ABSTRACT

Title of Document: HOT SURFACE IGNITION OF R-32 AND R-410A REFRIGERANT MIXTURES WITH LUBRICATING OIL

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This study examines the flammability 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 were carried out to determine ignition temperatures and quantify the flammability risks associated with these refrigerants. Additionally, computational fluid dynamic (CFD) methods were used to model the vapor temperatures and concentrations of an R-32 jet impinging on a hot-surface. The laboratory results indicate that R-32 will ignite upon contact with a 764^{o}C surface. This is higher than the reported 648^{o}C autoignition temperature of R-32. R-410A was found to ignite upon contact with a 790^{o}C surface. Results with mixtures of refrigerant and polyolester (POE) oil were found to ignite at temperatures close to that of oil alone, 645^{o}C. CFD predictions show that ignition is likely to occur along the edges of the apparatus, where the fuel vapor concentrations and temperatures are within the limits of combustion.

HOT SURFACE IGNITION OF R-32 AND R-410A REFRIGERANT MIXTURES WITH LUBRICATING OIL

By

Adam Boussouf

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1. Introduction

The primary risks associated with refrigerants are their environmental impact and their flammability. This study was conducted to better understand ignition risks due to an accidental refrigerant leak within a residential AC system that uses either R-32 or R-410A. R-32 has entered service in Japan and is being considered for service in the United States. However, its adoption is being hindered due to concerns over its flammability in air. 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, refrigerant mixtures of R-32 and R-410A with lubricating oil are impinged onto a heated flat metal surface to examine hot surface ignition behavior. The ignition temperatures of R-32 and R-410A were determined using a unique hot surface ignition testing method. 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.

1.1 History

The need for an effective way of cooling ones shelter is arguably as old as humanity itself. Modern day air conditioners have provided an effective means of addressing this need, by using a cyclic process that manipulates the phase change properties of refrigerants. Willis Haviland Carrier created the first modern day air conditioner in 1902. Early HVAC cooling systems were primarily used in large scale industrial operations with ammonia and carbon dioxide as the working fluid.

In these early years there were several work related accidents due to the toxicity of carbon dioxide and explosive hazard of ammonia use as a refrigerant. This led to the invention of Freon, by chemist Thomas Midgley in 1928. These modern refrigerants are typically prefixed with the letter R and a number relating to the molecular structure of the chemical, examples include R-11, R-22, R-134A, R-410A. For the most part of refrigeration history two refrigerants were used, R-12 was used for A/C in the automotive industry, while R-22 was used in homes and small retail operations.

1.2 Environmental Concerns

The refrigeration industry went through a drastic change when concerns over the adverse effects of greenhouse gasses on the earth's ozone were discovered. Damages were attributed to the release of large amounts of chlorofluorocarbons and hydrochlorofluorocarbons into the atmosphere. In response to environmental concerns, the 1989 Montreal Protocol and the 1997 Kyoto Protocol were adopted worldwide. These new regulations triggered a phase out of ozone depleting gasses, including the widely used refrigerant R-22 (Bennett, 2011). As a result, scientists around the world began to develop alternative refrigerants, like R-134A and later R-410A, which had a much lower GWP than their predecessors. R-32 and R-410A are both non-ozone depleting refrigerants, however R-410A has a GWP of 2088 (Lewandowski, 2012), more than three time that of R-32's GWP of 675 (Hung, 2010). More recently, other refrigerants like R-32, having a very low GWP, have been implemented in Japan, however its adoption in the United States has been hindered due to its slight flammability in air. It is likely that flammability concerns stem from the history of accidents associated with ammonia and propane based refrigerants, however new test standards and regulations have helped lower these risks (Kataoka, 2013).

1.3 Safety Concerns

It is important to evaluate the dangers and ignition potential of R-32 and R-410A, as they are used in proximity to humans and the life safety risk may outweigh the potential environmental benefit. Under certain conditions a refrigerant line may rupture or leak refrigerant creating a localized flammable concentration of refrigerant vapor in the surrounding air. If this flammable region comes into contact with an ignition source it may cause a flash fire causing injury to people nearby. Because refrigerant vapors are heavier than air, higher concentrations may develop near the floor or near the bottom of an AC unit, and this region may remain flammable for an extended period of time.

Recent laboratory tests conducted by Vivien Lecoustre at the University of Maryland have not be successful in reproducing a refrigerant ignition scenario using a PTAC heater as the ignition source. These tests were performed with and without operation of the blower fan. Lewandowski conducted a risk assessment study in 2012 comparing the risk of refrigerant ignition to that of other relevant hazards within a home. He determined that the risk of a heat pump ignition of R-32 is $9*10^{-5}$ (per home per year), far below the risk and severity of other hazards that are commonly accepted by public (Lewandowski, 2012).

1.4 Chemical Properties

Difluoromethane, also called R-32, HFC-32, Freon-32, carbon fluoride hydride, methylene difluoride, or methylene fluoride has the chemical formula CH_2F_2. It is a non-ozone depleting refrigerant with a global warming potential (GWP) of 675 (Hung, 2010). R-32 is slightly flammable and has flammability limits between 13.3 and 29.3% by volume in air. ASHRAE Standard 34 classifies R-32 as an A2L refrigerant, where the letter A characterizes its low toxicity and the number 2 identifies it as a lower flammability refrigerant as compared to the "non-flammable" number 1 and the "highly flammable" number 3 (ASHRAE, 1992). R-32 has a laminar flame speed of 6.7 cm/s (Jabbour, 2004). It is a nontoxic gas with a vapor pressure of 1.6 MPa at a room temperature of 25^{o}C. It has a molecular weight of 52 g/mol, a boiling point temperature of -52^{o}C. It has a heat of combustion of 9.4 kJ/g (Goetzer, 1998). It has an enthalpy of formation of -8.7 kJ/g (Womeldorf, 1999).

R-410A, also known by its trademark names Forane-410A, Puron, EcoFluor, Genetron, and AZ-20 is made of a 50:50 ratio (by weight) 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 (Lewandowski, 2012). R-410A has flammability limits between 15.6 and 21.8 % by volume in air (Takizawa, 2012). ASHRAE Standard 34 classifies R-410A as an A1 refrigerant, where the letter A characterizes its low toxicity and the number 1 identifies it as a "non-flammable" fluid (ASHRAE, 1992). It is a nontoxic gas with a vapor pressure of 1.38 MPa at a room temperature of 21^{o}C. It has a molecular weight of 72.6 g/mol and a boiling point temperature of -48.5^{o}C. The laminar flame speed and heat of combustion properties could not be found.

Previous refrigerant flammability studies have examined the flammability of refrigerants by measuring the minimum and maximum vapor concentrations, minimum ignition energy, and laminar flame speed. Though there is little research on the ignition of R-32 and R-410A due to hot surface contact, a likely ignition source within wall mounted heating and air conditioning units.

1.5 Autoignition

The autoignition temperature of a fuel, or AIT, is the lowest temperature at which a quiescent isothermal fuel/air mixture will spontaneously ignite unaided by an external ignition source. Under certain conditions a mixture of fuel and oxidizer can result in a combustion reaction. This will only occur if the mixture can reach a critical temperature and the concentrations of fuel and oxidizer are within their flammable concentrations. In localized areas where fuel is in the gaseous phase, combustion will rapidly slow then cease as fuel and oxidizer are consumed in the reaction (Quintiere, 2006). Figure 1.1 highlights the relationship between autoignition and the balance between fuel vapor pressure, temperature, and vapor concentrations required for the phenomena to take place.

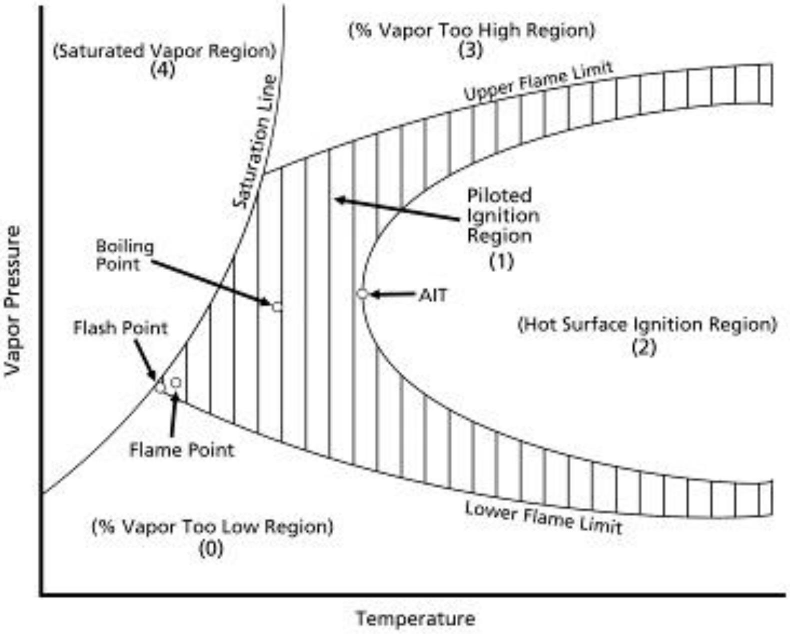


Figure 1.1 Fuel Vapor Pressure vs. Temperature (NIST, date)

The burning of R-410A and R-32 can be harmful and there is an increased risk due to the production of hydrogen fluoride (HF) as one of the primary products of combustion. During combustion fluorine acts as an oxidizer resulting in the H-F bond making up approximately 30% of the product species (Womeldorf, 1999). Risk associated with HF inhalation or skin contact include respiratory damage, severe irritation and pulmonary edema, eye, nose, and respiratory track irritation. Inhalation of high doses can result in convulsions, cardiac arrhythmias, and death. Inhalation of HF has been known to cause damage to the liver and kidneys (EPA, 1998).

1.6 AIT Design Considerations

Flammability can be characterized by numerous properties all of which are dependent on many variables. The autoignition temperature (AIT), hot surface ignition temperature, flammable concentration range, minimum ignition energy, flame speed are just some of these variable that can be measured as a means of classifying the flammability of various chemicals. When comparing the flammability and ignition likelihood of R-32 with R-410A it is important to consider the situation where the refrigerants will be used. In this case the primary use will be within a PTAC unit, where operational heating element temperatures are above 1000^{o}C, well above the listed AIT of both refrigerants. For this reason it was decided that the most likely ignition scenario will be from an internal refrigerant leak and vapor contact with one of these heating elements. The test method that most closely matches this application is the hot-surface method where a fine tuned vapor jet impinges on the plate center.

1.6.1 ASTM E659

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 this test 100 microliters of liquid is released into a 500 ml glass flask, the flask is uniformly heated by a furnace, and the liquid in the flask begins to vaporize forming a fuel air mixture within the flask. The tests is repeated for various fuel volumes and the lowest temperature at which ignition occurs is labelled the AIT of the chemical. Testing under these conditions are considered close to ideal and represent the lowest possible temperature that a chemical can ignite without the presence of an external ignition source (i.e. flame, spark) (Davis, 2009). This test method is conducted under atmospheric pressure conditions and ignores the effects of pressure changes on AIT. Figure 1.2 illustrates the ASTM E659 test apparatus used to determine the minimum AIT of a liquid fuel.

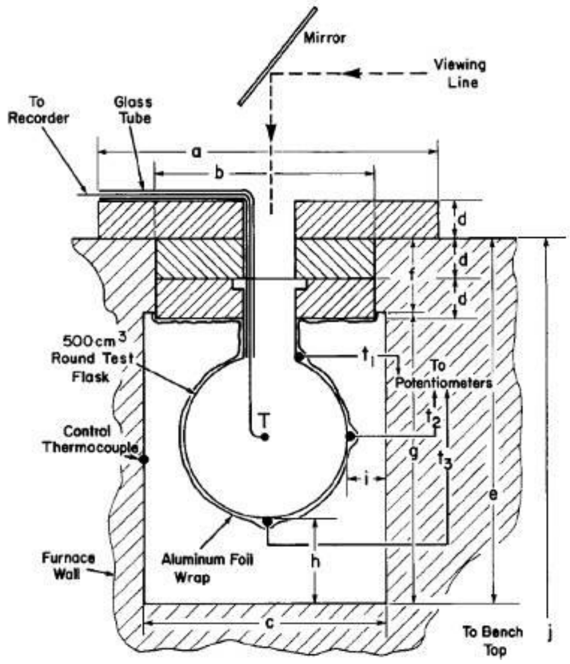


Figure 1.2 ASTM E659 Test Apparatus (Wendellhull)

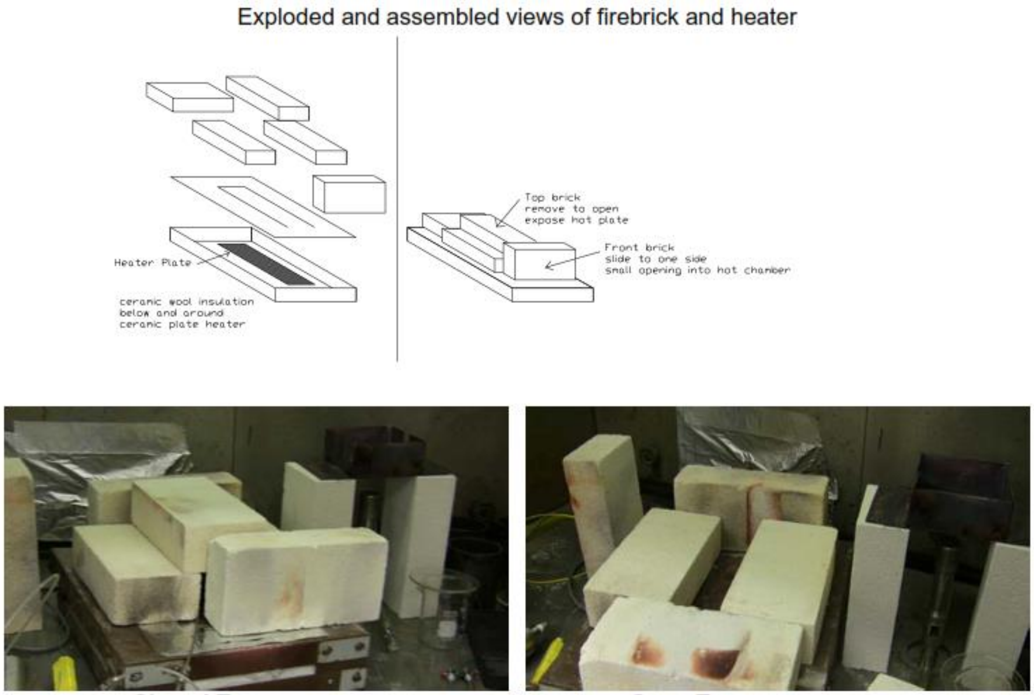
In such conditions, the reported AIT for R-32 is 648 °C (Goetzler, 1998). However, the original source of this measurement is a personal communication and the original test method could not be verified in literature. There is currently no published AIT for R-410A using this test method. In terms of risk analysis, these conditions are unlikely to occur in practice and therefore can be considered as conservative. Additionally, variables such as the use of a glass surface, leak rate control, and the use of non-liquid chemicals are not addressed by this test method.

1.6.2 Hot-Surface Ignition

Based on similar principles of autoignition, a flammable substance can ignite when it comes into contact with a heated surface. Though there is no current standard method to examine this phenomena many argue that this is a more realistic representation of real world scenarios involving the ignition of fuels. For the purposes of this research, the hot-surface ignition temperature of a fuel is defined as the lowest surface temperature at which a fuel/air mixture will ignite upon contact with the heated surface. Previous studies used a hot-surface ignition method to examine the ignition of various performance fuels, specifically within the aircraft and automotive industries. It is argued that fuel leaks within mechanical systems have a high probability of coming into contact with a heated metal surface, such as a heat exchanger, an electrical resistance heater, or various engine and exhaust components. This complex phenomena involves many variables, all of which can affect the end result, such as the fuel discharge rate, angle of discharge, catalytic effects due to heating a metal surface, contact time, temperature uniformity, geometry, roughness, humidity, and airflow. The National Fire Protection Association

(NFPA) notes that hot surface ignition can be several hundred degrees higher than the reported AIT in literature from the ASTM 659 standard test method (NFPA, 2004).

Research conducted by Honeywell examined the hot-surface ignition of R-32 in horizontal and vertical configurations. They used a closed top and open top method showing how confinement differences can affect the AIT of the refrigerant vapor/air mixture. The maximum surface temperature that could be reached by their apparatus was 700^{o}C. Their results indicated an R-32 ignition temperature of 675^{o}C in the closed top configuration and no ignition in the open top configuration (Richard, 2012). They argue that open top configuration reflect the most likely ignition scenario in commercial and residential use. The apparatus used in these tests are shown in Figure 1.3. The apparatus consisted of a 14 gauge steel plate heated by a 10 kW propane burner and insulated using refractory brick.


Exploded and assembled views of firebrick and heater

Closed Top

Open Top

Figure 1.3 Honeywell Test Apparatus

2. Methodology

The present tests aim to characterize the ignition temperature (IT) of refrigerants through contact with an isothermal, hot metallic surface. The hot surface method was used because it reflects the most likely ignition scenario within a PTAC unit, where operational heating element temperatures are well above the listed AIT. This test method best matched the application where a refrigerant leak could results in a flammable vapor cloud within the unit. The apparatus was designed specifically for a refrigerant release scenario. The design and construction was motivated by a 2008 study, *Hot Surface Ignition of Performance Fuels* by Scott Davis, where 900 ignition tests of high performance motorsport fuels were performed to better understand the hot surface ignition behavior of automobile fuels, helping to limit the damage and deaths caused by vehicle fires (Davis, 2009). Figure 2.1 below shows the apparatus used in Davis's study.

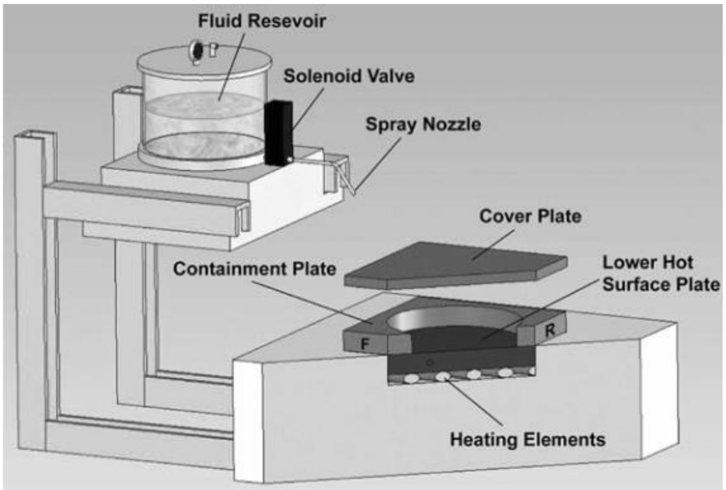


Figure 2.1 Test Apparatus from Davis's Study

The apparatus used in this study was constructed specifically for the use with refrigerants. Several designs were developed throughout the testing process in an effort to reach a high enough plate temperature while maintaining a uniform temperature distribution across the plate surface. Figures 2.2 and 2.3 below show a schematic of the test apparatus, delivery system and hot plate design that was built for use in the collection of this data. Because the primary product of combustion is HF all combustion tests were performed under a fume hood. The control variables were discharge angle, discharge height, discharge rate, plate size and material. The external variables that could have an effect on the results are the fume hood exhaust fan, room temperature fluctuations, and humidity.

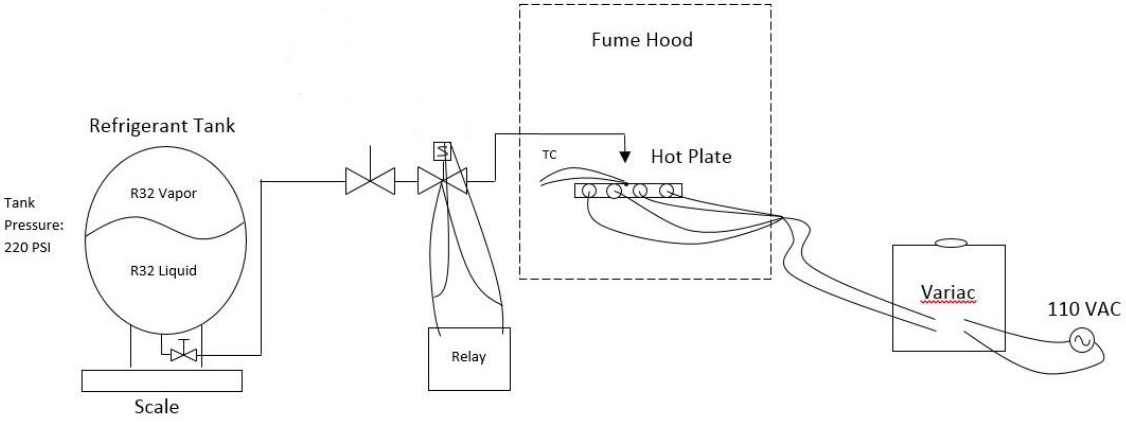


Figure 2.2 Experimental Hot Surface Ignition Apparatus

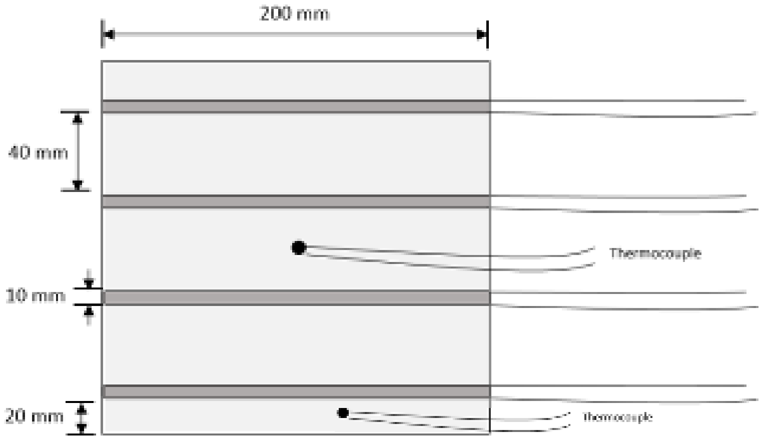


Figure 2.3 Hot plate schematic.

2.1 Description of Apparatus

A unique test apparatus was designed and constructed for the purpose of determining the hot surface ignition temperature of R-32 and R-410A, this posed challenging because no standard design approach exists to collect the data needed. The design went through several phases and modifications were made as issues in testing arose. The apparatus consisted of two parts, the first was the refrigerant delivery apparatus and the other was the hot plate apparatus. The delivery apparatus was constructed to ensure that the predetermined refrigerant release rate and total duration of discharge remained constant throughout testing. The hotplate apparatus was constructed for control and monitoring of the surface temperatures across the exposed surface. With every new test method or apparatus design, the ignition testing process was restarted to ensure that these discrepancies did not affect the results.

2.1.1 Refrigerant Delivery Apparatus Design Considerations

The design of the delivery apparatus played an important role in testing and its use was essential in maintaining the consistency of control variables throughout the testing process. Variables such as refrigerant discharge rate, discharge angle, distance from the hot-plate surface, duration of discharge, and nozzle temperature were maintained constant throughout testing. Initial testing did not show a strong correlation between the refrigerant ignition temperature and discharge rate. Preliminary flow rate tests showed a negligible influence on the recorded ignition temperatures. To reduce excessive refrigerant release, all subsequent tests were conducted with a constant refrigerant discharge mass flow rate of 1.1 g/s. A consistent flow rate of 1.1 g/s was achieved through calibration of the needle valve using a series of timed releases and measuring the change in weight of tank.

A discharge time of 1 – 2 seconds was used throughout testing. Duration of discharge did not affect the ignition temperature observed and it was kept short to reduce the amount of refrigerant released as well as the amount of HF produced. In all tests the refrigerant discharge nozzle remained at a 90 degree angle and approximately 5 centimeters from the hot plate surface.

2.1.2 Hot-Plate Apparatus Design Considerations

In the initial phases of experimentation the hot-plate test apparatus was made up of a top and bottom 8 inch by 8 inch, 1/8th inch thick carbon steel plate, and 4 high temperature Firerod Watlow cartridge heaters, with 3/8 inch thick steel blocks in between each heating element. Several issues arose with this set up and modifications were made to address the concerns. Initially the hot plate was unable to reach temperatures above 500^{o}C, so the apparatus was modified by adding kaowool and fire resistant insulation to reduce heat loss along the sides and base of the hot plate. With these corrective measures in place the apparatus could be heated to a maximum temperature of around 950^{o}C.

The second issue that arose was with the warping and rapid oxidation of the hot plate surface. Thermal stresses due to rapid heating and cooling caused the steel plate to warp and bend. This heating and cooling also increased the amount of oxidation along the plate surface, which caused the steel surface to become abrasive and flake, and there were concerns that this could affect the accuracy of the test results. The issue with warping was addressed by using a thicker ¼ inch steel plate and the surface abrasiveness was corrected by rubbing the plate surface with a steel wool cleaner between testing.

After review of testing footage there was evidence of “hot spots” which highlighted a concern of temperature uniformity across the surface of the hot plate. Later testing confirmed the issue of irregular temperature distribution by taking several temperature readings at various locations along the hot plate surface. Due to the nature of the apparatus and placement of the heating elements it was not feasible to achieve an acceptable level of temperature uniformity using steel. This concern was addressed by modifying the apparatus via replacing the steel elements with copper. Due to the higher thermal conductivity of copper, heat was able to disperse more evenly across the hot plate surface and temperature uniformity remained +/- 5^{o}C along the new surface. Figure 2.4 below shows a side by side comparison of a heated steel plate (left) and a copper plate (right), where “hot spots” are evident on the steel surface and there is much more temperature uniformity along the heated copper plate.

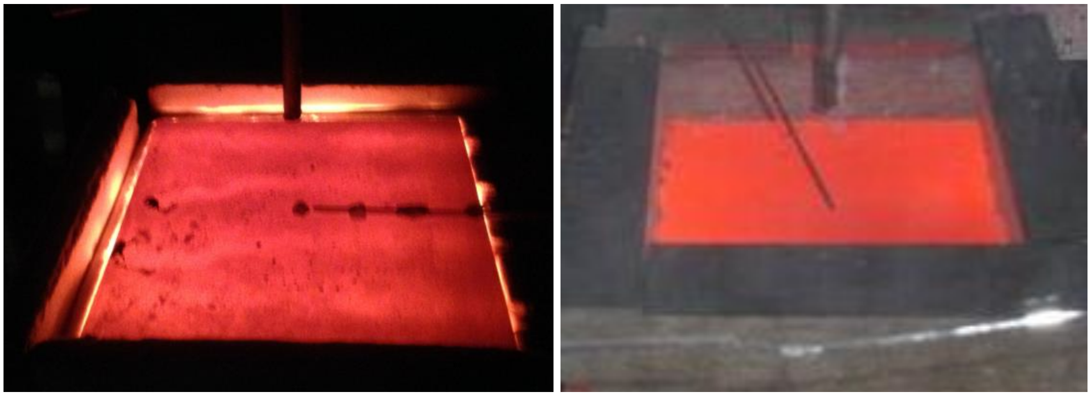


Figure 2.4 Heated Steel Plate (left). Heated Copper Plate (right)

Another area of concern was the possibility of refrigerant ignition upon contact with one of the heating elements. Because the heating elements were operating at a much higher temperature than the plate surface temperature it was important that the ignition temperature measurements reflected the location where ignition occurred. To achieve this, the apparatus was modified by sealing all gaps where refrigerant could pass through the insulation and under the plate surface. Additionally, video footage was reviewed to pinpoint the location where ignition occurred.

2.1.3 Refrigerant Delivery Apparatus

The refrigerant delivery apparatus consisted of the original refrigerant tank cylinder, the refrigerant hose line, a 3/8th inch ODF solenoid valve (Danfoss 032F7110), a 110 VAC solenoid valve coil (Danfoss 018F7692), a solenoid valve actuation switch, a single shot timer relay with 0.1 to 10 second range (7630K41/7122K19), a needle valve (Parker N400B/1A862), high temperature soft silicone rubber tubing, and an aluminum discharge nozzle. Both refrigerants, 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, 1.1 g/s. 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. The control board, shown in Figure 2.5 below, was set up for the solenoid valve, timer relay, and needle valve assembly.

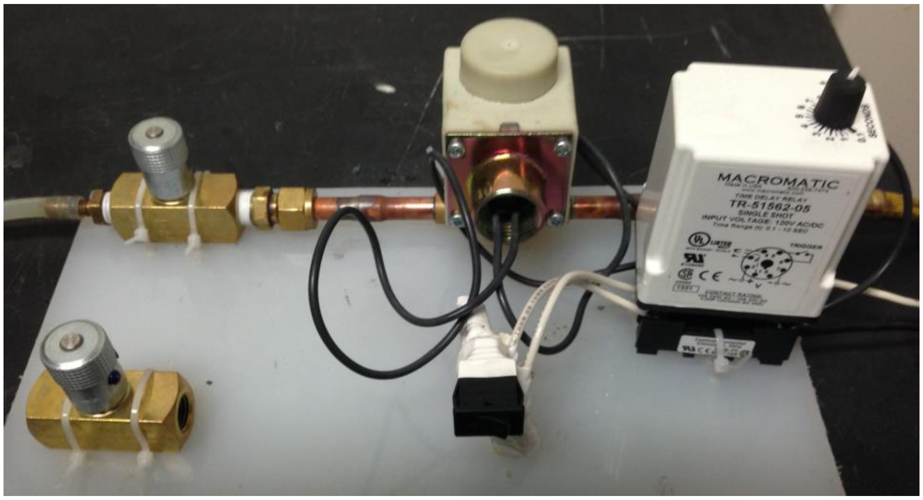


Figure 2.5 Refrigerant Delivery Control Board

2.1.4 Hot Plate Apparatus

The final apparatus consisted of two 20 × 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 were reached. The temperature of the hot plate could then be controlled by varying the power delivered by the autotransformers.

The temperature across the surface 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, or 10 temperature measurements per second. Data collected at this frequency provided a time temperature plot with enough resolution to pinpoint disturbances in the plate temperature at the moment of refrigerant contact with the hotplate surface. The experimental uncertainty of the measured temperatures was ± 10^{o}C. These measurable temperature fluctuations were most noticeable at elevated temperatures (above 500 °C). This is attributed to the increased turbulent motion caused by natural convection. The hot plate apparatus described above is illustrated in Figure 2.6.

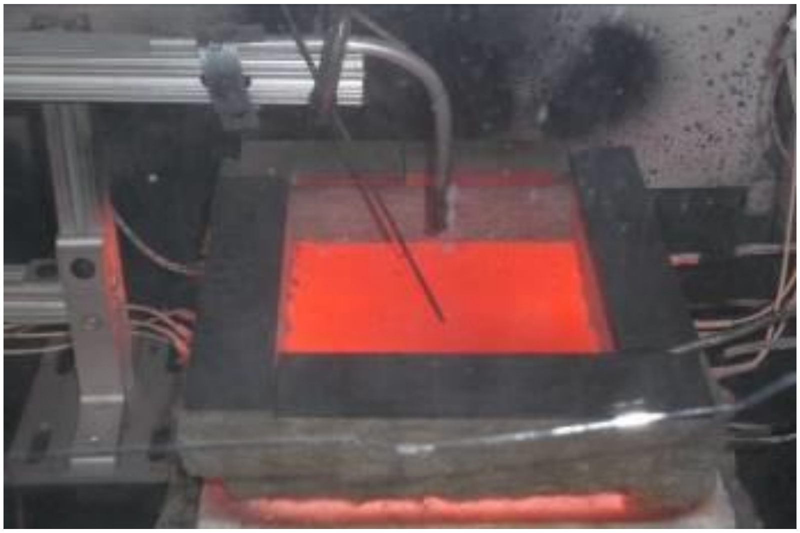


Figure 2.6 Hot Plate Design

2.2 Test Procedures

Final testing was conducted over a several week period and data for 4 different cases were collected: pure R-32, pure R-410A, POE oil, and R-32 mixed with oil. Pure refrigerant was delivered in the gas phase. Throughout the weeks of testing many of the heating elements would fail, likely due to overheating, and were replaced with new ones. Due to time constraints, some of the replacement heating elements did not match the make and model of the others, however their design specifications were comparable and these changes did not affect the temperature uniformity across the plate surface.

Before each test, the hot plate apparatus was fully tested by verifying all electrical wiring connections, checking the thermocouple connections and ensuring adequate bead to hotplate surface contact. The data acquisition system was powered on and thermocouple temperature measurements and response characteristics were calibrated to ensure proper communication with the software and laboratory computer. The control board containing the timer relay and solenoid valves were powered on and tested without the release of refrigerant. The VARIAC was then powered on at a low voltage setting, approximately 30 V, to verify that all heating elements were operational.

For each test, the hot plate was first covered and gradually heated to 800-900 ^{o}C. These temperatures were reached with the VARIAC set to 130 V. Once heated, these conditions were maintained for approximately 30 minutes to ensure an even temperature distribution along the hot plate surface. Once steady state was reached, the plate temperature was slowly reduced by either removing the insulation cover or by reducing the power supplied to the heating elements. Refrigerant was then discharged by triggering the solenoid valve switch. As the plate surface cooled multiple releases were performed. All ignition occurrences were recorded and labeled with the time stamp from the data acquisition monitoring system. Each occurrence of refrigerant mixture ignition was first determined by visual inspection and later verified by the video recordings during further analyses. This method provided an accurate means to determine the lowest temperature at which ignition occurred, however due to rapid surface cooling in between each refrigerant discharge, the plate would have to be fully reheated after each test. This process was repeated until the temperature differential between the observed ignition temperatures and non-ignition temperatures were narrowed. In total, approximately 150 tests were conducted, with 4 to 6 refrigerant releases per test.

For tests involving a mixture of refrigerant and 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, which is the approximate ratio observed in residential HVAC and PTAC units.

3. Results & Analysis

This research presented a method to explore the ignition of refrigerants upon contact with a heated surface. This method was implemented because of the presence of hot surfaces and heating elements within HVAC units, and represents a likely ignition scenario. The hot plate apparatus was designed to analyze ignition criteria by controlling the plate surface temperature and observing the ignition temperature limits. The lowest temperatures where ignition was observed is further discussed and presented in Table 3.1.

3.1 Observations

Ignition was observed for all fuels tested. Figures 3.1(a), 3.1(b), and 3.1(c) 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 3.1 (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.

Ignition occurrences were closely monitored throughout testing. The approximate ignition time and hotplate temperatures were recorded manually upon each visual confirmation of ignition. However, due to human error and the sensitivity of the thermocouple readings, further review was needed. This was done by analyzing the measurements collected by the data acquisition system and also corroborated with the experimental video footage.

3.2 Measurements & Findings

After a series of ignition tests, the transient temperature data was extracted from the laboratory computer for further analysis. The time temperature curve, shown in Figure 3.2, depicts the raw data from a series of ignition tests using R-32 on a heated copper plate where the plate edge temperature is the solid line and the plate center temperature is the dashed line. In this series of tests, data was collected over the course of 3 hours and a total of 215,620 temperature values were examined.

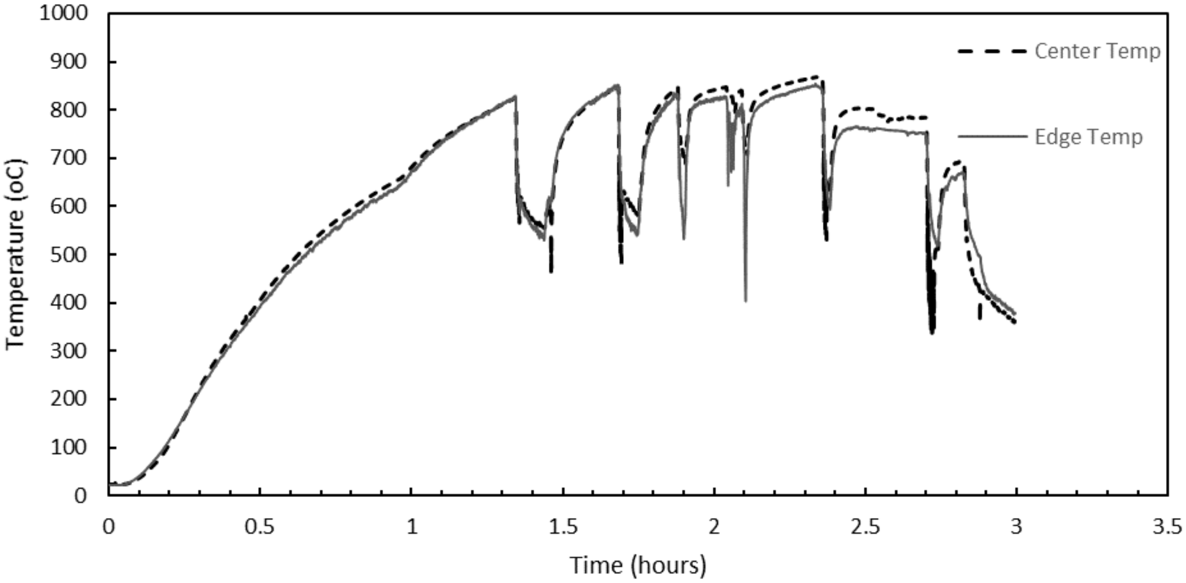


Figure 3.2 Raw Data R-32 Copper Hot Plate Ignition Test

In this test, Figure 3.2 shows that the plate was heated steadily over a period of 80 minutes up to the desired temperature of 800°C. Isothermal conditions were established with the plate edge measuring 794°C and the plate center measuring 791°C, or a temperature differential of 3°C. At this time, evident in the graph by the first peak followed by a steep drop, R-32 was released onto the hot plate and ignition was observed (t=1.2 seconds). Followed by 6 subsequent releases were no ignition was observed. Figure 3.3 shows a more detailed depiction of the first 7 releases and measurements are displayed within the trial's 47 second time frame.

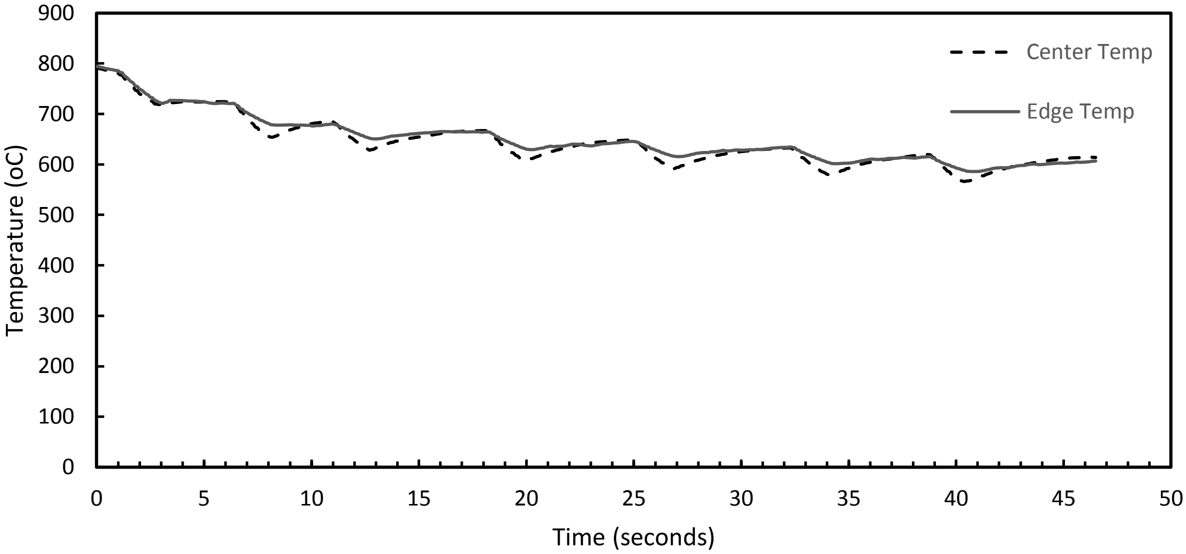


Figure 3.3 R-32 Copper Plate Ignition Test (Releases 1-7)

R-32 ignition occurred during the first release, however further analysis was needed to determine the exact temperature at which ignition occurred. Figure 3.4 shows the recorded temperature data during the time frame of the first release, over a 2.5 second interval.

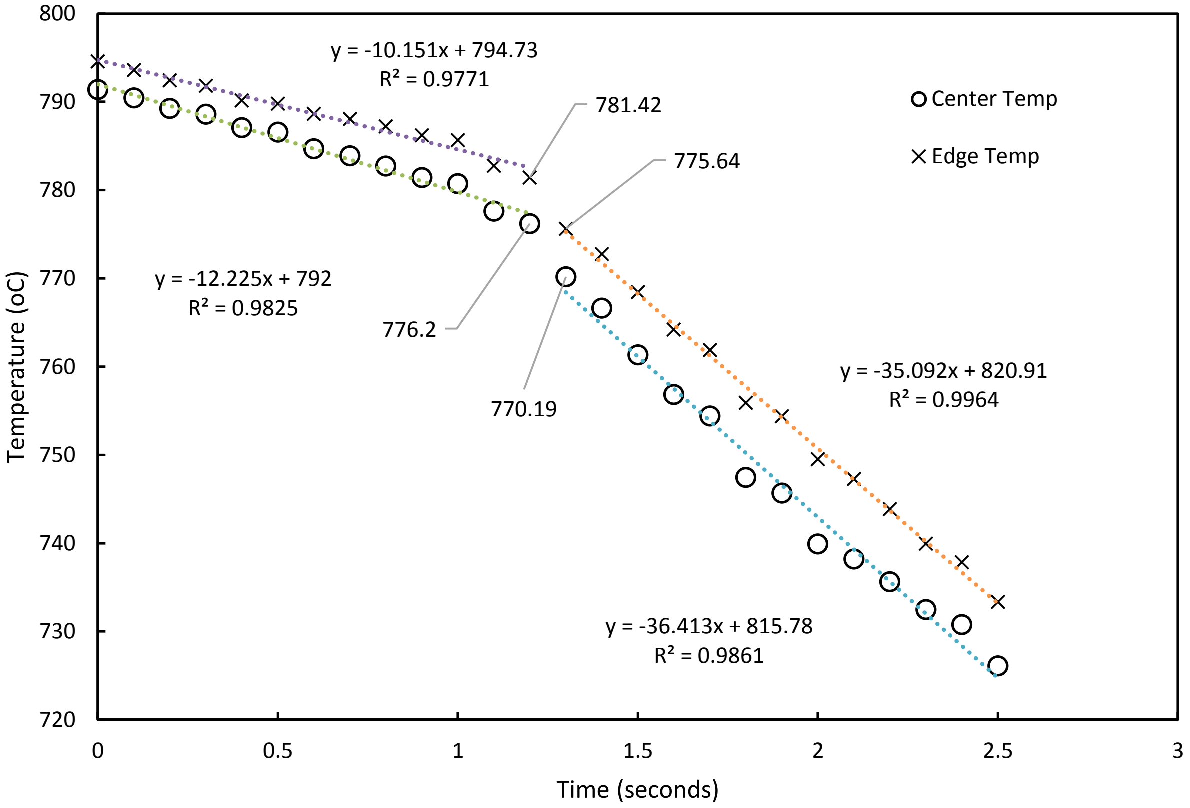


Figure 3.4 R-32 Copper Plate Ignition Test Release 1 Moment of Ignition

Figure 3.4 shows the laboratory temperature measurements recorded by both the center and edge thermocouples from the moment of refrigerant release through contact with the hot plate surface and ignition. The graph reveals several interesting phenomena. Both time-temperature curves react simultaneously with one another to a measurable difference of less than 0.1 seconds. This finding shows that both thermocouples have similar response times, which helped to alleviate any concerns of errors due to differences in the thermocouples used. Additionally, the temperature differential across the entire plate surface remains less than 10^{o}C throughout the entire release period.

Both time-temperature curves show two distinct linear regions. There is a linear trend for the first 1.2 seconds followed by a sharp change in slope for the remaining 1.2 seconds. For the first 1.2 seconds, the center of the plate time-temperature curve fits the linear regression line (y = -12.2x + 792) with an r^2 value of 0.982, and the edge of the plate curve fits the linear regression line (y = -10.1x +794) with an r^2 value of 0.977. This indicates a nearly constant plate surface temperature cooling rate of 10.1^{o}C to 12.2^{o}C per second during this interval, and shows that it is the same across the plate surface. This temperature reduction rate was due to the increase in heat losses which occurs when the insulation plate cover is removed before each test. This phenomena was also verified by comparing the time-temperature data to the experimental video footage recorded during testing.

For the next 1.3 seconds, the center of the plate time-temperature curve fits the linear regression line (y = -36.4x + 815.8) with an r^2 value of 0.986, and the edge of the plate curve fits the linear regression line (y = -35.1x +820.9) with an r^2 value of 0.996. This indicates a nearly constant plate surface temperature cooling rate of 35.1^{o}C to 36.4^{o}C per second, and was a 25^{o}C per second change from the previous (0 to 1.2 second) interval. The change in slope at (t=1.2seconds) is due to R-32 cooling and occurs the moment at which R-32 refrigerant gas contacts the hotplate surface. This value fits with our definition for hot-surface ignition temperature; defined as the lowest surface temperature at which a fuel/air mixture will ignite upon contact with the heated surface.

Further analysis of the experimental video footage was used to pinpoint where this initial ignition occurred in relation to the hot plate surface. For R-32 this occurred at the center of the plate at a temperature of 773^{o}C.

The same approach and measurement analysis was conducted for R-410A and the lubricating oil refrigerant mixtures. Figure 3.5 shows the ignition test results extracted from the time-temperature plots for R-410A, R-32, POE Oil, and 1% refrigerant oil mixtures. The lowest observed ignition temperature for each mixture is shown in red. All of the temperature data provided is within +/- 10 °C of uncertainty.

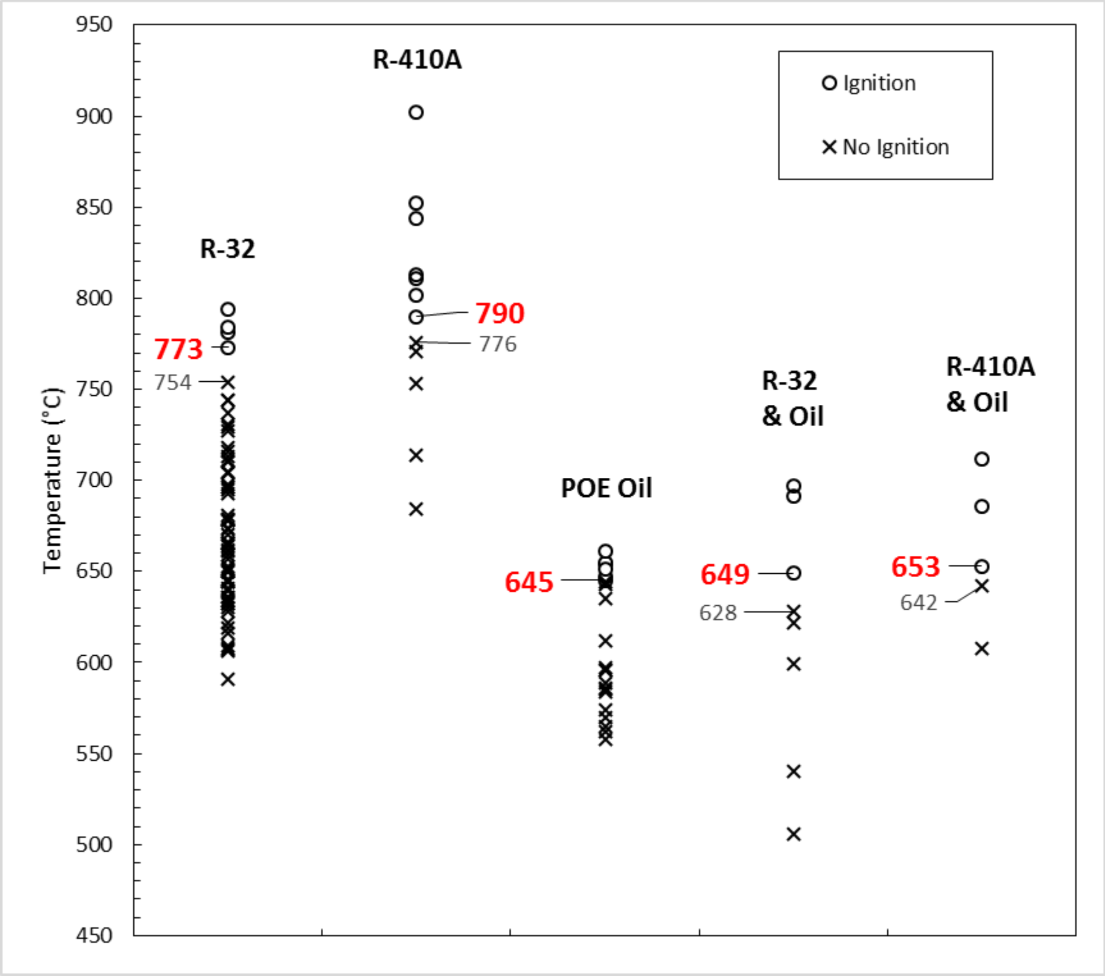


Figure 3.5 Hotplate Ignition Temperatures for R-32, R-410A, POE Oil, & Mixtures

The lowest R-32 ignition temperature observed was 764 °C. The lowest R-410A ignition temperature observed was 790 °C. The lowest ignition temperature of POE lubricating oil was 645 °C. The lowest R-32 and 1% POE oil mixture ignition temperature observed was 649 °C. The lowest R-410A and 1% POE oil mixture ignition temperature observed was 653 °C. Differences between the observed ignition temperatures 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) who further discussed this, and highlighted the dependence on the fuel structure, surface material properties, surface temperature, fuel/air stoichiometry, surface size, surface orientation, and ambient pressure conditions.

Table 3.1 reports the critical ignition temperatures recorded and compares them with published values. The lowest R-32 IT observed was 764 ^{o}C, which is 116 ^{o}C higher than the published, albeit in a different setup. Richard (2012) reported that the autoignition temperature was above 700 ^{o}C in an open top measurement. This measurement is closer to ours.

Table 3.1 Present Work Observed Ignition Temperature & Values Reported in Literature

Fuel	**Ignition Temperatures (°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	-
R-410A mixed with POE Oil	653	-

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 ^{o}C higher than pure R-32. Furthermore, the addition of 1% POE oil lowers significantly the ignition temperature 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 °C. Tests show that when mixed with this oil, the ignition temperature of R-32 is reduced to 649 °C; a decrease of 125 °C. The oil provides sufficient energy to ignite the refrigerant vapors

Table 3.2 below shows a side by side comparison of combustion properties of pure R-32 and R-410A as found in the literature with the addition of the hot surface ignition temperatures collected in our tests. Here, HSIT represents the hot-surface ignition temperature, AIT represents the autoignition temperature, LFL represents the lower flammable limit, UFL represents the upper flammable limit, MIE represents the minimum ignition energy, BV represents the laminar flame speed or burning velocity, and Δh_c represents the heat of combustion of the refrigerants.

Table 3.2 Combustion Properties of R-32 and R-410A

Fuel Properties	HSIT (oC)	AIT (oC)	LFL (vol%)	UFL (vol%)	MIE (mJ)	BV (cm/s)	Δhc (kJ/g)
R-32	764[a]	648[b]	13.3[c]	29.3[c]	15[c]	6.7[d]	9.4[e]
R-410A	790[a]	-	15.6[f]	21.8[f]	-	-	-

[a] Ref (Current testing)
[b] Ref (Downing, 1988) test method not verified
[c] Ref (Hihara, 2012)
[d] Ref (Jabbour, 2004)
[e] Ref (Goetzler, 1998)
[f] Ref (Takizawa, 2012)

3.3 Closed Cup Oil Ignition Results

The closed-cup ignition tests, performed by Vivien Lecoustre, compared the ignition temperatures of POE and mineral lubricating oil using a slightly different approach. The ignition temperature results were much closer to that of the published AIT value found in literature sources.

These test used the same delivery apparatus, however the hot plate was no longer square, and it consisted of a copper pan with a 14 cm diameter as seen in Figure 3.6. POE autoignition occurred at 445°C, and mineral oil autoignition occurred at 338°C.

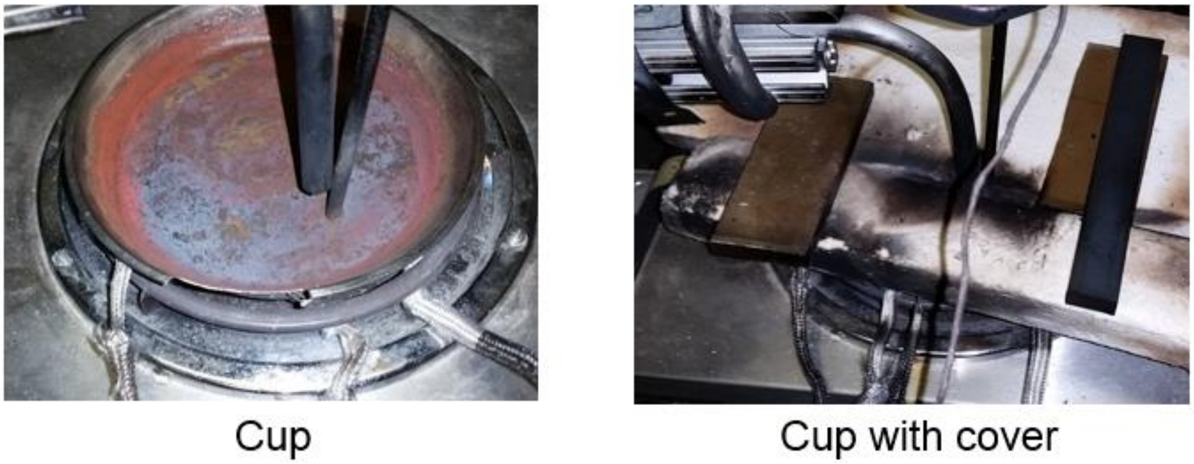


Figure 3.6 Closed-Cup Hotplate Ignition Temperature Apparatus

3.4 CFD Model

To provide an improved understanding of the experiments, a LES code, the Fire Dynamics Simulator (FDS, McGrattan, 2013) was employed by research team member Vivien Lecoustre. 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 °C. FDS does have the ability incorporate combustion capabilities in the CFD model, however these methods were not used here.

Fire Dynamics Simulator (FDS) is an open-source Fortran program written by the National Institute of Standards and Technology (NIST) and it is widely used in the fire protection engineering field. It is a Large Eddy Simulation (LES) 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 configuration of this model is based on the setup of the hotplate ignition experiments. The mesh consists of a three dimensional plane measuring 130 by 130 by 49, in the x, y, and z planes respectively. 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. As depicted in Figure 3.7 below.

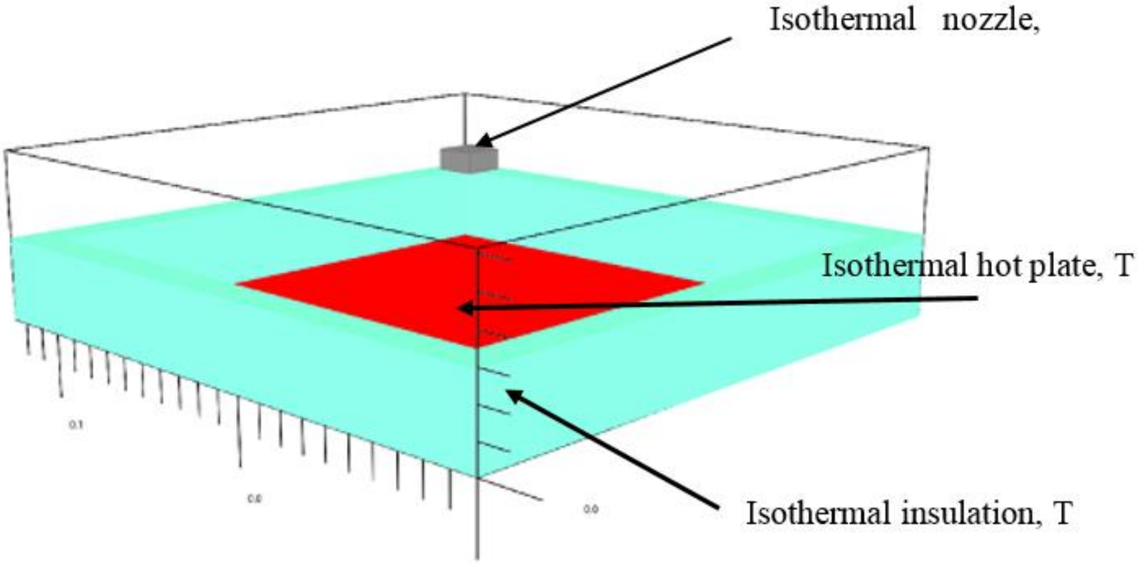


Figure 3.7 Hotplate Ignition Temperatures for R-32, R-410A, POE Oil, & Mixtures

One code limitation requires the use of rectangular Cartesian geometry, which is why the nozzle is not circular. The dimensions of the nozzle outlet injection zone were adjusted to loosely match the area of the cylindrical nozzle used in the experiment. Input variables are as follows:

The mass flow rate of injected R-32 is set to 1.1 g/s. The nozzle temperature is set to 0 ^{o}C, 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 the 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 ^{o}C. The insulated draft shield is also modeled as an isothermal surface, with a surface temperature of 394 ^{o}C as opposed to room temperature. This value was chosen to account for the heat addition that originates from the hot plate. Ambient conditions were set to 25 ^{o}C and 1.01 bar. A 2 s refrigerant release delay was included to allow for the development and stabilization the heat induced hotplate boundary flow fields. Discharge was a 1.5 second release using a linear ramp of 0.1 s, and a constant discharge up to 3.5 s, ceasing with a linear ramp decay. The primary goal was to study local concentrations and temperatures of R-32 vapor after the injection and compare these findings to the ignition locations observed in the laboratory.

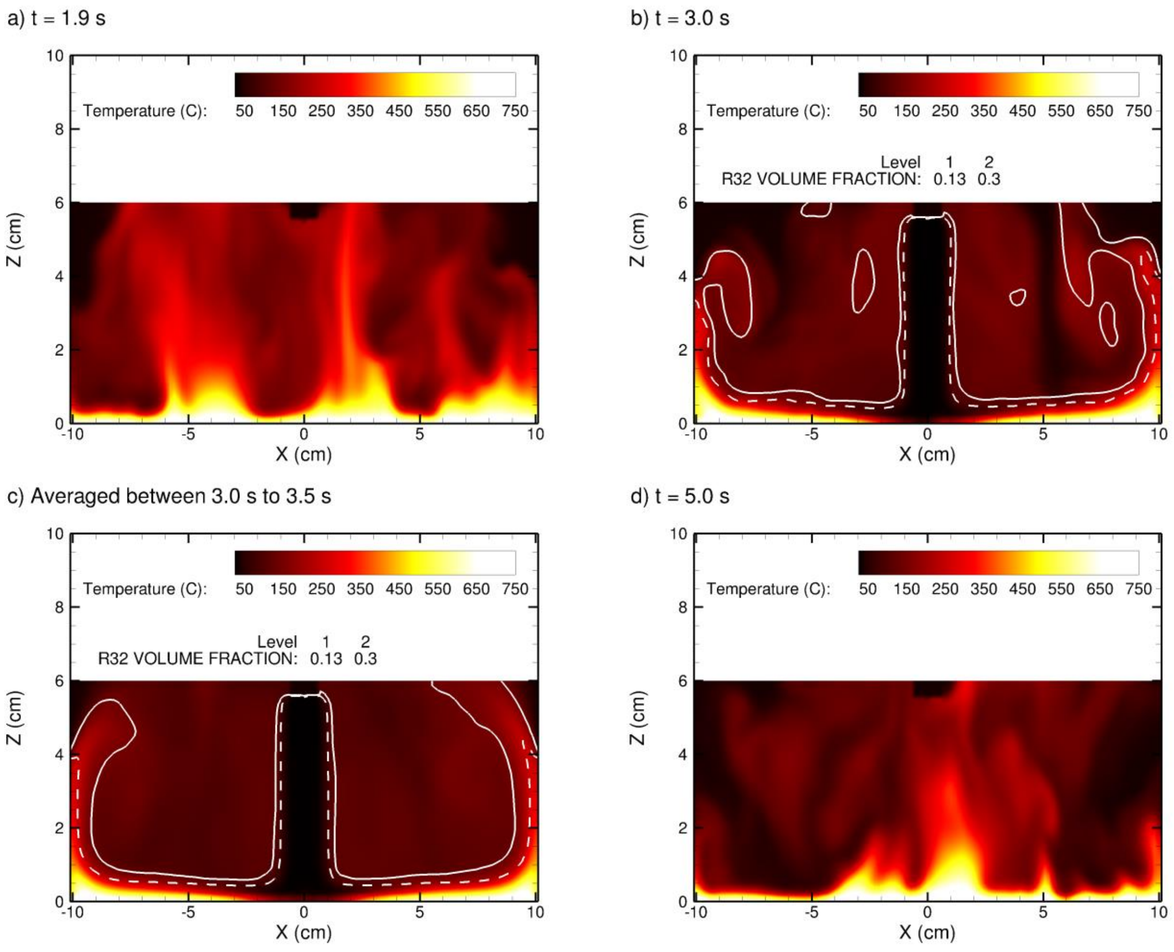


Figure 3.8 Model of R-32 Concentration and Temp Fields upon Contact with Isothermal Heated Surface

Figure 3.8 plots the temperature fields and the contours of constant R-32 concentration corresponding to the ambient lower flammability limits of 13 %/vol and the ambient upper flammability limit of 30 %/vol of R-32 in air. 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.

This model gives insight into the buoyancy physics driving hotplate ignition. Initially the hotplate induces flow naturally, with a vertical speed of approximately 0.5 m/s. When the R-32 jet comes into contact with the hotplate, the vapor jet moves radially toward the edge of the plate. Vapor temperatures reach 600 °C near the draft shield, a relatively stagnant zone having elevated temperatures and slow velocities. This implies that, in this configuration, R-32 is most likely to ignite near the draft shield and away from the jet point of impact.

4. Conclusions & Future Work

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 ^{o}C. The hot-plate ignition temperature of R-32 was found to be 764 ^{o}C (± 10 ^{o}C), while that for R-410A was found to be at 790 ^{o}C (± 10 ^{o}C). 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 ^{o}C) 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 ^{o}C 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.

Future work should examine:

- Effects of variations in surface material
- Realistic leak scenarios and likely flow rates
- Flammable concentrations in real world scenarios
- Design for a standard test method to determine the hot-surface ignition temperatures of compressed gasses
- Other variables such as configuration, gas disbursement, angle of discharge
- HF production and protection methods

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