

1996

Flammability Evaluation of HFC-32 and HFC-32 / 134a Under Practical Operating Conditions

O. Kataoka
Daikin Industries

M. Yoshizawa
Daikin Industries

H. Ohnishi
Daikin Industries

S. Ishida
Daikin Industries

Follow this and additional works at: <http://docs.lib.purdue.edu/iracc>

Kataoka, O.; Yoshizawa, M.; Ohnishi, H.; and Ishida, S., "Flammability Evaluation of HFC-32 and HFC-32 / 134a Under Practical Operating Conditions" (1996). *International Refrigeration and Air Conditioning Conference*. Paper 297.
<http://docs.lib.purdue.edu/iracc/297>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.

Complete proceedings may be acquired in print and on CD-ROM directly from the Ray W. Herrick Laboratories at <https://engineering.purdue.edu/Herrick/Events/orderlit.html>

FLAMMABILITY EVALUATION OF HFC-32 AND HFC-32/134a UNDER PRACTICAL OPERATING CONDITIONS

Osami Kataoka, Masahito Yoshizawa
Alternative Refrigerant Application Project

Haruo Ohnishi, Satoshi Ishida
Mechanical Engineering Laboratory
Daikin Industries, Ltd.
Sakai, Osaka, 591, Japan

ABSTRACT

Refrigerants were pooled in a pan whose size is typical of a small room in Japan and were ignited, in order to evaluate the potential of ignition and observe the nature of the flame propagation. Combustion of HFC-32 occurred, but not explosively, although explosions of HFC-32 in small vessels have been reported.*¹⁾ Furthermore, combustion of HFC-32 was shown to be quite different from that of HFC-152a, even though they are classified in the same flammability group by ASHRAE. Typical ignition sources under practical operating conditions were also evaluated to assess the risk of ignition. For example, it was confirmed that typical ignition sources such as a lit pilot burner could not ignite the blend.

DISCLAIMER

This paper was prepared by Daikin Industries, Ltd. according to its best knowledge regarding the flammability of these refrigerants to date. It explains the results we observed and our best judgment, but Daikin accepts no responsibilities for damages, if any suffered by any third party as a result of decisions made or actions taken based on this paper.

INTRODUCTION

The CFC phase out was completed at the end of 1995 in developed countries, and limit on HCFC production amounts according to Montreal Protocol also began this year, illustrating the steady progress being made in the protection of the stratospheric ozone layer. However, the air conditioning industry is also deeply concerned about the issue of global warming. For this reason, hydrocarbons, ammonia and flammable HFCs have been suggested as alternatives by the U.S. EPA and environmental groups. However, air conditioner manufacturers have avoided the use of these refrigerants in most residential and commercial applications, since non-flammable and non-toxic refrigerants have been used in these applications for decades.

U.S. DOT regulations allow handling of ammonia as a non-flammable gas. The Japanese High Pressure Gas Control Law considers even HFC-32 to be non-flammable. We understand this to mean that these moderately flammable gases can be handled as non-flammable, if the application and charge amount are appropriately specified. Flammability and toxicity risks of these refrigerants must be assessed, but the global warming effect of refrigerants should also be considered. The global warming increase due to CFC's emission (direct warming) from 1981 to 1990 is approximately 25% of total warming increase resulting from human activity in this decade.*²⁾

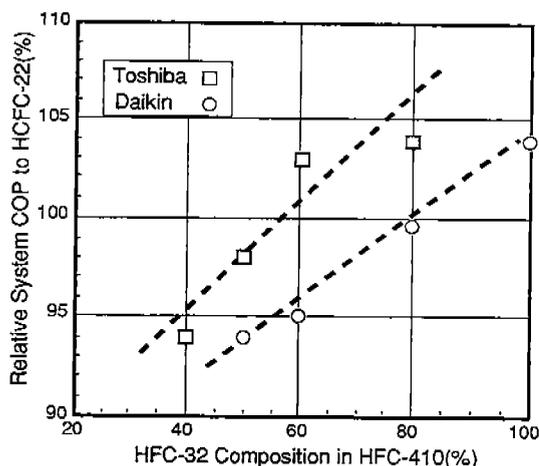


Figure 1 Effect of HFC-32 Composition

The EPA reported to Congress in 1989 that if the CO₂ concentration in the atmosphere doubles, there would be at least 958 mortality increase (1042 increase in summer and 84 decrease in winter) in 15 major cities in the United States those have about 21 million populations in total.*³⁾ Since Japan has a population over 120 million, we could assume that there would be 5500 mortality increase in Japan. If the ratio of warming impact of CFC's to the total during the decade of 1981-1990 was applied, CFC's would be responsible for 25% or 1400 mortality increase per year. Even if the warming effect was reduced to 10% by refrigerant recovery, it would still be responsible for 140 deaths in Japan. On the other hand, there are about 50 deaths due to fuel gas fire or accidents annually in Japan.*⁴⁾ This suggests that global warming is a critical issue in comparison to flammability risk. As the next step in the CFC and HCFC phase out, we should consider both the flammability and global warming risks quantitatively to select the most appropriate refrigerant.

COP is another key issue in choosing the most appropriate

alternative refrigerant. We should also take into account future energy conservation regulations. In addition, COP is dominant for indirect warming effect (CO₂ emission in power plant). Since HFC-125 has a relatively low critical temperature and high molecular mass, it has rather poor thermo-physical properties and practical COP. Consequently, reduction of the HFC-125 composition in blends increases the system COP. Figure 1 illustrates this tendency.⁵⁾ However, a certain amount of HFC-125 has been required in order to classify HCFC-22 alternative blends as non-flammable.

Flammability of refrigerants may be determined by a small vessel test such as that specified by ASTM E-681, but the flammability risk can not be assessed by this type of test. A risk assessment based on various factors such as ignition consequence, leak probability, pooling probability is necessary. In the study described below, we conducted flammability tests of HFC-32 and HFC-32/134a under practical operating conditions, as well as testing some potential ignition sources. This testing enabled us to obtain basic data for the risk assessment and to better understand the moderate flammability of these refrigerants.

DIFFUSION EVALUATION

Before starting the combustion test, we evaluated the diffusion of the leaked refrigerant in order to design an appropriate test set-up and to determine the appropriate test conditions. We first performed a small scale diffusion test to understand and confirm the diffusion behavior of a gas which is heavier than air. A cylinder of 0.3 m I.D. (1') x 1 m (3.3') height was used this test. We then conducted the practical size diffusion test to evaluate the phenomena quantitatively. Figure 2 shows the size and measurement points of the room that was used for this test. Refrigerant concentration in air was measured by gas chromatography. Since about 0.5 kg (1 lb.) of refrigerant charge is necessary to air condition a room this size, we evaluated about 1 kg (2 lb.) of leaked refrigerant for conservatism.

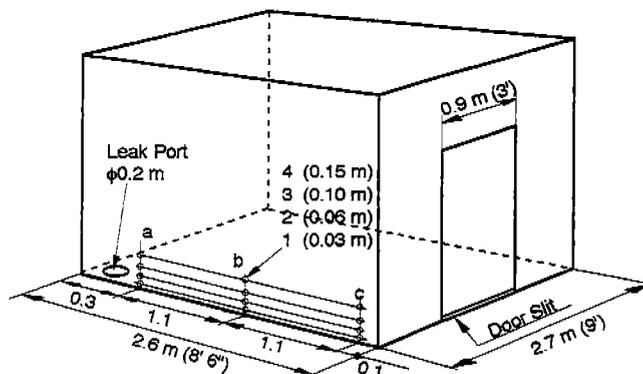


Figure 2 Diffusion Test Room Dimensions

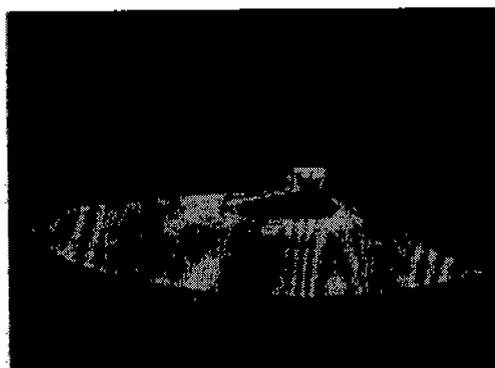


Figure 3 FEA Diffusion Analysis

The homogeneously mixed condition of air and refrigerant is most conservative for flammability evaluation, but about 5 kg (10 lb.) of refrigerant is required to make the entire room flammable in a homogeneously mixed condition. This scenario was judged to be impractical. HFC-134a and CO₂ instead of HF-32 and HFC-32/134a were used for the experimental evaluation to get more conservative result. Finally we conducted finite element analysis (FEA) using DYNA-FLOW[®] to simulate the room diffusion test and to interpolate data between measured points in order to understand the phenomenon visually. Figure 3 shows a typical FEA result.

Diffusion of leaked refrigerant is affected by many factors such as leak velocity, leak rate, height of leak, tightness of room, convection in the room, molecular weight of refrigerant, so it is impossible to evaluate the phenomena at every condition. However, we know the general effects of these factors, so we can predict the worst case condition that causes a higher concentration of leaked gas. Major factors we evaluated and their impacts are listed in Table 1.

It is confirmed experimentally that the leaked refrigerant pools at a height less than 0.3 m (1') above the floor in high concentration, although a lean concentration occurs at higher positions. Figure 4 shows a typical concentration gradient in the room test. Although we see a large concentration gradient in the vertical direction, the gradient in horizontal direction is negligible, as shown in Figure 4.

Major findings of these analyses are as follows;

- The mass transfer caused by gravity or kinetic energy is more dominant than physical diffusion caused by molecular movement. Therefore, leaked gas spreads very quickly in the horizontal direction and

Table 1 Major Diffusion Parameters

Parameter	Room Test Conditions
Leak Velocity	Minimized
Leak Rate	100% of charge/hr.
Leak Height	Leak at the floor
Horizontal Location	Most far position from the door
Opening(Door Slit)	Standard, Halved, No slit
Tightness of wall	Sealed with vinyl sheet
Ventilation	Without ventilation
Heat conduction	Heat effect from the window was confirmed

downward, but very slowly in the upward direction, if refrigerant is leaked at low velocity.

- The concentration increases as the leak rate increases.
- The highest concentration appears at the end of leak and on the floor, though the concentration may increase after that at higher positions.
- Velocity caused by pressure or gravity dilutes the concentration, so low velocity and low position of leak are necessary to generate flammable concentration with a specified amount of refrigerant.
- A fairly large portion of spilled refrigerant leaks out of the room through the paper covered plaster board wall unless it is sealed by a vinyl sheet.

We determined the test conditions and the set-up of the room flammability test according to the results of the diffusion tests and FEA results.

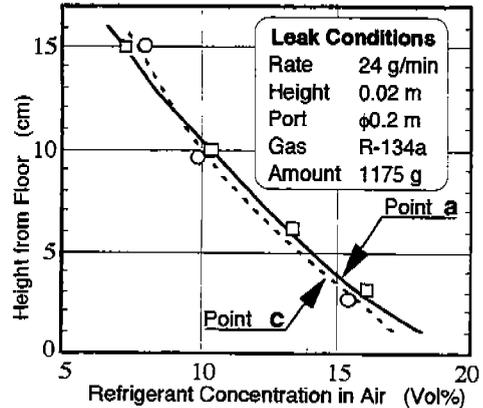


Figure 4 Typical Diffusion Test Data

ROOM FLAMMABILITY TEST

Test Room and Pan

Room tests were conducted at the Factory Mutual Test Center in West Glocester, Rhode Island, in the United States. Since the diffusion test indicated that leaked refrigerant pools at a low position in a room, we prepared a pan that is rather shallow but has sufficient depth to test the combustion of refrigerants. The floor area of the pan was chosen to match the smallest room that is likely to be equipped with a room air conditioner in Japan. The dimensions of the pan were 2.7 m by 2.7 m by 0.6 m depth (9' by 9' by 2'). The pan was placed in an explosion resistant room 4.5 m by 4.5 m by 3 m high (15' by 15' by 10'). We prepared a steel plate corner to increase the local concentration to obtain the worst condition, though its effect is insignificant. Since we found a "flame holder" to be effective in sustaining the combustion of HFC-32 and the blend after several tests, we provided a few in the pan during testing. Figure 5 shows the test set-up.

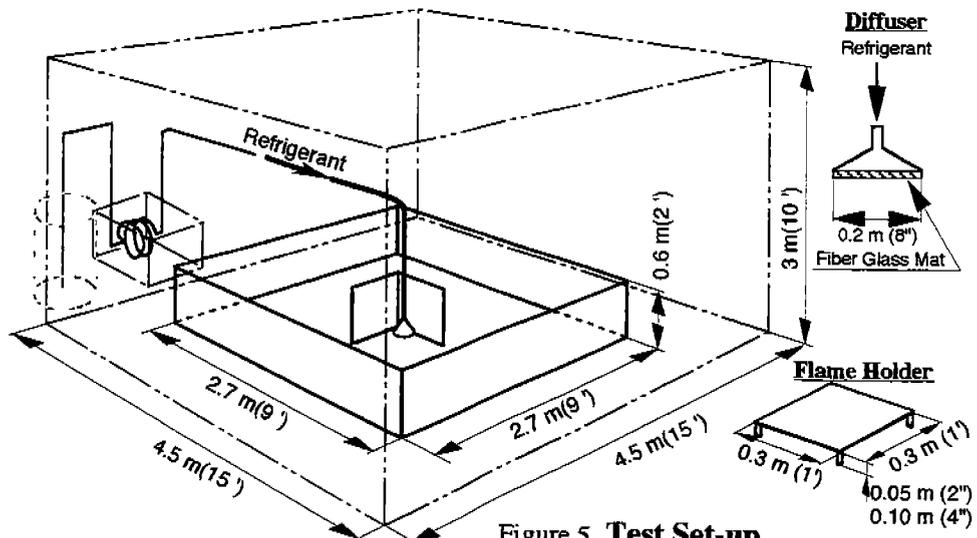


Figure 5 Test Set-up

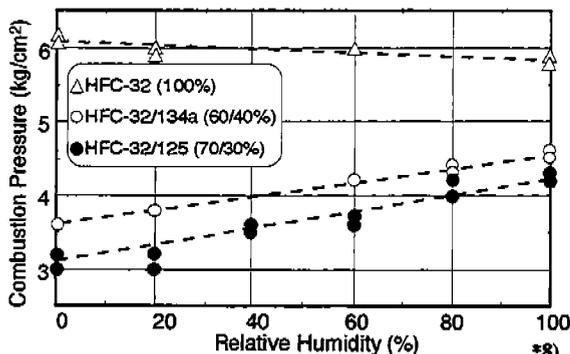


Figure 6 Humidity Effect on Combustion

The room was equipped with a heater and a humidifier to control the temperature and humidity at the specified condition. Since the flammability of HFC-32/134a increases with humidity (See Figure 6), the relative humidity of the air was controlled at approximately 80% when the blends were tested. In addition, combustion tends to be stronger at higher ambient temperature, so tests were conducted at about 30 °C (86 °F). Three video cameras were provided to record the combustion phenomena. Pressure and temperature were also measured and stored in a data acquisition system.

Ignition Source

We used DC spark igniter that generates a spark energy of about 19 J, except during later testing of various ignition sources. Since the energy required to ignite HFC-32 and the blend was reported to

be about 200 mJ^{*6)}, we judged 19 J to be sufficient. Three igniters were provided to observe the effect of location and local concentration. The first igniter was placed just beneath the release port. The second one was located 0.1 m (4 ") from the edge of the release port. The third one was the same horizontal position but the height was increased. The first two igniters were located 2.5 cm (1 ") from the bottom and third one was 5 cm (2 ") from the bottom. When the flame holders were used, igniters were moved to the position just beneath the edge of them. Every five seconds, one igniter was activated, so each igniter sparked every 15 seconds.

Refrigerant and Release System

HFC-32 and HFC-32/134a were the primary refrigerants tested. Since HFC-32/134a is a zeotropic blend, various compositions were tested to cover the worst case fractionation scenario. In addition HC-290 (propane) and HFC-152a were tested in order to compare their behavior to HFC-32 and the blends. Blend refrigerants were mixed and charged to the cylinder at the chemical laboratory of National Refrigerants Inc., and the composition was confirmed by gas-chromatography. The refrigerants were drawn out from the cylinder in liquid phase to prevent the blend from fractionating and to maintain a constant flow. A heat exchanger and a water heat sink were prepared to evaporate the liquid refrigerant. Evaporated refrigerants were spilled into the pan through one of the two release ports. The first release port is a 0.2 m I.D. (8 ") diffuser that consists of a funnel and glass wool pad at the bottom. This setup allows large release rate while minimizing velocity. The second one is a 7.7 mm (0.305 ") I.D. tube opening vertically downward from a height of 34 cm (13 ").

Procedure

The room was sealed tightly, and the room air was then heated to the specified temperature. The room air was humidified to the specified condition also when the blends were tested. Refrigerants were then spilled. The sparking normally began at the end of the spill because the highest concentration appears at or after the end of the spill. However, a few special tests were conducted with sparking during the spill, in order to observe behavior under these conditions. Ignition was continued until a substantial combustion occurred or until 10 minutes passed without combustion.

Results and Findings

Table 2. Major Test Results

Test No.	Refrigerant *	Release Amount kg	Release Rate g/min.	R.H. %	Flame Holder	Diffuser	Results
1	60/40%	1.00	11	90	Yes	No	No sustained ignition, Small puffs of flame
2	60/40%	1.02	62	78	No	Yes	Small flame sustained 25 sec. on the funnel
3	60/40%	1.00	68	75	No	No	Puff of fire balls around 50 cm dia.
4	HFC-32	1.14	300	40	No	Yes	Small flame grown over the corner
5	40/60%	1.00	79	75	Yes	No	Sustained for 55 sec. above the holder
6	35/65%	1.00	100	70	Yes	No	No Ignition
7	HFC-32	1.00	72	40	Yes	No	Sustained above the holder
8	Propane	0.12	70	38	No	No	Explosive combustion
9	HFC-152a	1.00	64	63	No	No	Explosive combustion slower than propane
10	60/40%	0.28	71	80	Yes	No	No ignition
11	60/40%	0.25	110	80	No	Yes	Small flame sustained for 40 sec.

*Percentages indicate the blend HFC-32/134a with that composition.

Major results are tabulated in the Table 2, and selected video segments are shown in Figure 7. Small puffs of flame were observed when we ignited the pooled refrigerant at a release rate about 10 g/minute, but at release rates of about 70 g/minutes, small fire-ball about 50 cm in diameter were observed. The combustion of HFC-32 and the blends was not self-sustaining in the absence of a flame holder. However, when a flame holder was provided, self-sustained combustion occurred, but not explosively. The combustion nature is quite different from that of HFC-152a which is classified in the same flammability class by ASHRAE 34. Flames of HFC-32 and the blends did not propagate horizontally except above the flame holder. In contrast, HFC-152a and propane flames propagated explosively in the horizontal direction. Although HFC-32 and propane have shown similar pressure rises in tests in small vessel^{*1)}, the combustion behavior of HFC-32 is quite different from that of propane.

Combustion is stronger when a thick flammable layer is present, which is a condition generated by moderate release velocity. However, the minimum refrigerant amount required to sustain a flame occurred at slow release velocity condition. Since 175 g of blend (60/40%) did not but 250 g sustained the flame, the minimum refrigerant amount to sustain a flame in this size of room seems to be about 200 g with the blend.

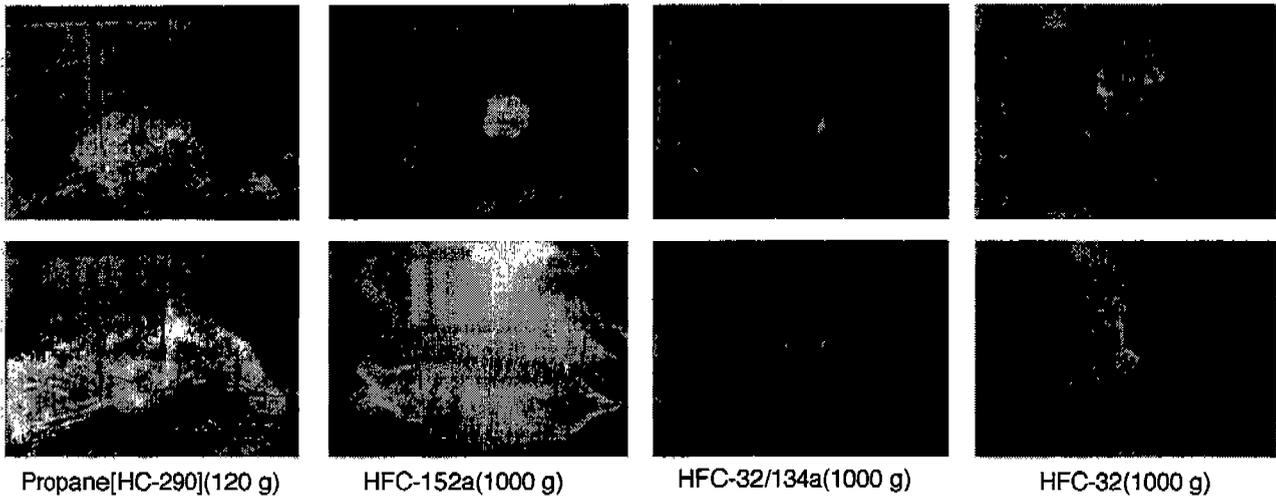


Figure 7 Combustion Nature of Refrigerants

Since HFC-32/134a blend (40/60%) sustained the flame but HFC-32/134a (35/65%) did not, the boundary between flammable and non-flammable seems fairly consistent with bench scale tests such as ASTM E-681. (See Figure 8)

IGNITION SOURCE TEST

Background

Most flammability tests, including this room flammability test, employ ignition sources which are sufficiently strong to evaluate the flammability of a substance conservatively. However, in order to better evaluate flammability risk quantitatively, we should reduce this excessive conservatism. The energy in a 20 J spark is far in excess of a typical household ignition source. Therefore, an evaluation of the potential for ignition by typical sources is necessary. We evaluated such sources experimentally to better understand the potential for ignition. The minimum ignition energy for HFC-32 is reported to be 1000 times higher than that of hydrocarbons.*6)

We chose a glowing Ni-Cr wire, a magnet relay and a pilot burner as typical ignition sources. A match head was not tested because ASTM E-681 testing had shown that an electrically activated match head is strong enough to ignite HFC-32 and the blends. However, ignition by match in a practical operating condition requires stroke movement and a live person to generate convection in the room that dilutes the gas concentration, so this scenario needs to be investigated further.

Glowing Ni-Cr Wire Test

We used the same procedure specified by ASTM-E681, but replaced the match with a Ni-Cr wire for the ignition source. The wire was formed as a vertical spiral so that a heated mixture flowing upwards would contact the glowing wire repeatedly. We fill the flask with a mixture of air and HFC-32 or the blends at stoichiometric composition, and then energized the Ni-Cr wire. No ignition occurred with the blends or HFC-32.

Magnet Relay Test

In this test we used a steel vessel instead of the ASTM flask in order to charge the relay with a high current. (See Figure 9.) Test required eight terminals to charge the relay with a 3 phase, 60 Hz, 220 V and 21 amp power line, which is representative of the power line used in a 16 kW (56000 Btu/h) capacity air conditioner. The vessel had terminals and a sight glass so combustion can be confirmed visually. The test procedure was similar to the Ni-Cr wire test. We filled the vessel with a stoichiometric mixture of air and refrigerant. We then cycled the load on and off several times with the relay in the vessel. No combustion was observed with HFC-32 or the blends.

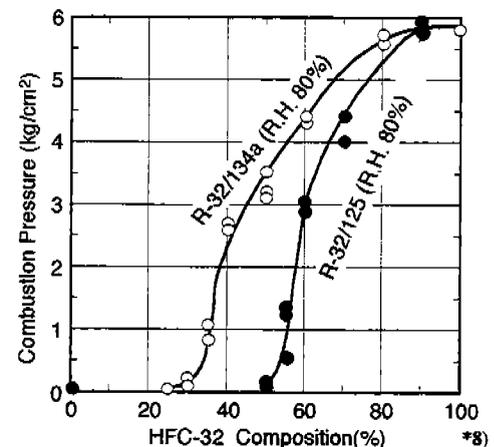


Figure 8 Combustion in Small Vessel

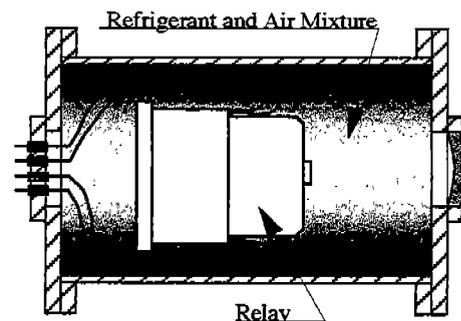


Figure 9 Magnet Relay Test

Pilot Burner Test

Pilot burners of boilers are an important potential ignition source but also representative of other open flame such as a main burner of boiler, a gas stove or a fireplace. We conducted a test in which a lit pilot burner was placed in the pan, and refrigerants were spilled. The pan was the same one used for the room flammability test. The room was humidified to about 80% relative humidity at the start of the test. The HFC-32/134a (60/40%) blend was then spilled at a rate of about 70 g/minute. The result was that the pilot flame temporarily enlarged somewhat but the flame then went out after a short time because of insufficient oxygen.

DISCUSSION

HFC-32 and the blend of HFC-32/134a with a flammable composition did not show horizontal flame propagation practically. This is probably because its combustion velocity is lower than the convection velocity caused by its heat of combustion. The flame temperature is greater than 1300°C (2372 °F) so it could generate fairly high speed convection (Buoyancy of the flame theoretically generates acceleration more than 50 m/sec²). However, the combustion velocity is only about 10 cm/second.*7) Therefore, convection rapidly reaches the combustion velocity which prevents flame propagation in the horizontal direction and generates only a small fire ball. However, if a sufficient turbulence occurs above an object (flame holder), HFC-32 and blends sustains flame. Because, part of the reacting mixture can stay above the object due to the turbulence and can continuously ignite the newly sucked gas.

We did not observe ignition of the blend with any of three typical ignition sources. We believe that the Ni-Cr wire and the magnet relay could not ignite the stoichiometric mixture of air and HFC-32 because the flame quenching distance of HFC-32 is about 7 mm (0.28 ")*7). The distance between the contact surfaces of the relay was not long enough. In the case of the Ni-Cr wire, boundary layer thickness required to reach the ignition temperature of HFC-32 seems to be insufficient to generate a flame, although surface temperature of the wire exceeds the HFC-32 auto ignition temperature of 648 °C (1198 °F).

CONCLUSION

The flammability of HFC-32 and HFC-32/134a blends were evaluated under practical operating conditions. The primary conclusions of this study are as follows:

- Although some regulations classify gases with high LFL (lower flammable limit) and narrow flammable range as a non-flammable gas, these gases can sustain flame in some practical conditions.
- The risk associated with use of these gases seems to be fairly low. Because, they burn under very limited conditions. In addition, typical ignition sources do not ignite the gas. Therefore, the flammability risk should be compared quantitatively to the global warming risk.
- Small scale test such as ASTM E-681 or pressure measurement in a steel vessel are useful for judging the boundary between flammable and non-flammable gases. However, the combustion behavior under practical condition is very different from that of small scale tests. Therefore, some refinements to small scale test procedures are necessary in order to better evaluate the flammability risk with small scale tests.

REFERENCE

- *1) MCLR Report "Methods Development for Measuring and Classifying Flammability/Combustion of Refrigerants", Heinonen, Tapscott, et al., University of New Mexico, Dec. 1994.
- *2) AFEAS/DOE Report "Energy and Global Warming Impacts of CFC Alternative Technologies", Fischer, Kusik et al., Oak Ridge National Laboratory, Arthur D. Little, Dec. 1991
- *3) "The Potential Effects of Global Climate Change on the United States - Appendix G - Health", "The Impact of CO₂ and Trace Gas-Induced Climate Changes upon Human Mortality" Kalkstein, University of Delaware, May 1989.
- *4) "Shoubou Hakusho" [Fire Defense White Paper] Fire Defense Agency Japan, 1993
- *5) "Performance Evaluation of Residential Air Conditioner with HFC-32/125 Mixture", Furuhashi, Komazaki, Toshiba Corporation, Dec. 1994
- *6) "Research on HFC-32 flammability - Measurement of the quenching distance and the minimum ignition energy", Mizomoto, Ueda, et al., Keio University Japan
- *7) "Research on HFC-32 flammability - Measurement of the laminar flow combustion velocity", Ikeda, Ueda, Keio University Japan
- *8) "Flammability Evaluation of Alternative Refrigerants for HCFC-22", Ishida, Ohnishi, Domestic Report of Daikin, March 1996.