



# The combined effect of pressure and oxygen concentration on piloted ignition of a solid combustible

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## ABSTRACT

There are a number of situations when fires may occur at low pressures and oxygen concentrations that are different than standard atmospheric conditions, such as in buildings at high elevation, airplanes, and spacecraft. The flammability of materials may be affected by these environmental conditions. Since ignition delay is a measure of material flammability and directly influences whether a fire will occur, experiments were conducted to assess the variation of the ignition delay of PMMA in sub-atmospheric pressures and elevated oxygen concentrations. Three sets of experiments were performed at different pressures and in air, in an atmosphere having 30% oxygen/70% nitrogen by volume, and in a “normoxic” atmosphere (constant oxygen partial pressure). It was observed that as the pressure is reduced, the ignition time decreased, reached a minimum, and then increased until ignition did not occur. Several mechanisms were considered to explain the “U-shaped” dependence of ignition time on pressure, and three regimes were identified each having a different controlling mechanism: the transport regime where the ignition delay is controlled by changes in convection heat losses and critical mass flux for ignition; the chemical kinetic regime where the ignition delay is controlled by gas-phase chemical kinetics; and an overlap region where both the transport and chemistry effects are seen. The results provide further insight about the effect of the environmental conditions on the flammability of materials, and guidance about fire safety in low pressure environments.

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## 1. Introduction

There are a number of situations when fires may occur at pressures and oxygen concentrations that are different than standard atmospheric conditions. Atmospheric pressure is not constant with elevation and there are cities such as Wenzhuan, Tibet (elevation 5100 m) where the atmospheric pressure is as low as 55.3 kPa [1,2]. In some cases, the reduction in atmospheric pressure is offset by an increased oxygen concentration. One hotel in Cuzco, Peru, located at 3400 m, is offering their guests the option to enrich their room with oxygen to help combat the effects of altitude sickness [3]. The atmospheric pressure at this altitude is only 68 kPa so to offset the reduction in oxygen partial pressure due to altitude, the rooms are enriched to an oxygen concentration of 24% by volume.

Another situation of an environment with non-standard pressure and oxygen levels is onboard aircraft and spacecraft. The FAA requires airplane cabin pressures to be higher than 75.9 kPa,

or an equivalent altitude of 2440 m [4]. NASA is designing the next generation of space vehicles to operate with a different cabin environment than has been used previously [5,6]. To reduce the time required to pre-breathe before going on an extra-vehicular activity (EVA) and the mass of consumables required during a long-duration mission, the nitrogen partial pressure will be decreased. To maintain human comfort and performance, the oxygen partial pressure will be maintained at the equivalent of 2347 m (7700 ft) elevation which provides adequate human performance and health in long-term low-gravity. However, the net result is an elevated oxygen concentration. The currently proposed cabin environment is a pressure of 52.7–58.6 kPa with an oxygen concentration of 30–34% by volume. Since costly and deadly fires can occur at these non-standard pressures and oxygen concentrations, the effect of these conditions on material flammability should be understood.

Measuring the piloted ignition delay time is one method to evaluate material flammability [7], and when flame spread is viewed as a series of piloted ignition events, the trends in ignition delay can be used to predict trends in flame spread rates. Unfortunately, the combined influence of pressure and oxygen concentration on piloted ignition is not well understood. There are several works in the literature that examine autoignition, such as [8–13]. However autoignition is strongly influenced by gas-phase chemis-

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try effects [14] whereas in piloted ignition, the pilot minimizes the gas-phase chemistry effects. The dominant mechanisms of auto-ignition are therefore different from those of piloted ignition and conclusions about piloted ignition cannot necessarily be drawn from the autoignition results. Cook et al. [15] is one of the few works that examined the role of pressure on piloted ignition. In this early work, the piloted ignition delay and the ignition temperature of filter paper were measured in air for pressures ranging from atmospheric to 920 kPa. The igniter was an electrically heated wire in contact with the filter paper, and its temperature at ignition was reported as the ignition temperature of the paper. Interestingly, the temperature of the igniter at ignition was shown to decrease as the pressure increased, but the ignition delay time showed a slight increase with pressure. If these trends are relevant for pressures below atmospheric, one might infer that the piloted ignition delay will be shorter in reduced pressure environments. Investigating this phenomenon is one of the objectives of this study.

Though piloted ignition occurs near the lean flammability limit and should therefore not be affected by an elevated oxygen concentration, an increase in oxygen concentration can decrease piloted ignition delay times due to its influence on the solid pyrolysis and gas-phase chemical kinetics [16–19]. For PMMA Cordova et al. [22] saw that the ignition delay time decreased when the oxygen concentration was increased from 21% to 25%, but noted that any further increase in the oxygen concentration did not have an effect. Similar results were seen by Heitaniemi et al. [20] and Atreya and Abu-Zaid [21]. The magnitude of the effect of oxygen concentration, however, seems to depend on the external heat flux level [22,23]. Cordova et al. [22] found the decrease in ignition time ranged from 15% to 40% depending on the external heat flux, with the greatest decrease noticed at high heat fluxes. Though the ignition delay times were not measured, Cook et al. [15] examined the ignition temperature of paper strips at different pressures and oxygen concentrations. At high pressures, the ignition temperature decreased as the oxygen concentration increased. The greatest decrease (10.4%) was observed at the highest pressure tested (1022.4 kPa) but the decrease in temperature became less pronounced as the pressure was reduced and no clear trend was seen at atmospheric pressure. The interaction between pressure and oxygen concentration and their impact on ignition temperature and ignition delay time will be investigated in this study.

## 2. Description of experiments

All tests were performed in the forced-flow ignition and flame spread test (FIST) apparatus [22]. A simplified schematic and photograph of the FIST apparatus are shown in Figs. 1 and 2, respectively. The version of the FIST used in this work has a tunnel 0.39 m long in the streamwise direction, 0.15 m wide, and 0.075 m high. A fan at the downstream end of the tunnel can induce forced flows from 0 to 70 cm/s. At the upstream end, an array

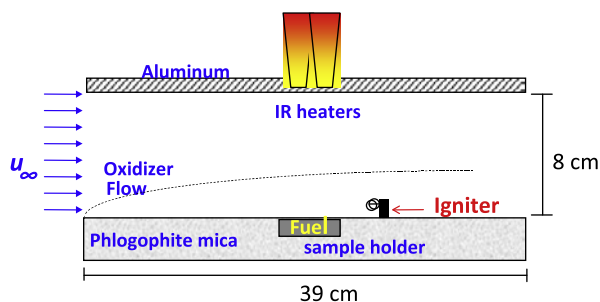


Fig. 1. Simplified schematic of the FIST tunnel.



Fig. 2. Photograph of the FIST tunnel and the containment chamber.

of louvers is used to straighten the flow. The fuel samples are mounted flush with the tunnel floor 0.20 m from the tunnel downstream end. An infrared radiant heater placed in the ceiling of the tunnel is used to preheat the samples and is arranged to produce a nearly constant heat flux from 0 to 15 kW/m<sup>2</sup> over the surface of the sample. The radiant heater produces 99% of the steady-state heat flux in three seconds. Piloted ignition is induced with a 3-mm diameter coiled Kanthal wire mounted 10 mm downstream of the sample. The igniter is kept above 1000 °C in all tests to minimize the gas-phase induction time. To perform an ignition test, the fan is turned on and the flow is allowed to reach steady state. The sample heating is initiated by turning on the heater. When the initiation of pyrolysis of the fuel sample is visually observed, the igniter is turned on and ignition is determined by the onset of sustained flaming of the sample surface.

The FIST apparatus is mounted horizontally in a containment chamber, shown in Fig. 2, in which experiments can be conducted at a range of ambient pressures and oxygen concentrations. The chamber has an ID of 0.40 m and a length of 0.83 m, three windows, and three ports for electrical and gas flow connections. The chamber pressure is monitored and controlled using a pressure transducer. The oxygen concentration is set via partial pressures. The desired oxygen concentration is achieved by evacuating the chamber to a pressure lower than the desired test pressure and adding pure oxygen to the chamber so that the mixture is at the desired final pressure and oxygen concentration. To ensure good mixing, the fan in the tunnel is turned onto a high setting and the gases are allowed to mix for at least 5 min. The ambient gas temperature inside the chamber is monitored with a thermocouple placed near the inlet of the tunnel to make sure the chamber does not heat excessively during the tests. The maximum recorded temperature increase was 5 °C.

In the present work, all the tests were conducted with commercially available black polymethylmethacrylate (PMMA, Type G, Atoglas), and with a flow velocity at the fan end of 0.3 m/s and a radiant flux of 14 kW/m<sup>2</sup>. The PMMA samples used were 30 mm by 30 mm with a thickness of 10 mm and were mounted so that they were flush with the surface of the tunnel. One K-type thermocouple was embedded on the top surface of the sample to record the surface temperature. Although care was taken to ensure that the thermocouple bead was embedded flush with the sample surface, the measured temperature should only be viewed as an approximation to the actual surface temperature due to movement of the thermocouple resulting from surface density changes. Ignition was recorded manually based on observation but was verified by the surface temperature traces. The ignition delay time was measured as the time required for the sample to ignite after the external heat flux was activated. All tests were repeated three times to estimate the experimental repeatability and obtain an average value.

Three series of tests were performed to explore the effect of reduced pressure and the combined effect of reduced pressure and increased oxygen concentration on the ignition delay of PMMA. In the first series of tests, the pressure was varied from 101.3 kPa to the lowest pressure at which ignition was observed while the oxygen concentration was fixed at 21% by volume (air). To understand the flammability of materials in reduced pressures and elevated oxygen concentrations, the pressure was also varied from 101.3 kPa to the lowest pressure for ignition but the oxygen concentration was fixed at 30% by volume. In the final series of tests, the chamber atmosphere was kept at the “normoxic” equivalent identified by NASA in [5,6] as possible atmospheres for space vehicle cabins. Tests were performed in pressures ranging from 101.3 kPa to 37.6 kPa while the oxygen concentration was increased such that the partial pressure of oxygen remained constant at 21.3 kPa (see Table 1). The normoxic equivalent environments are chosen because oxygen transport across aveoli in the human lung depends primarily on the partial pressure of oxygen. Maintaining the partial pressure the same as at standard atmospheric conditions prevents hypoxia in the crew as the ambient pressure is decreased.

### 3. Results

The measured ignition delay times as a function of pressure are shown in Fig. 3 for all three oxidizer mixtures tested. For all results, each data point represents the average of three tests. The average standard deviation was 3.95% in air, 3.68% in 30% O<sub>2</sub>, and 2.55% in the normoxic equivalent environments.

In air, it is seen that as the pressure is decreased below atmospheric, the ignition delay time decreases until about 28 kPa where a minimum occurs. This minimum is 22% lower than the ignition time in sea-level air. If the pressure is decreased below 28 kPa, the ignition time sharply increases until no ignition is observed at pressures below 7 kPa.

As the pressure is reduced, the appearance of the flames changes radically. Fig. 4 compares the appearance of the flame in standard atmospheric pressure to that at a pressure of 27.6 kPa in air. In addition to the shape, the most noticeable difference is the change in color. The atmospheric flame is yellow whereas the low pressure flame is blue. The shape and color of the flame at low pressure are similar to those observed in microgravity tests [24,25], which is understandable since reducing the ambient pressure reduces buoyancy [26].

Also shown in Fig. 3 is the ignition delay time as a function of pressure for an oxygen concentration of 30% by volume. Similar trends in the ignition delay times are seen here as in air. The ignition time decreases until a minimum is reached and any further pressure reduction results in an increased ignition time. However, the minimum occurs at a slightly higher pressure (41 kPa) than for the air tests. This minimum ignition time is 17.5% less than it is at atmospheric pressure for the same oxygen concentration. In addition, the no-ignition point occurs at a lower pressure than for the air tests (below 3.4 kPa). In the case with 30% oxygen, as the pressure was reduced below 7 kPa, the gases would flash for extended periods of time before the sample would ignite. Because of this increased flashing and the dimness of the flame, it was extremely difficult to determine the exact ignition time so no data is reported here. However, at 3.4 kPa, the gases continued to flash and no sustained ignition occurred. The results indicate that oxygen concen-

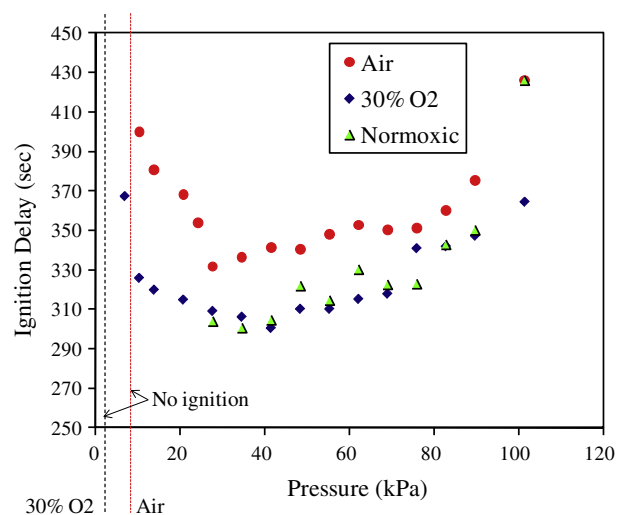


Fig. 3. Ignition delay time as a function of pressure for different oxygen/nitrogen mixtures.



Fig. 4. Photographs of the flames in air at atmospheric pressure (above) and at 27.6 kPa (below).

tration affects the ignition delay at least up to 30%, as observed by Cordova et al. in [22], and that the effect of changes in pressure varies slightly with the oxygen concentration.

The ignition delay times in normoxic equivalent atmospheres (Table 1) are also shown in Fig. 3. As observed before, the ignition delay times decrease as the pressure is reduced and the oxygen concentration is increased following the normoxic curve. The total reduction in the ignition delay time was 29.5% between sea-level air and the normoxic atmosphere at 34.5 kPa. Because the partial pressure of oxygen is kept at 21.3 kPa, no tests can be performed at lower pressures. The ignition delay time decreases when the oxygen concentration is increased from air to 24% (corresponding

Table 1

Pressure and oxygen concentrations for “normoxic” environments. The partial pressure of oxygen is a constant 21.27 kPa.

|                  |       |      |      |      |      |      |      |      |      |      |      |
|------------------|-------|------|------|------|------|------|------|------|------|------|------|
| Pressure (kPa)   | 101.3 | 89.6 | 82.7 | 75.8 | 68.9 | 62.1 | 55.2 | 48.3 | 41.4 | 34.5 | 27.6 |
| % O <sub>2</sub> | 21.0  | 23.8 | 25.7 | 28.1 | 30.9 | 34.3 | 38.6 | 44.1 | 51.5 | 61.7 | 77.2 |

pressure of 89.6 kPa), but no additional decrease in the ignition time is observed for higher oxygen concentrations. Though only tested in atmospheric pressure, Cordova et al. in [22] found a very similar result – that the ignition delay time is independent of oxygen concentration for values greater than 25%.

#### 4. Discussion

The ignition of a solid can be viewed as a series of three events [27,28]. In the first, the solid must be heated to a high enough temperature for pyrolysis to occur. Once the pyrolysis gases are produced, they must mix with the oxidizer to form a combustible mixture. A gas-phase induction process must then be initiated by the igniter for thermal runaway to ignition and flaming to occur. Once the mixture near the igniter has ignited, a pre-mixed flame may propagate back towards the solid. In order to initiate sustained burning (equivalent to the fire point), enough pyrolysis gases must be generated at the surface so that the heat release rate of the approaching flame is great enough to overcome the heat losses to the solid do not extinguish the flame. If this is the case, a diffusion flame will become anchored at the surface. By viewing ignition in this manner, it is apparent that there is a critical mass flow rate of pyrolysis gases from the solid in order for sustained burning to occur [29–31]. Flashing ignition (equivalent to a flash point) occurs when sufficient pyrolysis gases are produced so that the mixture at the igniter is near the lean flammability limit. However, the heat release rate of this lean pre-mixed flame is too low to overcome the heat losses to the solid and it is extinguished before a diffusion flame can become anchored at the surface.

Pyrolysis of a solid is strongly temperature dependent. The rate of mass loss from the solid due to pyrolysis can be expressed by the following Arrhenius-type equation:

$$\dot{m} = A_p \rho \int_0^l \exp(-E_p/RT) dx \quad (1)$$

where  $A_p$  is the pre-exponential factor,  $\rho$  is the solid density,  $E_p$  is the activation energy,  $T$  is the solid temperature, and  $l$  is the solid depth. Given the exponential character of the reaction and that the activation energy is typically large, pyrolysis is very slow at low temperatures but increases very quickly above a temperature usually identified as the pyrolysis temperature. During the heating phase of ignition, the solid is heated by the radiant flux at its free surface while it loses heat to the gas flowing past its surface due to convective cooling (here surface re-radiation is a minor effect because of the experiment geometry). If the radiant heating rate is greater than the heat loss by convection, the solid temperature increases and a temperature gradient forms inside the solid that propagates deeper with time. Pyrolysis will occur in regions of the solid with sufficiently high temperatures and consequently the volume of the solid undergoing pyrolysis and the local pyrolysis rates increase with time as the solid is heated. Under certain conditions, the pyrolysis rate would be sufficient to create a combustible mixture near the igniter and ignition may occur. This pyrolysis rate is often referred to as the critical mass flux for ignition [29–31], as discussed above.

An approximate analytical expression for the ignition time can be written as the sum of the pyrolysis time and the chemical induction time (from [28]). In atmospheric pressure conditions, the mixing time is typically on the order of a few seconds [27] is normally considered relatively unimportant. The resulting expression for the ignition time is then [28]

$$t_{ig} = \frac{\pi}{4} \frac{k\rho c_p (T_{ig} - T_0)^2}{(\dot{q}_e'' - h_{eff}(T_{ig} - T_0))^2} - \frac{c_1 \chi}{u_\infty} \ln \left( 1 - \frac{\Gamma}{A_x} \right) \quad (2)$$

where  $k$  is thermal conductivity,  $\rho$  is the solid density,  $c_p$  is the solid specific heat,  $T_{ig}$  is the ignition temperature,  $T_0$  is the initial temperature,  $\dot{q}_e''$  is the external heat flux,  $h_{eff}$  is the effective heat transfer coefficient including both radiation and convection,  $c_1$  is a constant of proportionality,  $\chi/u_\infty$  is the flow residence time,  $\Gamma$  is the critical Damkohler number for ignition, and  $A_x$  is the characteristic Damkohler number. The critical and characteristic Damkohler numbers are given by, respectively:

$$\Gamma = 4c_2 \left( \frac{E}{RT_{pilot}} \right) \left[ \frac{2 - \beta}{e^2(1 - \beta^2)} \right]$$

$$A_x = \frac{A\Delta H_R \rho_g n W_o EX_{o,\infty} X_{F,S} (P/RT_{pilot})}{c_{p,g} RT_{pilot}^2 u_\infty / \chi}$$

where  $c_2$  is a constant of proportionality,  $E$  is the gas-phase activation energy,  $R$  is the ideal gas constant,  $T_{pilot}$  is the pilot temperature,  $\beta = T_{pilot} c_{p,g} / Y_{f,s} \Delta H_R$ ,  $c_{p,g}$  is the gas specific heat,  $X_{f,s}$  is the mole fraction of fuel,  $A$  is the gas-phase pre-exponential factor,  $\Delta H_R$  is the heat of reaction,  $\rho_g$  is the gas density,  $n$  is the reaction order,  $W_o$  is the molecular weight of oxygen, and  $X_{o,\infty}$  is the mole fraction of oxygen. However, the ignition temperature in Eq. (2) is not a constant and is a function of the critical mass flux for ignition and the rate of pyrolysis (Eq. (1)), i.e.  $T_{ig} = \text{fn}(\dot{m}_{cr,fire}'', \dot{m})$ . An analytical expression for the critical mass flux for sustained ignition was developed by Rich et al. in [30]:

$$\dot{m}_{cr,fire}'' = \frac{h_{conv}}{c_p} \ln \left[ 1 + \frac{Y_{O2,\infty}(1 - \chi_r)(\Delta H_R/r) - c_p(T_s - T_0)}{(1 - \chi_r)\Delta H_R - (rc_p/Y_{O2,\infty})(T_s - T_\infty + (1 + \frac{Y_{O2,\infty}}{r})(T_{f,cr} - T_\infty))} \right] \quad (3)$$

where  $h_{conv}$  is the convective heat transfer coefficient,  $\chi_r$  is fraction of flame radiation lost to the environment,  $r$  is the stoichiometric oxygen to fuel mass ratio,  $T_s$  is the surface temperature at ignition,  $T_\infty$  is the ambient temperature, and  $T_{f,cr}$  is the critical flame temperature for ignition (see [31]).

The above phenomenological and analytical descriptions of piloted ignition can be used to understand the observed experimental trends. Changing the pressure and oxygen concentration impacts mass and energy transport during the two stages of the ignition process. The effect of changes in pressure, oxygen, and the associated interactions between pressure and oxygen during the heating and chemical induction phases of ignition as predicted by Eq. (2) are used to explain the experimental results.

#### 4.1. Effect of pressure

##### 4.1.1. Convection heat loss

Pressure affects the solid heating process through the convection heat loss. Because the forced flow velocity in these experiments is low (maximum Reynolds number of  $10^3$ ), a mixed flow (free and forced) is expected. For mixed forced and natural convection over a flat plate, the convective heat transfer coefficient can be represented as

$$h \propto \text{Re}^{1/2} \text{Pr}^{1/3} \sqrt{1 + \frac{\text{Gr}}{\text{Re}^2} \text{Pr}^3} \quad (4)$$

where  $\text{Re}$  is the Reynolds number,  $\text{Pr}$  is the Prandtl number, and  $\text{Gr}$  is the Grashof number [32]. For relatively high velocity flows, Eq. (4) reduces to  $h \propto \text{Re}^{1/2} \text{Pr}^{1/3}$ . The Prandtl number is not a function of pressure but the Reynolds number is directly proportional to pressure through the density term. In the limit of pure natural convection, the relation for the mixed convection heat transfer coefficient becomes  $h \propto \text{Gr}^{1/4} \text{Pr}^{1/4}$ . If the oxidizer is assumed to be an ideal gas, the Grashof number is proportional to the pressure squared.

Thus, no matter what form of convective flow, the heat transfer coefficient is proportional to the square root of the pressure. Consequently, when the pressure is decreased, the heat transfer coefficient is decreased resulting in a reduced convective heat loss for the fuel surface and in turn a faster solid heating and shorter ignition time as shown in Eq. (2).

The surface temperature histories provide evidence of the change in the heat transfer coefficient with pressure. Fig. 5 shows the surface temperatures as a function of time for a range of pressures in air. It is seen that the rate of temperature increase is greater as the pressure is reduced, at least for pressures above 34.5 kPa. For pressures below 34.5 kPa the surface temperatures follow roughly the same path (as shown in Fig. 6) suggesting that the effect of pressure on the heat transfer coefficient is smaller below 34.5 kPa. This effect may be due to reduced buoyant flow or the heat transfer coefficient decreasing more rapidly as the pressure decreases due to the square root dependence. Though not shown here, the rate of surface temperature rise was also observed to increase with pressure for increased oxygen concentrations.

#### 4.1.2. Critical mass flux for ignition

Pressure may also affect the heating time by changing the critical mass flux of fuel for sustained ignition, thereby changing the ignition temperature in Eq. (2). As shown in Eq. (3), the critical mass flux is a function of the convective heat transfer coefficient which decreases with pressure. 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. Thus, for a given mass flow rate of fuel the reduced oxidizer mass flow rate results in an increased equivalence ratio above the solid. Because the temperature of pre-mixed flames is a function of equivalence ratio, less fuel is required to produce a sufficiently hot pre-mixed flame between the igniter and solid for sustained ignition, reducing the critical mass flux for ignition. This effect is seen in the relatively constant lean flammability limit as pressure is varied. Due to the strong temperature dependence of pyrolysis, the temperature at which the critical mass flux is generated would be lower and therefore attained sooner during the heating process, thereby reducing the heating time. To support this argument, the surface temperature at ignition is plotted in Fig. 7 as a function of pressure in air (21% O<sub>2</sub>) and in 30% O<sub>2</sub>. In air, it is seen that ignition occurs at a lower surface temperature when the pressure is reduced, supporting the reduced critical mass flux concept. However, at sufficiently low pressures (about 50 kPa in air) or with an increased oxygen concentration, other mechanisms begin to influence the surface temperature prior to ignition and are discussed below.

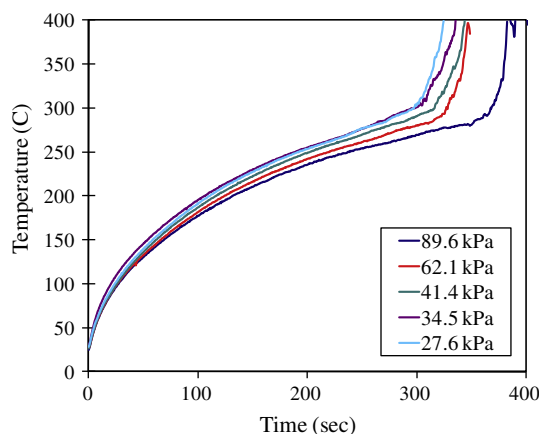


Fig. 5. Surface temperature as a function of time demonstrating the change in heat transfer coefficient for different pressures in air down to a pressure of about 34.5 kPa.

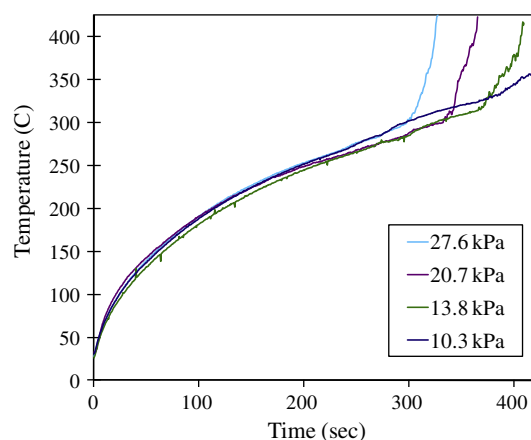


Fig. 6. Surface temperatures as a function of time in air at pressures below 30 kPa.

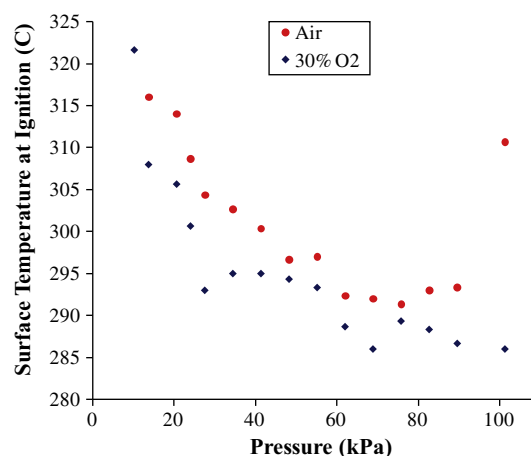


Fig. 7. Average surface temperature at ignition for air and 30% O<sub>2</sub>. The standard deviation for all point combined is 0.86% in air and 0.91% in 30% O<sub>2</sub>.

#### 4.1.3. Pyrolysis rate

Pressure may also affect the rate of pyrolysis. Koptelov and Karyazov [33] examined the thermal decomposition of several polymers, including PMMA, using thermogravimetry and calorimetry for pressures from 1.3 kPa to 13 MPa in various inert gases. For PMMA it was found that the rate of decomposition was insensitive to pressure. Previous researchers have noted that the atmospheric pressure can change the distribution of decomposition products formed, with lower pressures favoring heavier hydrocarbons [34,35]. Though the findings by Koptelov and Karyazov [33] were measured in inert atmospheres, this insensitivity of the pyrolysis rate in PMMA to changes in pressure was seen qualitatively during the experiments presented here. The formation of bubbles of pyrolysis gases escaping from the surface occurred at approximately the same surface temperature in all the tests. However, the rate of pyrolysis for PMMA is sensitive to oxygen concentration (as discussed below) so it is possible that there could be a pressure dependence in environments with higher oxygen concentration. If there were such an effect, pressure could affect the pyrolysis activation energy ( $E_p$  in Eq. (1)), the heat of combustion ( $\Delta H_R$  in both Eqs. (2) and (3)), and the stoichiometric oxygen to fuel mass ratio ( $r$  in Eq. (3)). By changing these properties, the ignition temperature would vary because both the pyrolysis rate and the critical mass flux change. The chemical induction time would also vary due to changes in both the critical and characteristic Damkohler

numbers. The determination of these effects, however, requires a more detailed study of the ignition process.

#### 4.1.4. Chemical induction time

In our tests, the igniter is maintained at a high temperature (above 1000 °C) with the objective of reducing the significance of the gas-phase chemical time [27]. However, as the pressure is reduced, the species concentrations decrease and therefore the gas-phase reaction rate is reduced. In other words, the characteristic Damkohler number in Eq. (2) decreases (via  $\rho_g$  and  $P$ ) and in turn the chemical induction time increases. At some point, the effect of pressure on the gas-phase chemistry becomes greater than its effect on the solid heating and critical mass flux, resulting in longer ignition times as observed in the “U-shaped” curve of Fig. 3. Eventually as the pressure is reduced further, ignition cannot occur.

#### 4.2. Effect of oxygen concentration

##### 4.2.1. Critical mass flux for ignition

Eq. (3) predicts that the critical mass flux for ignition is a weak function of the oxygen concentration. However, experiments performed by Rasbash et al. [29] and Rich et al. [30] have shown that the critical mass flux at ignition is insensitive to the oxygen content in the oxidizer for oxygen concentrations greater than 21% in atmospheric pressure. As suggested by Rich et al. [30], this insensitivity of the critical mass flux at ignition could be due to the increased flame temperature. Because sustained ignition is dependent on a sufficiently high heat release rate being generated over the solid surface, increasing the oxygen concentration means that a higher temperature flame can form at a reduced fuel mass loss rate. However, increasing the oxygen concentration may also change the pyrolysis products. As shown by Kashiwagi and Ohlemiller [36], in oxygenated environments the solid fuel can undergo oxidative pyrolysis, producing pyrolysis gases that are partially oxidized as they form, and resulting in a lower energy content fuel with more CO and CO<sub>2</sub> (changing the oxygen to fuel mass ratio,  $r$ , in Eq. (3)). These pyrolysis gases generally have a lower heat of combustion ( $\Delta H_R$  in Eqs. (2) and (3)) and therefore a lower flame temperature as compared to pyrolysis gases formed in inert environments. A solid undergoing oxidative pyrolysis would require a higher mass flux of fuel for ignition. The combination of these mechanisms (not fully captured in Eq. (3)) may result in the insensitivity of the critical mass loss rate on oxygen concentration at least for atmospheric pressures.

##### 4.2.2. Pyrolysis rate

Increasing the oxygen concentration not only changes the pyrolysis products that are generated, but can affect the rate at which pyrolysis occurs. For PMMA and other materials, the pyrolysis rate is increased by the presence of oxygen [17,18] by lowering the activation energy ( $E_p$  in Eq. (1)). As discussed above, if the critical fuel mass flux for ignition is constant with oxygen concentration [29,30], this increased pyrolysis rate means that the critical mass flux would be reached at a lower temperature, decreasing the surface temperature at ignition in Eq. (2) and ignition delay time at a given pressure. This has been observed in the present experiments and is shown in Fig. 7.

##### 4.2.3. Chemical induction time

When the oxygen concentration is increased, the reaction rate also increases and the effect of pressure on the chemical induction time is reduced. This is manifested in Eq. (2) as a change in the characteristic Damkohler number. It is for these reasons that ignition is possible in lower pressures for 30% oxygen concentration than in air. The same “U-shaped” dependence on the ignition time as a function of pressure is seen for elevated oxygen concentrations

as in air, indicating that the controlling mechanisms for ignition are basically the same at different oxygen concentrations.

#### 4.3. Combined effect of pressure and oxygen concentration

Table 2 summarizes the effects of pressure and oxygen concentration on the key mechanisms of ignition. Decreasing the pressure decreases the heat lost and the critical mass flux at ignition, changes the pyrolysis products, and increases the gas-phase chemical induction time. Increasing the oxygen concentration increases the pyrolysis rate, changes the pyrolysis products, and decreases the gas-phase chemical induction time.

Since the effects of pressure and oxygen concentration interact with each other, their combined effect becomes less clear to analyze. In low pressures, the decreased density results in less oxygen available at the solid surface. As a result, the effect of oxygen may decrease since the rate of pyrolysis and the role of oxidative pyrolysis decrease. The slower pyrolysis rate would increase the heating time, but the more energetic fuel generated due to reduced oxidative pyrolysis would tend to have the opposite effect. An additional complication arises because the solid experiences less convective heat losses as the pressure is reduced, resulting in a higher net heat flux on the solid. Rich et al. [30] showed that the critical mass flux for ignition increased as the external heat flux increased because more of the pyrolysis was occurring at the surface, resulting in more oxidative pyrolysis. As the pressure is reduced, if enough oxygen were still at the surface, the increased net heat flux on the surface in combination with the elevated oxygen concentration would tend to increase the critical mass flux for ignition. If the pressure is sufficiently low, not enough oxygen would be available at the surface to participate in oxidative pyrolysis and this mechanism would not take place. The surface temperatures at ignition for 30% O<sub>2</sub> are shown in Fig. 7. From this figure, it appears that the surface temperature prior to ignition is nearly constant as the pressure is reduced from atmospheric pressure down to about 70 kPa. It is possible that the increased oxidative pyrolysis due to the increased net heat flux is responsible for this trend in ignition temperature.

To summarize how these mechanisms effect the ignition delay time, three regimes have been identified and outlined in Fig. 8. As the pressure is reduced from atmospheric to about 50 kPa in air, both the reduction in heat transfer coefficient and in the critical mass flux for ignition are dominant and the ignition time decreases rapidly. This regime is defined here as the transport regime. Below 27.6 kPa, the increase in the chemical time strongly affects the ignition time, and is defined as the gas-phase chemical kinetics regime. Between 50 kPa and 27.6 kPa, the reduction in the heat transfer coefficient is competing with the increase in the gas-phase chemical time so the ignition time still decreases as the pressure is reduced but not as quickly, reaching a minimum at a pressure of 27.6 kPa. This region is where the transport and gas-phase chemical kinetics regimes overlap.

When the oxygen concentration is increased, similar regions can be identified. In the upper and lower ranges of pressures, the

**Table 2**  
Summary of pressure and oxygen effects on ignition processes.

| Process                        | Decreasing pressure | Increasing oxygen concentration |
|--------------------------------|---------------------|---------------------------------|
| Heat loss                      | ↓                   | –                               |
| Critical mass flux at ignition | ↓                   | –                               |
| Pyrolysis rate                 | –/?                 | ↑                               |
| Pyrolysis products             | ?                   | ?                               |
| Gas-phase chemical time        | ↑                   | ↓                               |

“–” Indicates no change.

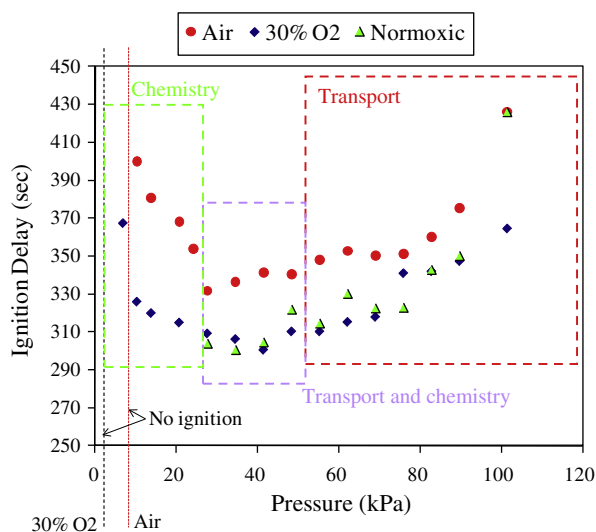


Fig. 8. Ignition delay times with the controlling mechanisms identified.

transport and gas-phase chemistry regimes act in the same manner as in air. Due to the increased gas-phase reaction rate, the chemical kinetics controlled regime occurs over a lower range of pressures. In between the two regions, the combined effect of reduced pressure and elevated oxygen concentration (oxidative pyrolysis) is responsible for flattening the curve and shifting the pressure at which the minimum ignition time occurs.

## 5. Concluding remarks

The results of the present work show that there are several controlling mechanisms that result in a “U-shaped” dependence of ignition time on pressure. Three regimes were identified in both air and elevated oxygen environments: the transport regime at the higher pressures where the ignition delay is controlled by changes in convection heat losses and critical mass flux for ignition; the chemical kinetic regime at the lowest pressures where the ignition delay is controlled by gas-phase chemical kinetics; and an overlap region where the transport and chemistry effects counteract each other. With an elevated oxygen concentration, the transport and chemistry regimes remain, but the intermediate region seems controlled by the balance of transport effects and oxidative pyrolysis effects.

The discussion presented here provides a phenomenological explanation of the experimental observations. Experiments that measure the mass loss rate of the material at ignition should be performed to further uncover the underlying mechanisms. These observations could also be evaluated using detailed models of the transport and chemical process.

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