15} \text{ cm}^3/\text{mol-s} with an activation energy of E_{gas}=165 \text{ kJ/mol} seems to delay the gas phase kinetics to the point that ignition time increases with pressure at the low pressure limit (14 kPa). With those kinetic parameters at 14 kPa the gas phase reaction is so slow that the chemical induction time increases significantly and dominates over the heating and mixing time. McAllister et al. [28] found similar trends for pressures around 40 kPa. I. Also, a better fit in the specific ignition delay values for 70kPa < P< 100 kPa translates in worse agreement in the mass flux and surface temperature at ignition, if compared to the baseline case.

Figure 5.32: Mass flux at ignition (a) and surface temperature at ignition (b) vs. pressure: variable E_{gas} (kJ/mol)
In summary, changing the gas phase kinetics (activation energy $E_{\text{gas}}$ or pre-exponential factor $B_{\text{of}}$) presents no overall benefit on the results compared to the baseline case, because it changes the shape of the pressure dependency. Except for the lower limiting value for the pre-exponential factor, the overall trends with pressure for ignition delay, mass flux and temperature are the same as in the baseline case. Although ignition delay results might be improved by decreasing $B_{\text{of}}$, this would significantly worsen the
values obtained for the mass flux and surface temperature at ignition. Therefore, for $E_{\text{gas}}=165\text{kJ/mol}$ a $B_{\text{of}}$ value on the order of $10^{16}$ cm$^3$/mol-s seems to describe the experimental trends best.

5.8.2 Solid Phase Kinetics

The influence of the solid phase kinetics was also explored and the results are shown in the following figures. The heat of the pyrolysis reaction (or heat of volatilization, $\Delta H_{\text{vol}}$) affects the ignition delay time for pressures $P>60$ kPa (Fig.5.35), but shows no substantial effect on either the mass flux at ignition (Fig.5.36.a) or on the surface temperature at ignition (Fig.5.36.b). Thus, for the range of values analyzed ($800 \text{kJ/kg} \leq \Delta H_{\text{vol}} \leq 1400 \text{kJ/kg}$) the optimum value is chosen based on the ignition delay behavior.

![Figure 5.35: Ignition delay vs. pressure: variable heat of pyrolysis reaction $\Delta H_{\text{vol}}$ (kJ/kg)](image_url)
Increasing the activation energy of the solid phase pyrolysis ($E_{\text{solid}}$) increases the ignition delay time without changing the actual shape of the pressure dependency (Fig. 5.37). However, it should be noted that the $E_{\text{solid}}$ value corresponding to the baseline case (142 kJ/mol) is the largest value found in similar models in the literature (see Table 5.2). Higher $E_{\text{solid}}$ values found in other pyrolysis models such as in Ref. [4, 5] correspond to very different computational models that only simulate the solid decomposition and determine ignition by imposing a particular criterion. Due to the substantial differences in the models, it was not found appropriate to further increase the $E_{\text{solid}}$ value from the baseline case even if this would yield a better agreement of the ignition delay results with the experiments. Moreover, finding a better match to the ignition delay results would come at the expense of worsening the temperature results, as Fig. 5.38 b suggests. The mass flux at ignition surprisingly does not vary substantially for the range of $E_{\text{solid}}$ investigated (Fig. 5.38 a).

**Figure 5.36:** Mass flux at ignition (a) and surface temperature at ignition (b) vs. pressure: variable heat of pyrolysis reaction $\Delta H_{\text{vol}}$ (kJ/kg)
The effect of varying the solid phase pre-exponential factor $A_{\text{solid}}$ (1/s) is explored in Figs. 5.39-5.40. Decreasing $A_{\text{solid}}$ improves the ignition delay results extraordinarily (Fig. 5.39) but it increases tremendously the surface temperature at ignition (Fig. 5.40 b). With $A_{\text{solid}} = 1 \times 10^9$ 1/s the surface temperature is over-predicted by 9% at pressures near 100 kPa, and with $A_{\text{solid}} = 4 \times 10^9$ 1/s the surface temperature is under-predicted also by 9% but near 13 kPa. The mass flux at ignition is not influenced substantially by the variation of $A_{\text{solid}}$ in the range of values tested (Fig. 5.40 a).
Combining the results from the grid refinement analysis (which shows a 15-30% decrease in ignition delay time for 69 ≤ P ≤ 100 kPa) and this parametric study, perhaps there is a slightly better match to the experimental results than the baseline case. With a smaller grid (Δx=1.1mm, Δz=0.6mm) the slope of the ignition delay curve vs. pressure (Fig. 5.28) was recovered by slightly increasing the \( E_{gas} \) from 165 to 170 kJ/mol. Reducing the solid phase pre-exponential factor \( A_{solid} \) by half improved the ignition delay time results slightly at the cost of overestimating the temperature. The optimization did not improve

![Figure 5.39: Ignition delay vs. pressure: variable solid phase pre-exponential factor \( A_{solid} (s^{-1}) \)](image)

![Figure 5.40: Mass flux at ignition (a) and surface temperature at ignition (b) vs. pressure: variable solid phase pre-exponential factor \( A_{solid} (s^{-1}) \)](image)
substantially the trends shown with the baseline case and consequently the results are not included here.

5.9 Discussion

The numerical model correctly simulates the physics of the piloted ignition of a solid fuel: a solid fuel thermally decomposes releasing fuel volatiles; the volatiles mix with the surrounding air forming a flammable mixture; subsequently a gas phase reaction appears at the pilot, and if the reaction (premixed flame) can overcome heat losses to its surroundings, it propagates upstream onto the solid surface, where a diffusion (non-premixed) flame is then established. The various processes involved in the ignition of a solid fuel (solid heating, mixing of volatiles with oxygen, and thermal runaway) are all influenced by the environmental variables (gas velocity, pressure, oxygen concentration), in different ways. Three parameters have been used to evaluate these processes and are discussed below: the ignition delay time, the mass flux at ignition and the surface temperature at ignition.

1. Ignition Delay Time

As described in Chapter 2, the time it takes a solid fuel to ignite is typically broken down into three characteristics times: heating time, mixing or transport time, and chemical induction time. Pressure affects each of these characteristic times in a different manner.

The heating time or time for the solid to pyrolyze is fundamentally a measure of the heat transfer processes involved. An externally irradiated solid fuel will heat up more quickly under lower ambient pressure (Fig.5.12) due to a reduction in the convective heat transfer from the solid to its surroundings (Fig.5.13). Thermal decomposition is a strong function of temperature due to an Arrhenius behavior, i.e. pyrolysis rate \( \sim A_{\text{solid}} \exp\left(-\frac{E_{\text{solid}}}{RT}\right) \). Thus, enhancing solid heating will lead to faster pyrolysis and to an earlier production of fuel volatiles (Fig.5.14).

The mixing of the pyrolysis gaseous products with the surrounding oxidizer also changes with ambient pressure. A characteristic diffusion time can be estimated by \( t_{\text{mix}} \approx \frac{l^2}{D} \). If the characteristic mixing length (l) is maintained over the range of pressures analyzed, then the mixing time decreases with pressure because the molecular diffusivity D varies as \( 1/\rho \). Additionally, the mixing/transport of the fuel volatiles is enhanced at low pressures by the development of a thicker species concentration boundary layer, as Fig.5.15 shows. In other words, under reduced pressure the gaseous fuel products are distributed over a wider area in the flow, facilitating the mixing with the surrounding oxidizer.
Chemical induction time increases with decreasing ambient pressure because chemical reactions are slower at low pressures. A global single-step reaction rate (Eq. 5.6) can be expressed in terms of pressure in the following way:

\[
\frac{d[C_{xH_y}]}{dt} = -B_{of} x_{C_{xH_y}O_2}^a \left( \frac{P}{RT} \right)^{a+b} \exp \left( \frac{-E_{gas}}{RT} \right)
\]  

(5.7)

Equation 5.7 reveals that the reaction rate will decrease with pressure (a, b in this model are 1). However, for the baseline case at the range of pressures analyzed, the reaction in the gas phase appeared earlier at lower pressures (see Fig. 5.16). Also the reaction induction time is very small at the range of pressures analyzed here. This result indicates that other processes are dominating the ignition time. More specifically, the heating times are dictating the overall process until $P \approx 10$ kPa when ignition does not occur.

The numerical model results show that ignition delay time decreases with ambient pressure similarly to the experimental findings from Chapter 3. This is primarily the result of both the heating and mixing times decreasing with decreasing pressure. Except at very low pressures, the chemical time is not sufficiently large to overcome the trends of the other two processes even at the low pressure range tested here. However, it was demonstrated that extreme values of the gas phase kinetic parameters can in fact produce an increase in ignition delay time at the lower pressure limit (Fig. 5.33).

2. Mass Flux at Ignition

The predicted mass loss rate trends also agree qualitatively with the experiments: the mass flux at ignition decreases at lower ambient pressures. Figure 5.14 shows the mass flux time history data for a range of pressures. It clearly indicates that ignition takes place with a lower mass flux at reduced pressures (except for $P=10$ kPa). This trend is not only due to a reduced heat transfer coefficient at lower pressures but also because a lower mass flux is needed to reach flammable conditions at reduced pressures (see Fig. 5.17). The gas phase reaction not only appears earlier at low pressures, it also requires a lower mass flux of pyrolyzate vapors.

The case of $P=10$ kPa requires further explanation. The PMMA samples did not ignite in the physical experiments at such low pressure, in fact the limiting pressure for ignition was found to be 14 kPa. In the numerical model it is unclear if sustained ignition is achieved at that point. The temperature traces revealed a change in slope at a particular instant, but the heat release rate shows a constant instability that indicates that the diffusion flame is not permanently anchored on the solid surface. At low Damköhler numbers ($Da = \frac{t_{conv}}{t_{chem}}$, ratio of flow characteristic residence time and chemical reaction time) such as situations where there is slow chemistry (low $P$ or low $O_2$, for example) it was found that ignition was
delayed or even prevented, but the model in Ref. [10] still predicted ignition. In any case, it seems that P=10 kPa is a limiting point in terms of ignition behavior.

3. **Surface Temperature at Ignition**

The trends found for the relationship between surface temperature at ignition and pressure do not exactly match the experimental findings; a few possible explanations are given below. The experiments show that the surface temperature at the moment of ignition grows with decreasing pressure. The model shows the opposite trend, although the temperature values are in the same ballpark.

First of all, the surface temperature measurements should be interpreted only as an approximation of the actual values. As explained in Chapter 3, it is difficult to get accurate temperature measurements with a single thermocouple bead in contact with a receding surface as the polymer melts and bubbles emerge during the pyrolysis.

Additionally, prior to sustained ignition, the premixed flame that appears at the pilot might be quenched (‘flashing’ conditions) if the heat released by this reaction cannot overcome the heat losses to the solid surface. This phenomenon is similar to the flash point in liquid fuels. Flashing consumes the pyrolysis gases produced at the solid fuel but it also increases the surface temperature, enhancing further fuel volatile production. Examples of this ‘flashing’ in the numerical simulations can be seen in Fig.5.41 where a series of sequential snapshots are shown. Flashing was more frequent at lower pressures. The ignition event in the numerical model is determined when the temperature traces show a peak and the convective heat transfer at the surface becomes positive. Now, as Fig. 5.41 shows this can very well correspond to a few seconds before sustained ignition occurs. From Fig 5.41 b (ignition in the model) to Fig.5.41 e (sustained burning) the surface temperature has increased from 318ºC to 339.7ºC. So, it is quite possible that the differences in temperature between the model and the experiments are due to a discrepancy in the definition of ignition. It should be noted that it is not possible to numerically determine the instant corresponding to Fig. 5.41 e because there are no abrupt changes in the surface temperature data with the current resolution.

Although most of the research focused on the effect of pressure on the ignition process, the influence of other environmental variables was also explored. The overall effect of the forced flow velocity is predicted correctly. However, the model seems to underpredict the heat losses from the solid surface, yielding similar temperature traces at different air flow velocities where the experiments present clear differences. The influence of oxygen concentration is also underpredicted with the numerical model most likely due to oxidative pyrolysis not being included in the model to complement the thermal decomposition.
Figure 5.41: Sequential snapshots showing flashing (baseline case, 41 kPa).
5.10 Conclusions

This research presents a two-dimensional numerical model developed with FDS 5 to investigate the effects of environmental variables on the piloted ignition of a solid fuel under external radiant heating. The focus is to confirm the hypotheses generated by experimental results of the effects on ignition of air flow velocity, oxygen and, in particular, ambient pressure. The phenomenological explanations thought to be responsible for those experimental findings, presented in Chapter 3, are then tested and confirmed by the numerical analysis.

The model correctly represents the complex physical mechanisms involved in the piloted ignition process and agrees fairly well with previous experimental results. It is confirmed that as ambient pressure is reduced, ignition occurs sooner and with a reduced mass flux of pyrolyzate gases required. The decrease in ignition delay time with pressure is attributable to a combination of reduction in convective heat losses and in the mass of fuel vapor required to reach a flammable mixture. The reduction in ambient pressure affects the flow field and, in particular, it leads to thicker temperature and species profiles above the solid surface. The present numerical analysis shows that the gas phase reaction (premixed flame) at the igniter appears earlier and requiring less fuel mass flux at lower pressures. The establishment of a diffusion (non-premixed) flame also appears earlier as pressure is reduced.

The numerical analysis represents a detailed first approach to modeling the effect of reduced ambient pressure on piloted ignition of solid fuels, establishing the groundwork for future development.
5.11 References


6.1 Conclusions

This research attempts to answer a series of questions that emerged when NASA was developing the Constellation Program and designed the internal atmospheres of its human space exploration vehicles with an increased oxygen concentration and an overall reduced pressure. The design choices led to an evaluation of how these new environmental conditions affect material flammability. Up until that time, the issue of how reduced ambient pressures affected the ease of ignition of solid fuels had not been widely investigated.

After the initial piloted ignition studies under reduced ambient pressure from McAllister et al. [1] and Olson [2] presented contradictory results, a question became apparent: is ignition hindered or promoted by low pressure environments? The answer is not simple. Subsequent studies, including the research presented here, have shown that piloted ignition is a complex problem with many different factors coming into play. The outcome depends on what type of physics dominates the process. That is, whether the most determining factor in an ignition event is the heat transfer between a solid fuel with its surroundings, the mixing of fuel vapor and oxygen, or the gas phase chemical reaction.

The ignition delay time in the experiments from McAllister et al. [1] showed an appreciable decrease with ambient pressure. However, the measurement of the ignition delay time did not clarify the underlying physics of why a material behaves the way it does under reduced pressure conditions. For this reason, it was necessary to explicitly measure the fuel mass loss rate or mass flux at ignition. In the present research, we have used the available tools (experimental measurements, theoretical analysis and numerical modeling) to explain why ignition can occur earlier at low pressures and how it relates to the fuel mass flux at ignition. The underlying objective is to examine the physical mechanisms responsible for solid fuel ignition and how environmental variables such as pressure affect those processes.

Throughout a series of experiments in a laboratory-scale combustion wind tunnel presented in Chapter 3, this research has shown that both the ignition delay time and the mass flux at ignition of a solid fuel such as PMMA decrease with pressure. To our knowledge this is the first time the mass flux at ignition of a solid fuel has been measured for a range of sub-atmospheric pressures. Chapter 4 presented a simplified theoretical analysis that
explained why the ignition delay time and the fuel mass loss rate decrease with ambient pressure. The theoretical analysis helped identify the governing processes and provided a preliminary answer to the questions we were seeking. Then a numerical model was applied to quantify the influence of pressure on the piloted ignition of PMMA. Similar models have been developed before, but none explicitly investigated the effect of pressure on ignition. The numerical model shows two important results: 1) the convective heat flux at the sample surface decreases with ambient pressure, resulting in solid fuels heating up more quickly and pyrolyzing faster when thermally irradiated, and 2) the mass flux of pyrolyzate vapors required for a gas-phase reaction to occur at the pilot is reduced under low pressures, leading to an earlier ignition. These results confirm the hypotheses offered as phenomenological explanations for the experiments in Chapter 3.

This research tackles a specific problem (do low pressure environments represent a higher fire risk?) and provides a comprehensive solution to the question posed based on experimental work, theoretical explanations and numerical simulations. The outcome of this research demonstrates that there are situations where low pressure environments represent an increased fire hazard. Polymers that are subjected to a low external radiant heat flux for extended periods of time will ignite more readily under low pressure. This scenario could easily take place in spacecraft or aircraft, where malfunctioning electronic equipment can produce constant low external heating on polymeric panels and covers that comprise the interior of a cabin in a low pressure environment, and an electrical spark could produce the ignition source. Since all ignition sources can never be completely eliminated, a strategy aimed at prevention is the best solution. This research also indicates that the conditions at which material flammability is generally tested (1 atm, standard sea level conditions) will not yield the most conservative results. Therefore, flammability testing should be revised according to the findings of this investigation.

6.2 Future Research

The research presented here represents the groundwork for future modeling studies. As exploratory work, the numerical model developed accomplishes the main objective of clarifying the physical mechanisms responsible for the piloted ignition of solid fuels. The main physical processes involved in an ignition event are correctly depicted in the numerical results. However, the model has some shortcomings.

First and foremost, the quantitative agreement between the model and the experimental results needs to be improved. The parametric study in Chapter 5, Section 7 indicates some possible avenues which can be explored in order to achieve this objective.
The modeling of the thermal decomposition of the polymer can be improved by coupling Gpyro [3], a generalized pyrolysis model, to the FDS simulations. Gpyro would include two-dimensional heat conduction throughout the decomposing solid (FDS only solves a 1-D heat conduction equation per cell) and the advantages of improving the heat transfer model within the solid could be evaluated. More complicated pyrolysis processes such as those found in charring materials could be simulated with Gpyro. In that sense, the model could be extended to a wide variety of materials, both charring and non-charring. Also, including oxidative pyrolysis in addition to simple thermal degradation in future models will most likely improve the sensibility of the simulations to oxygen concentration.

Finally, it would be very interesting to model the experiments from Olson [2] to see if the same type of model is capable of representing problems with different dominating phenomena, i.e. where heating times are not as important as the gas phase reaction chemistry. Further understanding in this area could help quantify the boundaries where low pressure or the combination of low pressure and high oxygen represent an increased fire risk.
6.3 References

