Autoignition of R32 and R410 Refrigerant Mixtures with Lubricating Oil

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ABSTRACT

This study examines the flammability risk of refrigerant and oil mixtures. The flammability risk associated with refrigerants is an important property to consider prior to their use in residential and commercial HVAC systems. This research was conducted to compare the ignition characteristics of R-32 with R-410A, and the effects of lubricating oil. Unpiloted hot-plate ignition tests and computational fluid dynamics (CFD) were used to determine the autoignition temperature and ignition probability data. The results indicate that the ignition temperature of R-32 impinging a hot plate is 764 ^{o}C. This is 116 ^{o}C higher than the reported autoignition temperature of R-32, but it is very close to the reported open top autoignition temperature. R-410A was found to ignite at a slightly higher temperature than R-32: 790 ^{o}C. Tests with polyolester (POE) oil indicate that the R-32 ignition temperature is reduced to nearly that of the ignition of oil alone. CFD predictions for a jet of R-32 impacting a hot plate at a temperature close to autoignition temperature of R-32 show that ignition should happen only away from the jet point of impact and in rich regions.

1. INTRODUCTION

Two important risks associated with refrigerants are their environmental impact and their flammability. Difluoromethane, or R-32 (CH_2F_2) is a non-ozone depleting refrigerant with a global warming potential (GWP) of 675. R-32 is slightly flammable, with flammability limits of 13.3 – 29.3% by volume in air, has a laminar flame speed of 6.7 cm/s (Jabbour, 2004), and has a heat of combustion of 9.4 kJ/g. It is classified as a 2L refrigerant (Hihara, 2012). R-410A is a mixture of R-32 (CH_2F_2) and R-125 (pentafluoroethane, formula $CH_2F_2CF_3$); it is a non-ozone depleting working fluid with a GWP of 2088, which is more than three time that of R-32. R-32 has entered service in Japan and is being considered for service in the US. However, its adoption is being hindered by its slight flammability in air.

This work is motivated by the possibility of an accidental release of working fluid within a refrigeration system. Under certain conditions, this release may produce mixtures with localized flammable concentrations of refrigerant vapors in the surrounding air. This scenario may lead to a subsequent fire if this flammable gas comes into contact with an ignition source. Because the vapors are heavier than air, higher concentrations may develop near the floor or near the bottom of a refrigerant unit, and this region may remain flammable for an extended period of time.

The autoignition temperature of a fuel, or AIT, is the lowest temperature at which quiescent isothermal fuel/air mixture will spontaneously ignite unaided by an external ignition source. Ignition occurs when the rate of heat produced exceeds the rate at which heat is dissipated.

This study was conducted to better understand ignition risks due to an accidental refrigerant leak within a system using R-32 or R-410A. Past research has examined the flammability of pure refrigerants without considering the effects of the presence of lubricating oil. The concentration of oil released in a refrigerant leak can vary depending on the location of the leak and the operating state of the equipment. In this study, mixtures of R-32 and R-410A with lubricating oil are impinged onto a hot horizontal metal surface to examine ignition behavior. The ignition temperatures of R-32 and R-410A were determined using hot surface ignition test methods. Additionally, computational fluid dynamics (CFD) simulations were performed to provide physical insight associated with hot-plate ignition, to validate ignition chemistry, and to aid a systematic risk assessment in various configurations.

2. METHODS

The most widely used method to measure the autoignition temperature of liquid fuels is ASTM E659, the Standard Test Method for Autoignition Temperature of Liquid Chemicals. This standard provides the conditions for sustained combustion of a quiescent, isothermal, homogeneous mixture (simulating a perfectly stirred reactor). In such conditions, the reported AIT for R-32 is 648 °C (Goetzler, 1998). However, the original source of this measurement is a personal communication with no documentation. In terms of risk analysis, these conditions are unlikely to occur in practice and therefore can be considered as conservative.

The present tests aim to characterize the ignition temperature (IT) of refrigerants through contact with an isothermal, hot metallic surface. Figure 1 illustrates the design and components of the isothermal hot plate. The apparatus consisted of two 20 $\times$ 20 cm square copper plates. The top cover plate, used as the testing surface, was 6.35 mm thick; the bottom plate was 3.175 mm thick. Copper was chosen due to its good thermal conductivity and its resistance to oxidation. The test plate was heated using four cylindrical electrical heaters with a diameter of 9.5 mm. Each heating element operated at a maximum power density of 11 W/cm^2. The maximum operating temperature of the heating elements indicated by the manufacturer is 1150 °C. The four heating elements were powered by two variable autotransformers, delivering 120 V and up to 33 A. Exposed sections of the apparatus were insulated with kaowool insulating panels (on the sides) and a thick mineral wool insulator minimized the heat losses from the sides and from the bottom plate. Additionally, insulation was placed on top of the hot plate surface, providing a 3 cm tall draft shield along the outer perimeter of the hot plate. With these precautions, the test plate was kept isothermal, and elevated temperatures (up to 900 °C) was reached. The temperature of the hot plate could then be controlled by varying the power delivered by the autotransformers.

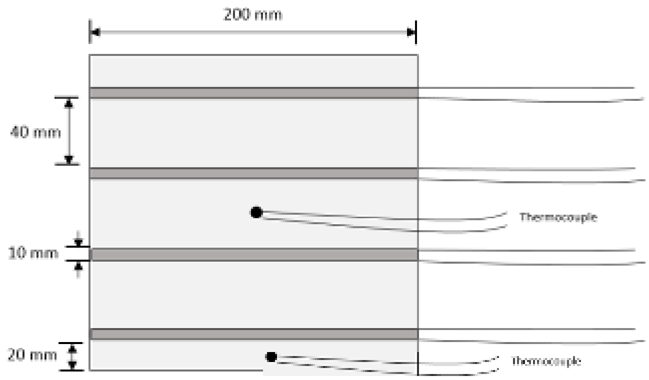

Figure 1: Hot plate schematic.

The temperature of the hot plate was monitored using two type-K thermocouples. Two small bead thermocouples were used, one peened into the center of the plate and the other fixed to the plate edge. The center thermocouple was directly under the discharge nozzle and the second thermocouple was used to verify temperature uniformity away from the center. The temperatures were recorded with a data acquisition software at a frequency of 10 Hz. The experimental uncertainty of the measured temperatures was ± 10 ºC. At elevated temperatures (above 500 °C), measurable temperature fluctuations were observed. This is attributed to the increased turbulent motion caused by natural convection.

R-32 and R-410A were delivered in the gas phase at ambient temperature through an aluminum circular nozzle, with an inner diameter of 1.58 cm. The delivery assembly consisted of refrigerant hose tubing, a solenoid valve, a single-shot timer relay, a needle valve, soft silicone rubber tubing, and an aluminum discharge tube. Prior to each discharge, the programmable timer relay was set to the desired discharge time, between 1 – 2 s, and the needle valve was set to the desired flow rate. For each discharge, the release of refrigerant was initiated with a switch, opening the solenoid valve. The vertical discharge nozzle was 5 cm above the hot plate. Figure 2 illustrates the experimental apparatus.

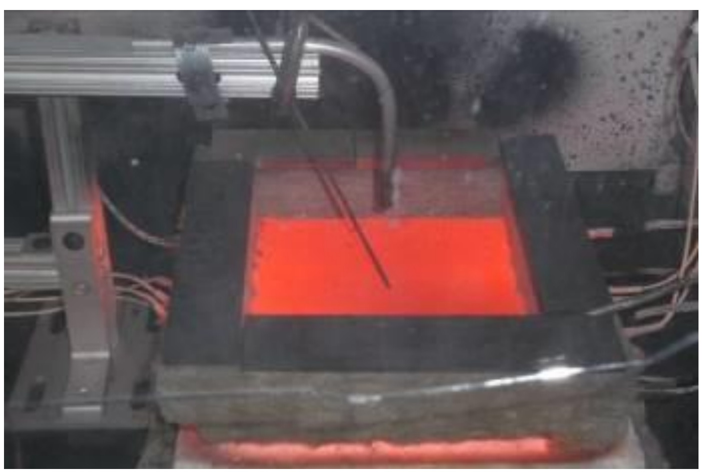

Figure 2: Color image of hot plate.

Four different cases were tested: pure R-32, pure R-410A, POE oil, and R-32 mixed with oil. Flow rate tests showed a negligible influence of the gas flow rate on the observed ignition temperatures. To reduce excessive refrigerant release, all subsequent tests were conducted with a constant refrigerant mass flow rate discharge of 1.1 g/s. Pure refrigerant was delivered in the gas phase. While the refrigerant supply tank was kept at ambient temperature, some frost was noted at the end of each refrigerant injection. For each test, the hot plate was first covered and heated to 800-900 ºC and maintained for approximately 30 minutes to ensure an even temperature distribution. Once steady state was reached, the plate temperature was slowly reduced by either removing the cover insulation or by reducing the power supplied to the heating elements. The occurrence of refrigerant mixtures ignition was determined by visual inspection and the tests were recorded by video for later analyses. For tests involving a mixture of refrigerant/oil, POE oil was introduced manually using a tube and syringe assembly discharging roughly 0.02 mL of oil. This corresponds to an oil-to-gas ratio of approximately 1% by volume. For each refrigerant mixture tested, the test was repeated at least three times. In total, approximately 150 tests were conducted.

3. RESULTS

Figures 3a, 3b, and 3c show photographs of R-410A, R-32, and POE oil ignition, respectively. They were captured at temperatures slightly above their critical ignition temperatures. Several differences in the burning characteristics of the fuels were observed: the refrigerants ignited more rapidly than oil, but combustion did not sustain burning after injection, whereas oil ignited with a slight delay but combustion lasted longer. A similar relationship was observed when oil and refrigerant are introduced simultaneously. For hot plate temperatures above the pure refrigerant critical IT, the refrigerant vapor and POE oil mixture ignited simultaneously. For hot plate temperatures below the refrigerant IT, oil ignited before the refrigerant.

(a) (b) (c)

Figure 3: (a) R-410A ignition at 820 ºC, (b) R-32 ignition at 789 ºC, and (c) POE oil ignition at 654 ºC.

For both R-410A and R-32, orange flames were observed close to the plate surface and blue flames were observed at the periphery of the burning region. A similar phenomenon was documented in the hot plate ignition report done by Bannister *et al.* (2005), where they described the blue flame regions of fuel/air mixtures as being lean, or oxygen rich, but lacked the heat to sustain ignition. This phenomenon is evident in R-32 and R-410A combustion tests. When unburned fuel vapors escape the heated plate area, the heat flux provided by the combustion reaction alone was insufficient to propagate to unburned vapors and thus the flame self-extinguished.

Table 1 reports the critical ignition temperatures recorded and compares them with published values. The lowest R-32 IT observed was 764 ºC, which is 116 ºC higher than the published, albeit in a different setup. Richard (2012) reported that the autoignition temperature was above 700 ºC in an open top measurement. This measurement is closer to ours.

The lowest R-410A IT was observed at 790 ºC. POE lubricating oil ignited at 645 ºC. Differences between the observed IT values and those in the literature arise from the differences in the test conditions or methods used, as explained by Affens (1974). Smyth and Bryner (1997) further discussed this, and highlighted the IT dependence on the fuel structure, surface material properties, surface temperature, fuel/air stoichiometry, surface size, surface orientation, and ambient pressure conditions.

Table 1: Present work observed ignition temperature along with values reported in literature.

Fuel	Ignition Temperature, in °C	
	Present work	Literature
R-32	764 (+/- 10)	648[a] to >700[b]
R-410A	790 (+/- 10)	-
POE Oil	645	371-427[c]
R-32 mixed with POE Oil	649	-

[a] Ref (Airgas, 2010)
[b] Ref (Richard, 2012)
[c] Ref (Kuchta, 1968)

Many literature sources report R-410A as a non-flammable refrigerant, but it was found here to burn. The measured critical ignition temperature of pure R-410A is 26 ºC higher than pure R-32. Furthermore, the addition of 1% POE oil lowers significantly the IT of R-32 refrigerant/oil mixtures, to a value very close to the ignition temperature of the oil. In this study, we found that the ignition temperature of the POE oil is 645 ºC. Tests show that when mixed with this oil, the ignition temperature of R-32 is reduced to 649 ºC; a decrease of 125 ºC .The oil provides sufficient energy to ignite the refrigerant vapors. Further results are depicted graphically in Figure 4.

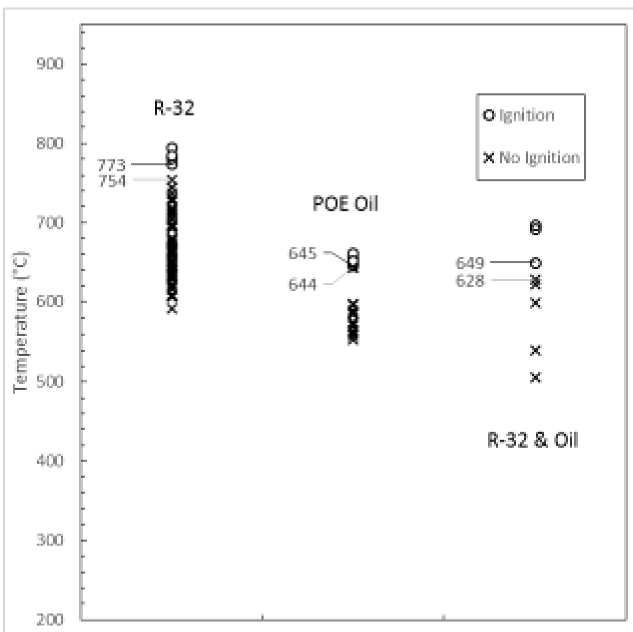

Figure 4: Hot-plate ignition temperature for pure R-32, POE oil alone, and a 1% mixture of R-32-oil.

4. CFD MODEL

To provide an improved understanding of the experiments, a LES code, the Fire Dynamics Simulator (FDS, McGrattan, 2013) was employed. This section presents results predicted for the configuration of pure R-32 injected at a mass flow rate of 1.1 g/s and impinging the hot plate set at a temperature corresponding to the measured ignition temperature of R-32, 764 ºC. Note that while the code features combustion capabilities, these were not used here.

The Fire Dynamics Simulator (FDS) is an open-source Fortran program written by the National Institute of Standard and Technology (NIST) and it is widely used in the fire modeling. FDS is a Large Eddy Simulation solver that solves the Navier-Stokes equations with the Low Mach Number assumption. See McGrattan *et al.* (McGrattan, 2013a) for a complete description of the code.

The numerical configuration for this work is similar to that of the experiment. The mesh consists of 130 points in the x and y directions and 49 points in the z-direction, taken as the vertical direction. The mesh spacing is 1.75 mm in the x and y direction and 1.25 mm in the z-direction. The dimensions of the computational domain are 227.5 mm in x and y directions, and 61.25 mm in z direction. The computational description is illustrated in Figure 5. The injection nozzle outlet is modeled with 8 points across in both directions. Due to the limitation of FDS, which can only model regular Cartesian geometry, the nozzle is modeled as a rectangular parallelepiped instead of a cylinder. The dimensions of the nozzle outlet (injection zone) were adjusted to match the area of the cylindrical nozzle used in the experiment. The mass flow rate of injected R-32 is set to 1.1 g/s. This corresponds approximately to an injection velocity of 2.8 m/s. The nozzle temperature is set to 0 ºC, as it was observed during the experiment that some frost was forming on the nozzle during the injection of R-32. The nozzle is located 55 mm above the hot plate. The hot plate spans 203 mm in x and y directions and it is flanked by an insulated 30 mm high draft shield. The hot plate is modeled as an isothermal surface with a surface temperature of 764 ºC. The insulated draft shield is also modeled as an isothermal surface, with a surface temperature of 394 ºC. This value was chosen to account for the heat addition that originates from the hot plate. Open boundary conditions are applied in $Z = Z_{max}$, and on the vertical sides. A rough wall log-law is used as a wall model to describe the interactions flow/hot plate.

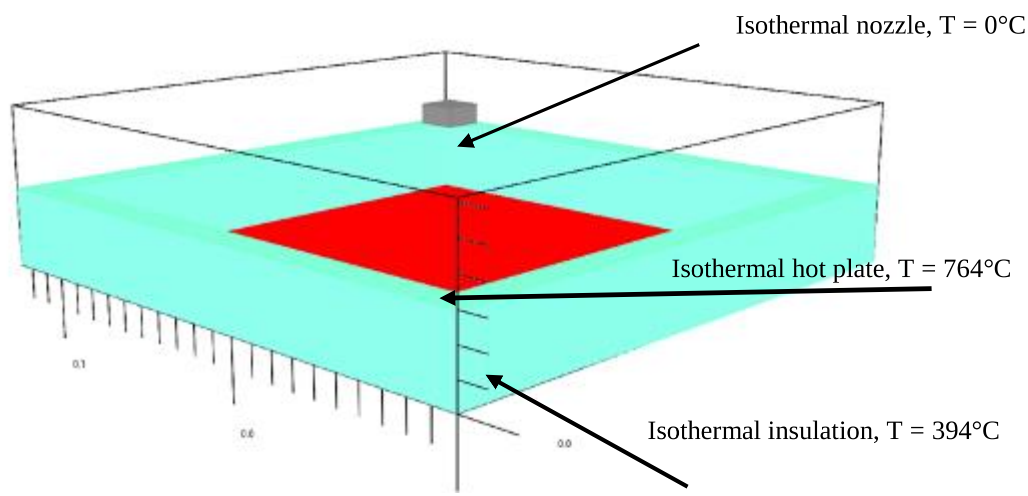

Figure 5: Geometrical description of the FDS computational domain. Open boundary conditions are used.

The simulation was initialized with still air at ambient condition (25 ºC and 1.01 bar) and was run for 2.0 s prior to R-32 discharge to simulate the development of a turbulent buoyant flow generated by the presence of the hot plate. The injection of R-32 at a mass flow rate of 1.1 g/s was imposed for 1.5 seconds using a progressive linear ramp of 0.1 s. It was maintained steadily until 3.5 s, after which time it was stopped, again using a linear ramp. The simulation was stopped at 5.0 s, as it was of interest to study the presence of R-32 after the injection.

The near-wall resolution on the hot plate was verified a posteriori by checking the value of y^+ at the first grid cell above the hot-plate. Its maximum value is 6, which corresponds to a considered highly resolved simulation (McGrattan, 2013b). An additional a posteriori test was performed to measure the error associated with the mesh discretization on the velocity and scalar fields. It consists of assessing the fraction of unresolved turbulent kinetic energy over the whole turbulent kinetic energy, referred to as the measure of turbulence resolution (Pope, 2004). This dimensionless criterion takes the value of 0 for a perfect resolution and 1 for a poor resolution. A recommended practice is to keep this value lower than 0.2. It is found that this criterion is observed everywhere in the domain except in a ring located between 1 – 2 nozzle diameters away from the point of impact of the jet with the hot plate (or stagnation point, located at the origin), where the maximum value is 0.3. This is considered satisfactory for this simulation as the area of interest is located away from the stagnation point.

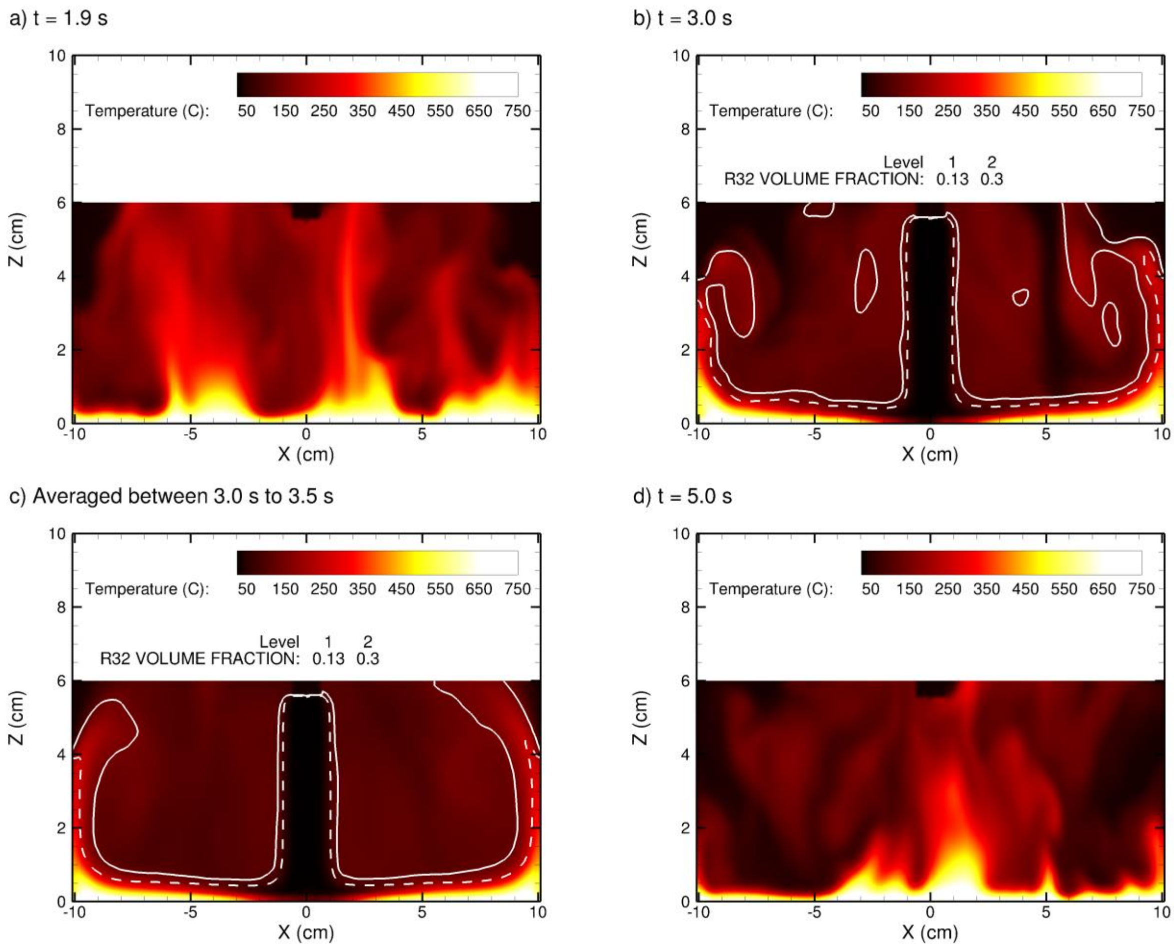

Figure 6: Cross section (at y = 0) of the temperature field and the contours of constant R-32 concentration at different times. The injection of pure R-32 from the nozzle starts at t = 2.0 s and continues for 1.5 s, until t = 3.5 s. The simulation ends at 5.0 s. Figure (a) plots the instantaneous conditions prior to R-32 injection at t = 1.9 s, (b) plots instantaneous conditions at t = 3.0 s during R-32 injection from the nozzle at x = 0 cm and z = 5.5 cm, (c) plots averaged conditions during R-32 injection between 3 and 3.5 s, and (d) plots the instantaneous conditions at the end of the simulation (t = 5 s), which is 1.5 s after the end of the R-32 injection. The solid line corresponds to where the R-32 concentration is at the lower flamability limit (13% in volume) and the dashed line corresponds to where the R-32 concentration is at the upper flamability limit (30% in volume). Neither (a) nor (d) has significant R-32 concentration levels.

Figure 6 plots the temperature fields and the contours of constant R-32 concentration corresponding to the ambient lower flammability limits (13% in volume) and the ambient upper flammability limit (30% in volume) of R-32 in air. The fields depicted correspond to the cross-section along the x and y directions at the location of y = 0 mm. Figure 6a plots the instantaneous fields prior to the R-32 injection, at 1.9 s. The turbulent nature of the buoyancy induced flow can be readily seen. As the air near the hot plate is heated, it rises and induces a turbulent motion, with a maximum vertical speed of 0.5 m/s. Some pockets of hot air are present in the domain. Figure 6b plots the instantaneous temperature field and the contours of constant R-32 concentration at t = 3.0 s. This is 0.5 after the start of injection and it corresponds to a turbulent steady state behavior. Figure 6c plots the average temperature field and contours of constant R-32 concentration over 0.5 s between 3.0 and 3.5 s. This plot illustrates the motion of the flow during the experiment. As the flow impinges the hot plate, it is conveyed toward the edge of the plate. During this process, it is heated and its temperature rises above 600 °C near the draft shield, more than 9 cm away from the point of impact. Near the draft shield, a stagnant zone exists, which is characterized by elevated temperatures and slow velocities. This implies that conditions propitious to R-32 ignition are to be expected near the draft shield and away from the jet point of impact. Figure 6d plots the temperature field at the end of the simulation. The discharge of R-32 had stopped 1.5 s earlier. Similar to Fig. 6a, buoyant turbulent structures can be readily observed. No significant concentration of R-32 remains; the concentration of R-32 falls below the lower flammability limit (13% in volume) about 0.9 seconds after the end of R-32 injection.

To gain a better understanding of the temperature variations with the distance from the jet point of impact (located at x = 0), values of temperature along the contours of constant concentration corresponding to the ambient lower flammability limit ($X_{R\text{-}32}$ = 0.13), stoichiometry ($X_{R\text{-}32}$ = 0.174) and the ambient upper flammability limit ($X_{R\text{-}32}$ = 0.30) were extracted from Fig.6c. Figure 7 plots these data along the location in the x direction. Away from the jet point of impact, the temperature increases with the concentration of R-32 (higher concentrations correspond to higher gas temperature) and, for a given concentration, the temperature increases away from the jet point of impact. Figure 7 shows that temperature at constant concentration reaches its maximum near the draft shield. Figure 7 indicates that conditions corresponding to the greatest R-32 concentration, $X_{R\text{-}32}$ = 0.30, has the highest temperature, 270 ºC, at |x| = 0.09 mm. This indicates that ignition is likely at locations in refrigerant rich conditions, *i.e.*, at locations where the R-32 concentration is above the stoichiometric value and far from the center of the plate and near its edges.

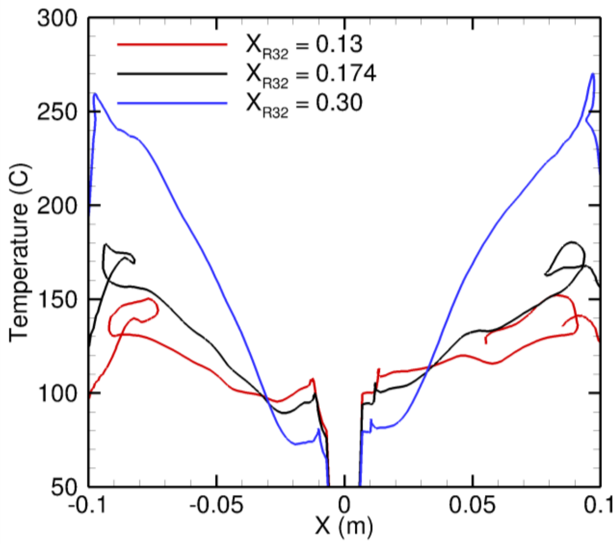

Figure 7: Temperature profiles along the x direction of different contours of constant R-32 concentration: 0.13 (which corresponds to lower flammability limit at ambient conditions) in red, 0.174 (stoichiometric) in black, and 0.3 (which corresponds to upper flammability limit at ambient conditions) in blue. Data were extracted from Figure 6c and correspond to averaged values over 0.5 s.

5. CONCLUSIONS

The experimental ignition temperatures of pure R-32 and R-410A refrigerants along with the ignition temperature of these refrigerants mixed with liquid POE oil were studied using a hot-plate configuration with a surface temperature varying from 200 – 900 ºC. The hot-plate ignition temperature of R-32 was found to be 764 ºC (± 10 ºC), while that for R-410A was found to be at 790 ºC (± 10 ºC). When mixed with POE oil, the ignition temperature of the R-32 refrigerant/oil mixture was found to be very close to that of the POE oil (649 ºC) employed in this study. The presence of ignited oil was found to be a driving factor of subsequent refrigerant ignition. CFD simulations using a LES code were performed to simulate the discharge of pure R-32. Simulations at 764 ºC suggest that ignition begins away from the jet point of impact and for R-32 concentrations above that of stoichiometry. This work is a first step in providing an extensive fire risk assessment associated with the use of R-32 in HVAC systems as a replacement for R-410A.

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