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Hazard assessment of the combustion of mildly flammable refrigerants

Tei Saburi[a*]

[a]National Institute of Advanced Industrial Science and Technology (AIST), Research Institute of Science for Safety and Sustainability

Acknowlegement

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Contents list

1. Background
2. Scale effect on flammability
3. Explosion severity evaluation
4. Summary

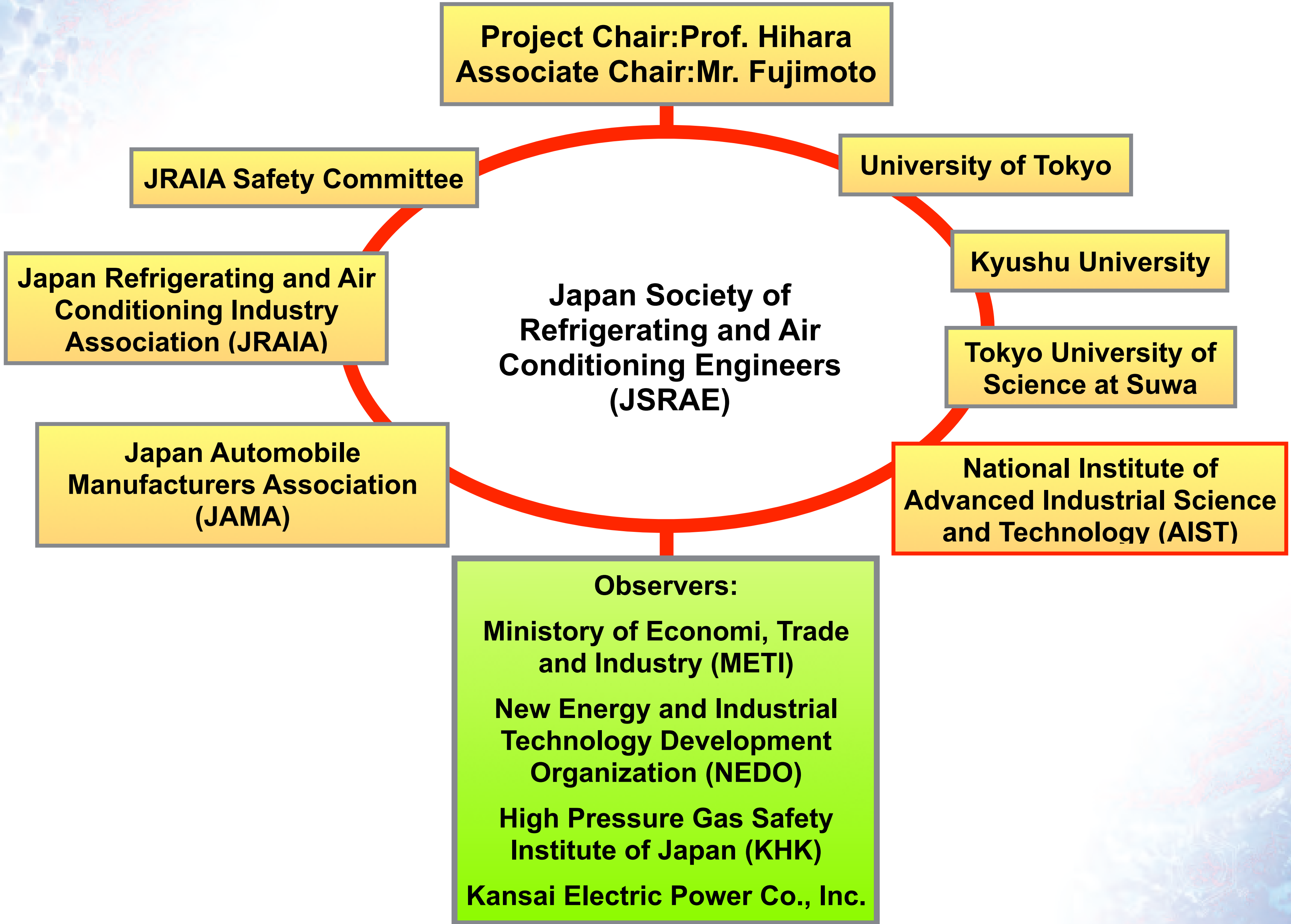
Background

- To promote A2L refrigerants effectively and safely, those ***fundamental flammabilities*** such as flammability limits, burning velocity, and MIE, etc. have been characterized (as shown by Dr. Takizawa).

- Hazard assessment on actual situation based on accidental scenario is also important ***to estimate the levels of extent of injury*** for the risk verification and the risk reduction measures.

- We should scale up and reflect the evaluation results by laboratory-scale standardized condition to ***the full-scale physical hazard evaluation***.

Research Committee for the risks associated with mildly flammable refrigerants



Research Committee for the risks associated with mildly flammable refrigerants

Physical Hazard Evaluation of A2L Refrigerants Based on Several Conceivable Handling Situations

National Institute of Advanced Industrial Science and Technology (AIST)

Hazard assessment of the combustion of mildly flammable refrigerants:

Combustion and explosion assessment

- **Explosion hazard assessment (scale effect)**
- **Explosion severity evaluation**

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Tokyo University of Science at Suwa

Hazard assessment based on accident scenarios

#1 the concurrent use of a wall-mount type room air conditioning system with a fossil-fuel heating system

#2 handling of A2L refrigerants at the factory for service and maintenance.

#3 use in the Variable Refrigerant Flow (VRF) system.

↓

Achievement of Hazard assessment in actual scale

Contents list

1. Background
2. **Scale effect on flammability**
3. Explosion severity evaluation
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Scale effect on flammability

- **The effects of temperature and humidity on the flammable behaviour of A2L refrigerants have been reported** (*Kondo, 2012); this is an important issue, especially with the hot and humid climate of Japan where over 30°C temperature and 80% humidity are often recorded in the summer.

*Kondo, S., Takizawa, K. & Tokuhashi, K. (2012), J. Fluorine Chem., 144; 130–136.

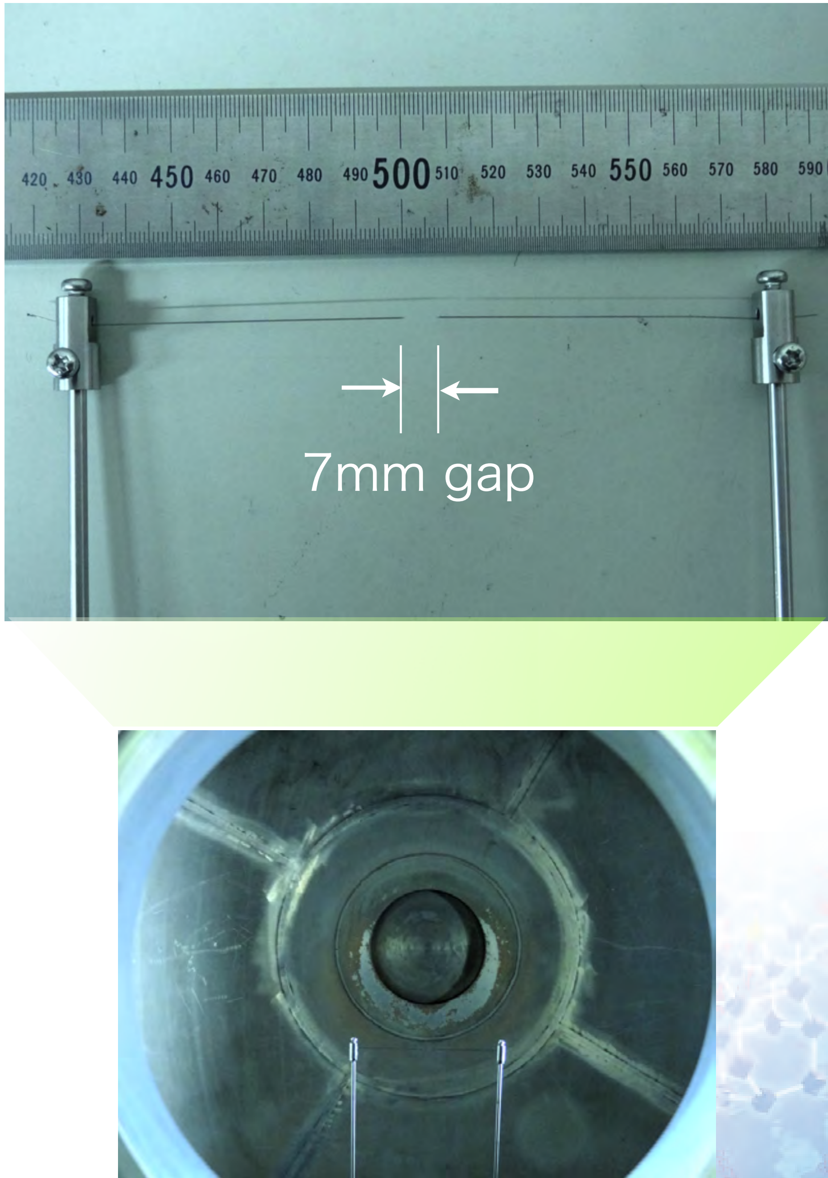
In this study

the flammable behaviour of A2L refrigerants in the presence of moisture and elevated temperatures was experimentally investigated using a large volume combustion vessel to see the scale and buoyancy effects.

Experiments

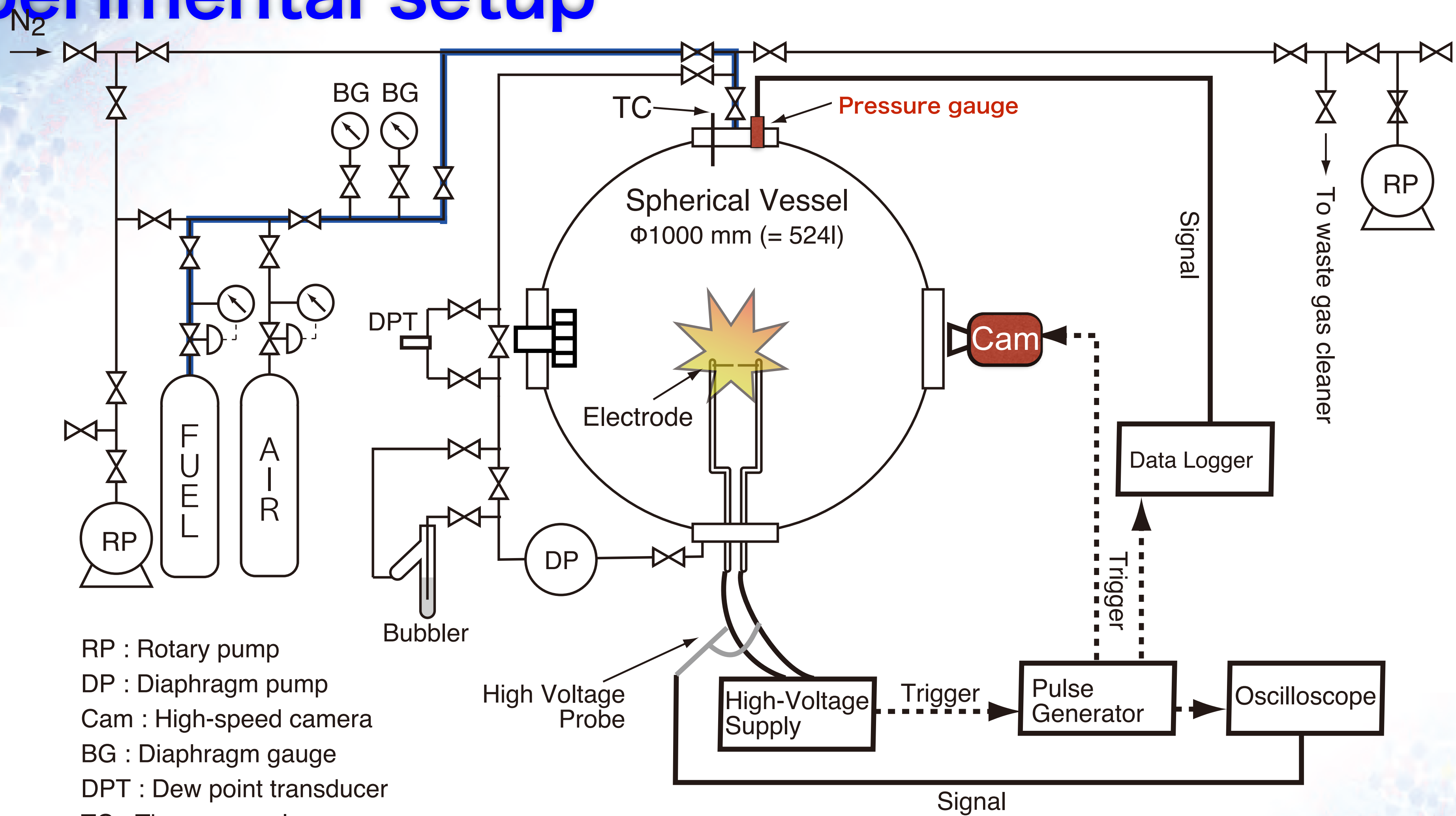
Experimental setup

Φ100cm **spherical combustion vessel**
equipped with mantle heater jacket



discharging electrode

Experimental setup



RP : Rotary pump
DP : Diaphragm pump
Cam : High-speed camera
BG : Diaphragm gauge
DPT : Dew point transducer
TC : Thermo couple

Strain gauge pressure sensor: KYOWA PHL-A (range: 2MPa, rate 100kS/s)
High speed video camera: Photon SA-Z (1024×1024pixels @ 1000fps)

Schematic illustrate of experimental apparatus

Experiments

Fuel/Air equivalence ratio Φ was determined from previous study.

- R32 Φ=1.1 (19 vol% in air)
- R1234yf Φ=1.325 (10 vol% in air)
- R1234ze Φ=0.8-1.325 (10 vol% in air)

Measurement

Premix combustion test was conducted by electric discharge using a Φ1m spherical vessel (524L)

- High speed video image observation
  - effect of buoyancy and viscosity on the flame propagation and shape
- Pressure measurement
  - peak pressure, rate of pressure rise

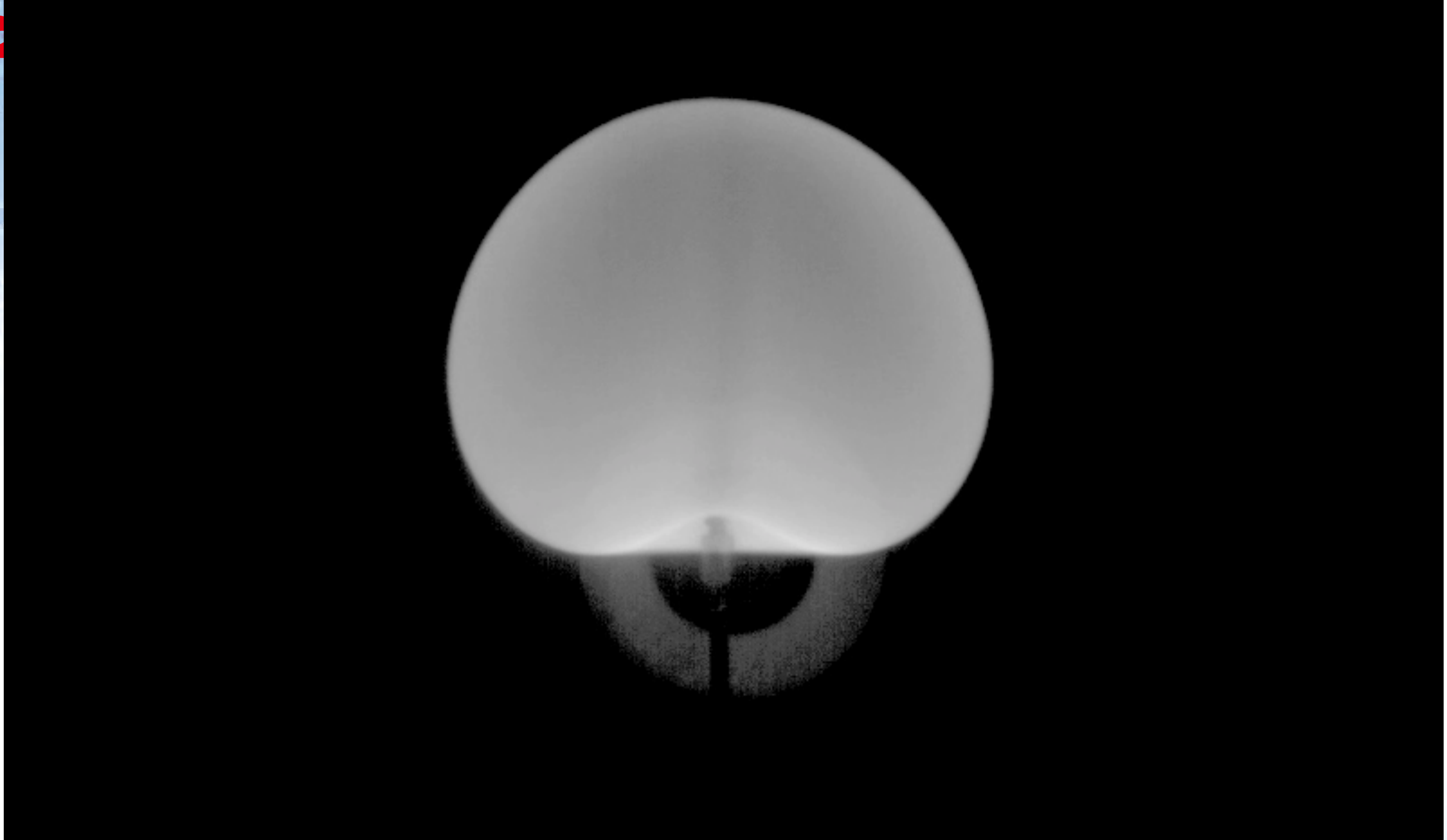
Evaluation

- Flame speed, burning velocity, and deflagration index(K_G)

Experimental condition

Refrigerant	Equivalence ratio (ϕ)	Temperature (°C)	Mositure (wet-dry condition)
R32	1	35	Dry
	1.1	35	Dry
		35	Wet (64% RH)
R1234yf	1.325	30	Dry
	1.325	35	Wet (78% RH)
R1234ze	0.8-1.5		Dry
	1.2	35	Wet(50%RH)
	1.325		Wet(55%RH)

High-speed video observation results



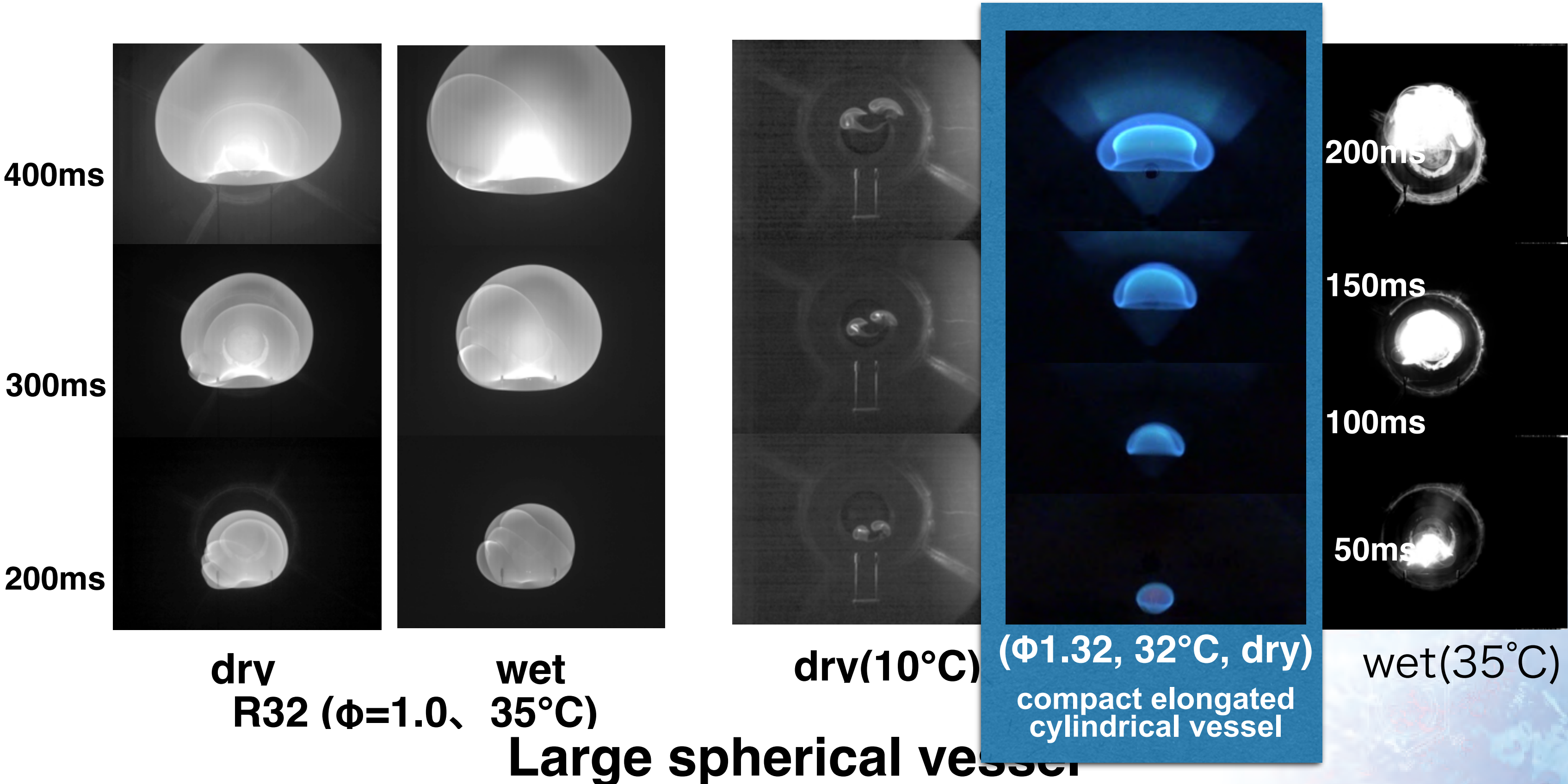
The flame expanded while slowly climbing upward and the shape of flame front was distorted under the influence of buoyancy, thermal expansion of the flame and thermal convection.

T+: +216.465 ms
Img#: 108 Rate: 500 Exp: 1998 µs

R32 30℃ dry

High-speed video observation

- Frame fronts of A2L refrigerants were smooth and wrinkled front was not seen in large volume vessel even under moisture and elevated temperature conditions.



A practical index for estimating safety

K_G:deflagration index*   (*ISO 6184-2, NFPA68 2007)

Deflagration index for gases K_G ($100\text{kPa}\cdot\text{s}^{-1}$) is described using maximum pressure rise rate in the vessel $(dP/dt)_{max}$ and the volume of vessel V_{vessel} as follows

$$K_G = \left(\frac{dP}{dt}\right)_{\max} \cdot V^{1/3}$$

P : Pressure (10^5Pa)

t : time (s)

V : the volume of vessel (m^3)

K_G is used for estimating **effect of deflagration in closed space** and designing explosion **venting area** of enclosures. Larger K_G value, larger venting area should be required for preventing enclosure burst.

Table of K_G and other flammable parameters for typical gases

Flammable Material	P_{max} (100 kPa)	K_G (100 kPa·m·s^{-1})	Burning velocity (cm·s^{-1})	Flammability limits (%)	Detonation limits (%)[*3] Cofined tube	Unconfined	Autoignition Temperature (℃)[*7]
Acetylene	10.6 [*1]	1415 [*1]	166[*2]	2.5—80.0[*3]	4.2—50.0		305
Hydrogen	6.8 [*1]	550 [*1]	312[*2]	4.2—75.0[*3]	18.3—58.9		400
Ethylene			80 [*2]	2.70—36.0[*3]	3.32—14.70		490
Diethyl ether	8.1 [*1]	115 [*1]	47 [*2]				
Benzene			48 [*2]	1.3—7.9[*3]	1.6-5.55		562
Ethane	7.8 [*1]	106 [*1]	47 [*2]	3.0—12.4[*3]	2.87—12.20	4.0–9.2	515
Propane	7.9 [*1]	100 [*1]	46 [*2]	2.1—9.5[*3]	2.57—7.37	3.0–7.0	450
Butane	8.0 [*1]	92 [*1]	45 [*2]	1.8—8.4[*3]	1.98—6.18	2.5–5.2	405
Ethyl alcohol	7.0 [*1]	78 [*1]		3.3—19.0[*3]	5.1—9.8		
Methanol	7.5 [*1]	75 [*1]	56 [*2]				
Methane	7.1 [*1]	55 [*1]	40 [*2]				
Ammonia	5.4 [*1]	10 [*1]	7.2[*4]	15—28[*5]			651

*1 Ref. (NFPA68, 2007), Table E.1 (0.005 ft^3 sphere; E = 10 J, normal condition).

*2 Ref. (NFPA68, 2007), Table D.1.

*3 Ref. (Mannan, 2005), Detonation limits obtained for confined tube. *4 Ref. (ISO/DIS 817, 2010)

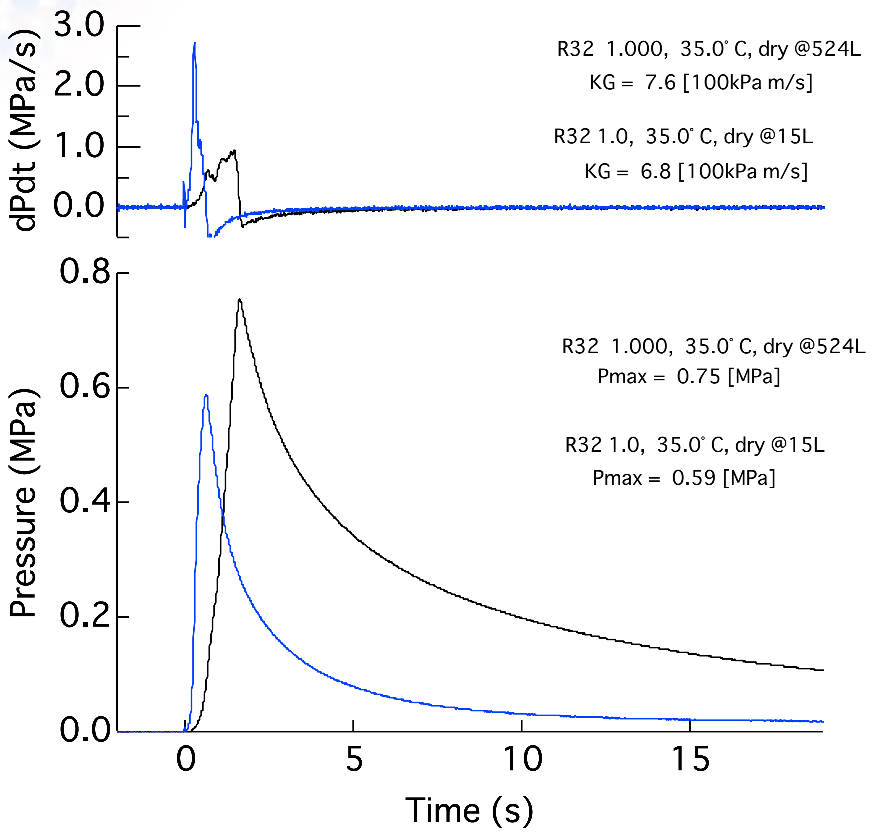
*5 Ref. (NFPA325, 1994) *6 Ref. (JFMA, 2013)

*7 Ref. (Mannan, 2005), Table 16.4

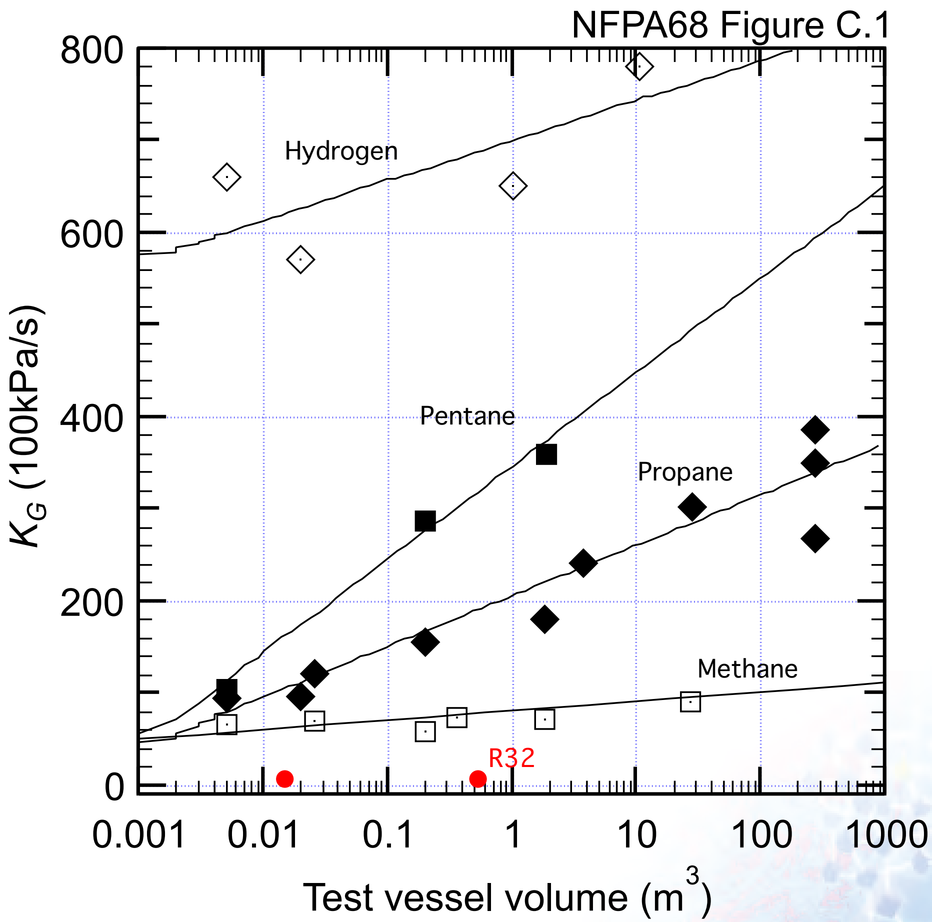
- The relative explosion severity of flammable gases was listed in order of K_G.
- We can know the relative severity of A2L refrigerants by estimating K_G.

K_G value in different volume

- K_G value is compared with that measured by 15L spherical vessel.
  - R32
  - Equivalence ratio Φ=1.0



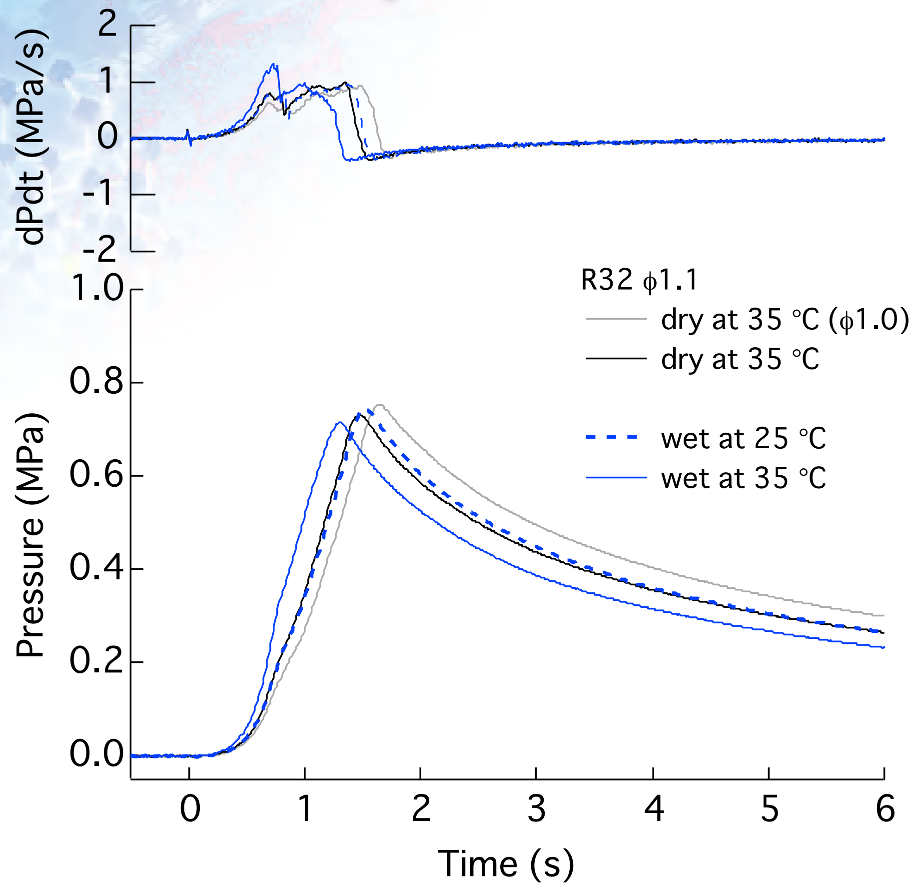
Pressure profile for R32 Φ1.0



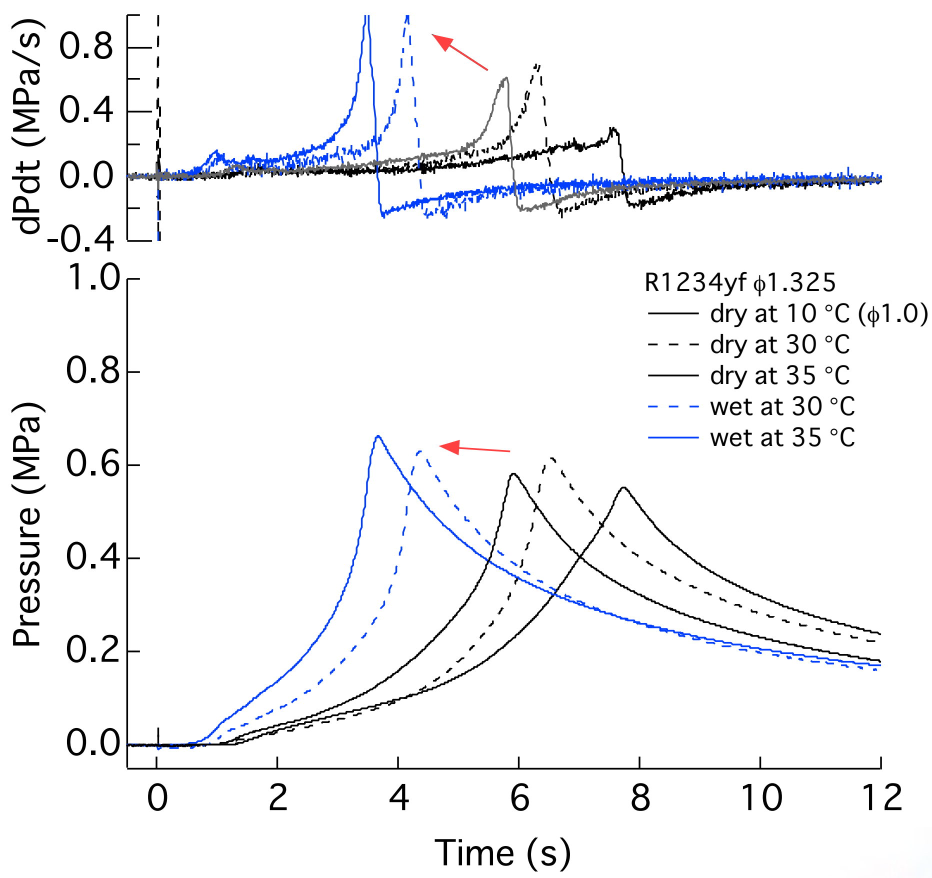
Effect of test volume on KG measured in spherical vessels.

- K_Gs are around 7-8 [100kPa•m/s]
- There is no significant potential of increase in K_G value at present.

Pressure profile



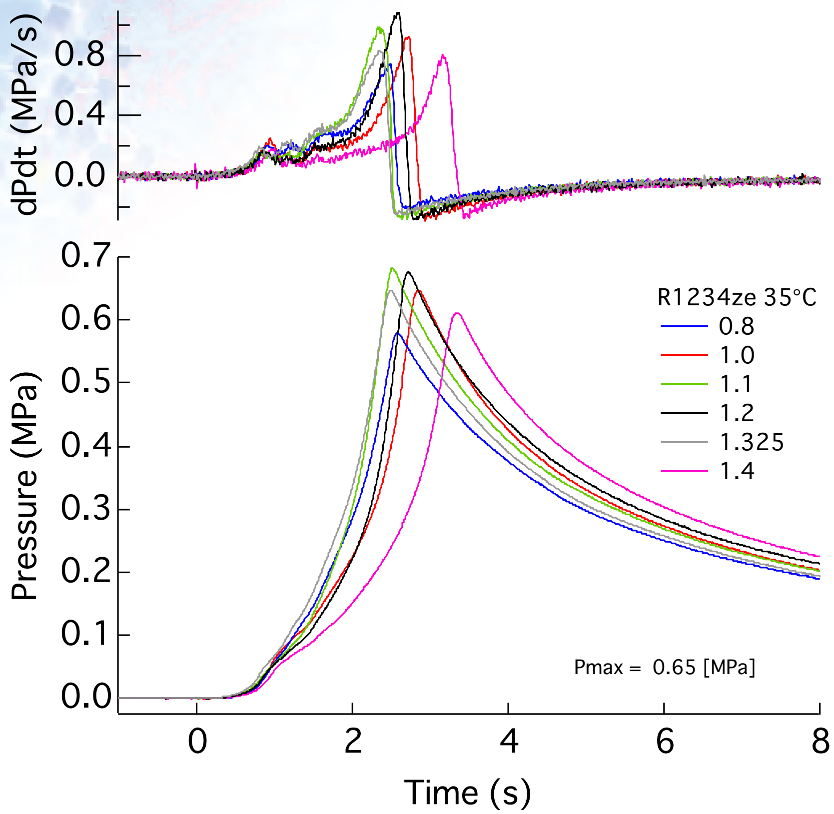
Pressure profile for R32



Pressure profile for R1234yf

- R32 is not so sensitive to temperature and moisture.
- R1234yf is obviously sensitive to temperature and moisture on temporal change of pressure (d*P*/d*t*).

Pressure profile and burning velocity for ze



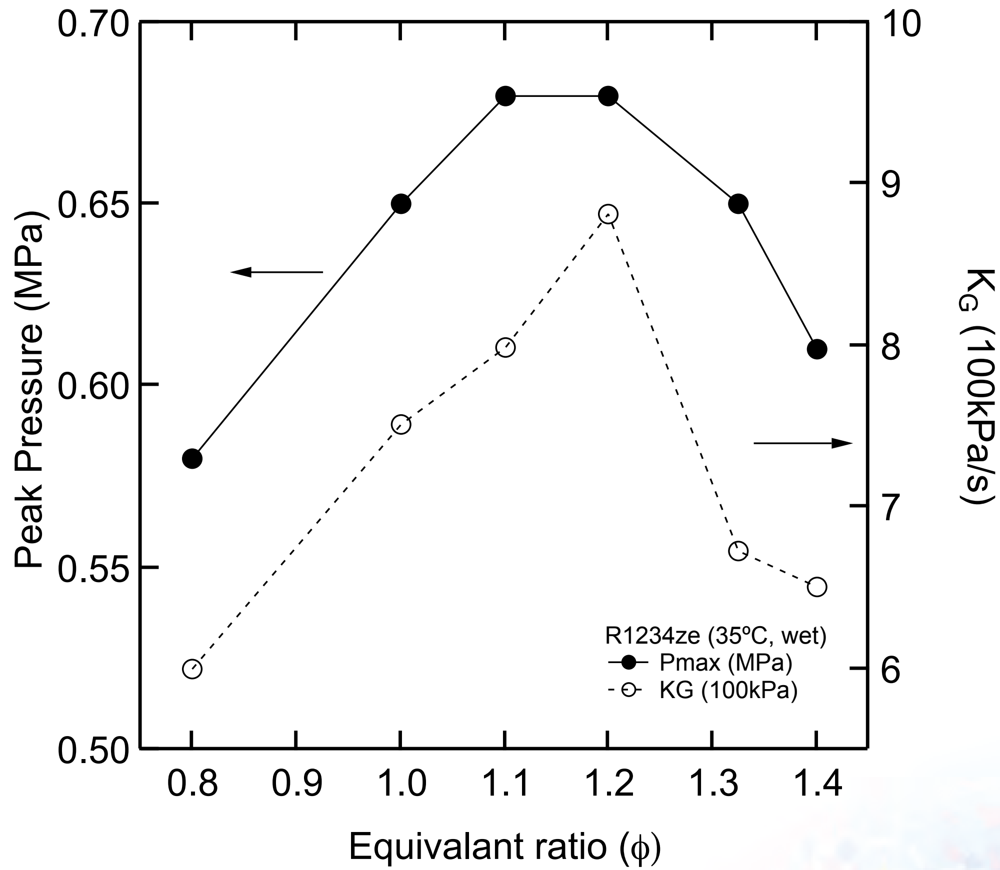


Fig. Example profiles of R1234ze at 35°C and wet condition (left: effect of equivalence ratio on pressure profile, right: effect of equivalence ratio on P_{max} and K_G).

Comparison between other gases

Table Comparison of P_{max}, K_G and other parameters with other typical gases.

Flammable Material	P_{max} (100 kPa)	K_G (100 kPa·m·s^{-1})	Burning velocity (cm·s^{-1})	Flammability limits(%)
Acetylene	10.6 *1	1415 *1	166 *2	2.5 – 80.0 *3
Hydrogen	6.8 *1	550 *1	312 *2	4.2 – 75.0 *3
Propane	7.9 *1	100 *1	46 *2	2.1 – 9.5 *3
Methane	7.1 *1	55 *1	40 *2	
Ammonia	5.4 *1	10 *1	7.2 *4	15 – 28 *5
R32 †	7.6 †	11 †	9 †	13.3 – 29.3 *6
R1234ze †	6.8 †	9 †	5 †	7.0 – 9.5 *6
R1234yf †	6.6 †	8 †	3 †	6.2 – 12.3 *6

*1 Ref. (NFPA68, 2007[5]), Table E.1 (0.005 ft^3 sphere; E = 10 J, norm. condition). *2 Ref. (NFPA68, 2007[5]), Table D.1.
*3 Ref. (Mannan, 2005[12]), Detonation limits obtained for confined tube. *4 Ref. (ISO/DIS 817, 2010[13])
*5 Ref. (NFPA325, 1994[14]) *6 Ref. (JFMA, 2013[15])
*7 Ref. (Mannan, 2005[12]), Table 16.4 † This work (at 35°C and wet condition)

- Flammable parameters were listed in order of K_G value.
- Judging from K_G value, R32, R1234yf and R1234ze remain nearly same risk as or less than Ammonia.
- It should be noted that we should directly compare Ammonia with A2L refrigerants under the same experimental setup conditions. => currently underway

Contents list

Explosion severity evaluation

- To apply refrigerants safely to air-conditioning equipment, the potential risk of combustion and explosion in actual situations should be evaluated by using the results of the laboratory-level fundamental evaluation.
  - Scale up from laboratory scale to actual scale.
  - Development of space from spherical closed vessel to rectangular unclosed room.
  - Development of the condition from premixed concentration and vertical concentration gradation in leakage.
- The relationship between the deflagration index and the influence on human and structures was considered with the help of the concept of vent design using K_G values.

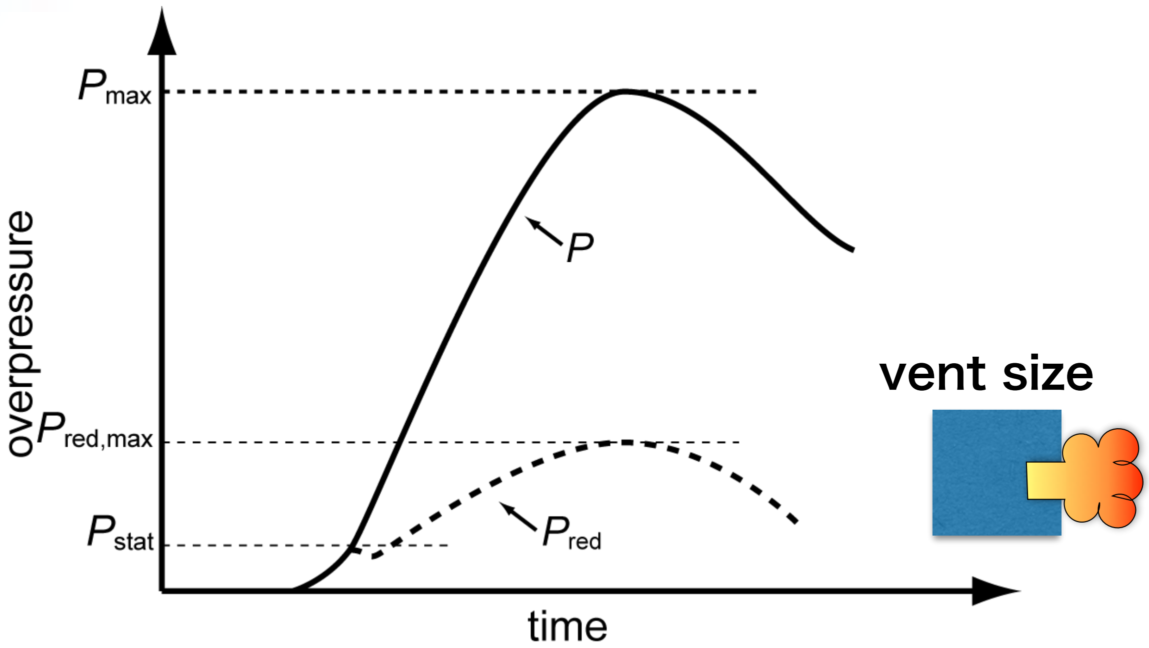
closed vessel — Rectangular and slit — Actual room

Venting effect on reduced pressure

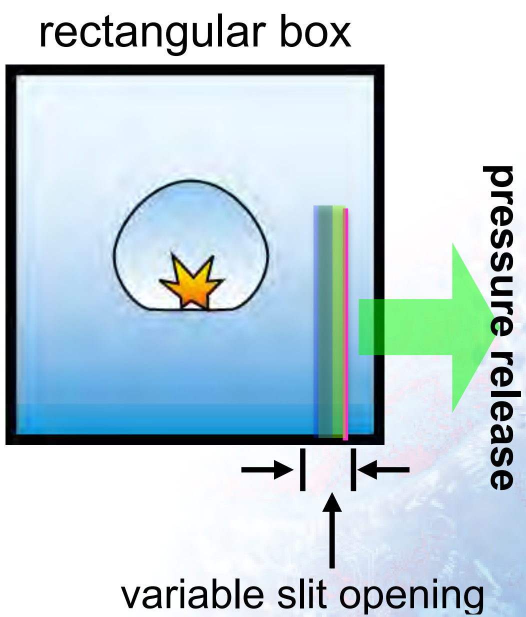
According to the venting design for explosion protection, the reduced pressure effect due to the presence of opening in the room was studied and effective area of venting was experimentally evaluated.

Parameters for Venting effects

P_{max}	Maximum Pressure
P_{red}	Reduced Pressure
$P_{red,max}$	Max Reduced Pressure
V	Volume
L/D	Length/Depth ratio
K_G	Deflagration index



Reduced pressure behavior for venting.



Explosion severity in room

Hazards due to internal explosion

- There are few quantitatively-established informations for internal explosion in a room.
- It is also difficult to find an internal blast-resistance standard for houseroom.

Typical Values of Failure Pressures in Building Structures
Lunn, G.A., 1984. Venting Gas and Dust.

	Failure Pressure (Pa)
Windows(normal)	3 – 4.6
Windows(strained)	1, or even 0.2
Chipboard(19mm)	7
Brick wall (114mm)	Survived at 23, destroyed at 35
Brick wall (228mm)	Survived at 70, destroyed at 105

Resistance design for wind pressure

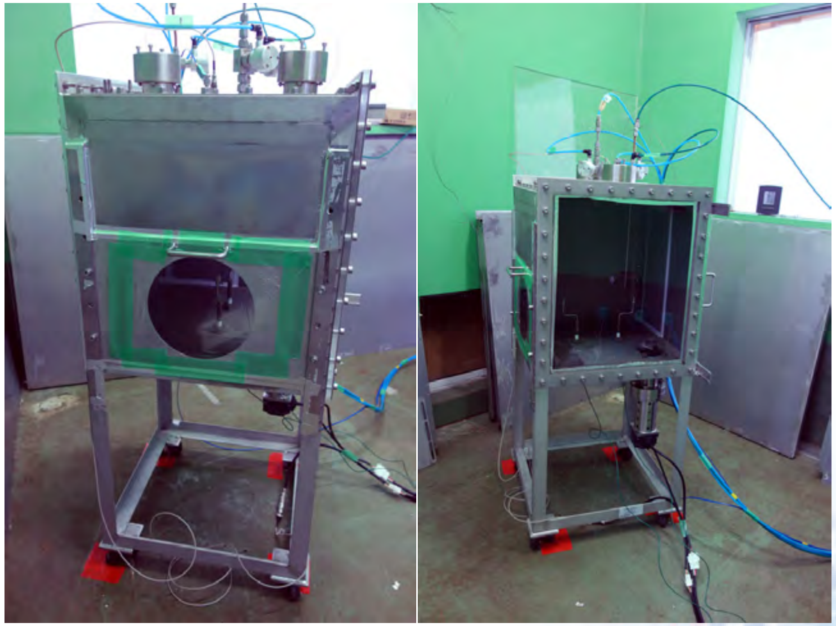
- There are standards for wind loads on buildings (Building Standards Act, AIJ). That is mainly concerning to external wall and roof.
- There is no standard for some kind of internal explosion load for internal wall and ceilings.
- There is a classification and standard for sash and door in JIS 4702/4706
- We set reduced overpressure P_{red} as 1.6k.
- If P_{red} exceeds the withstand pressure of the sash or door, the blast wind leads up to a breakup of open sash or door.

JIS classification for sash and door

Class	Over Pressure (Pa)	indication
S-1	0.8k	for 1st floor window (36m/s)
S-2	1.2k	for 2nd floor window (44m/s)
S-3	**1.6k**	for 3rd floor window (50m/s)
S-4	2.0k	
S-5	2.4k	
S-6	2.8k	
S-7	3.6k	

Venting effect on reduced pressure

A rectangular vessel 50cm on a side was prepared for the test.
A refrigerant was leaked into the vessel at the rate of 10g/min and was premixed to stoichiometric air-fuel ratio.
The flammable behavior and reduced pressure were observed under the presence of various vent shapes: circle, square, and rectangles with different ratio of long side and short side.
Reduced pressure effect was summarized according to vent area and aspect ratio of rectangles.



Experimental setup

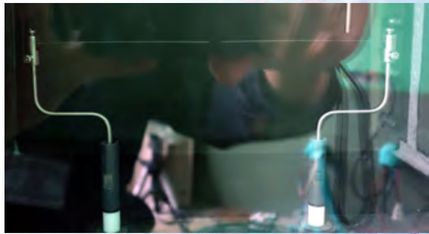
- Rectangular model space
- variable leaking area of slit aperture(width/height)
- Electric discharge

Conditions

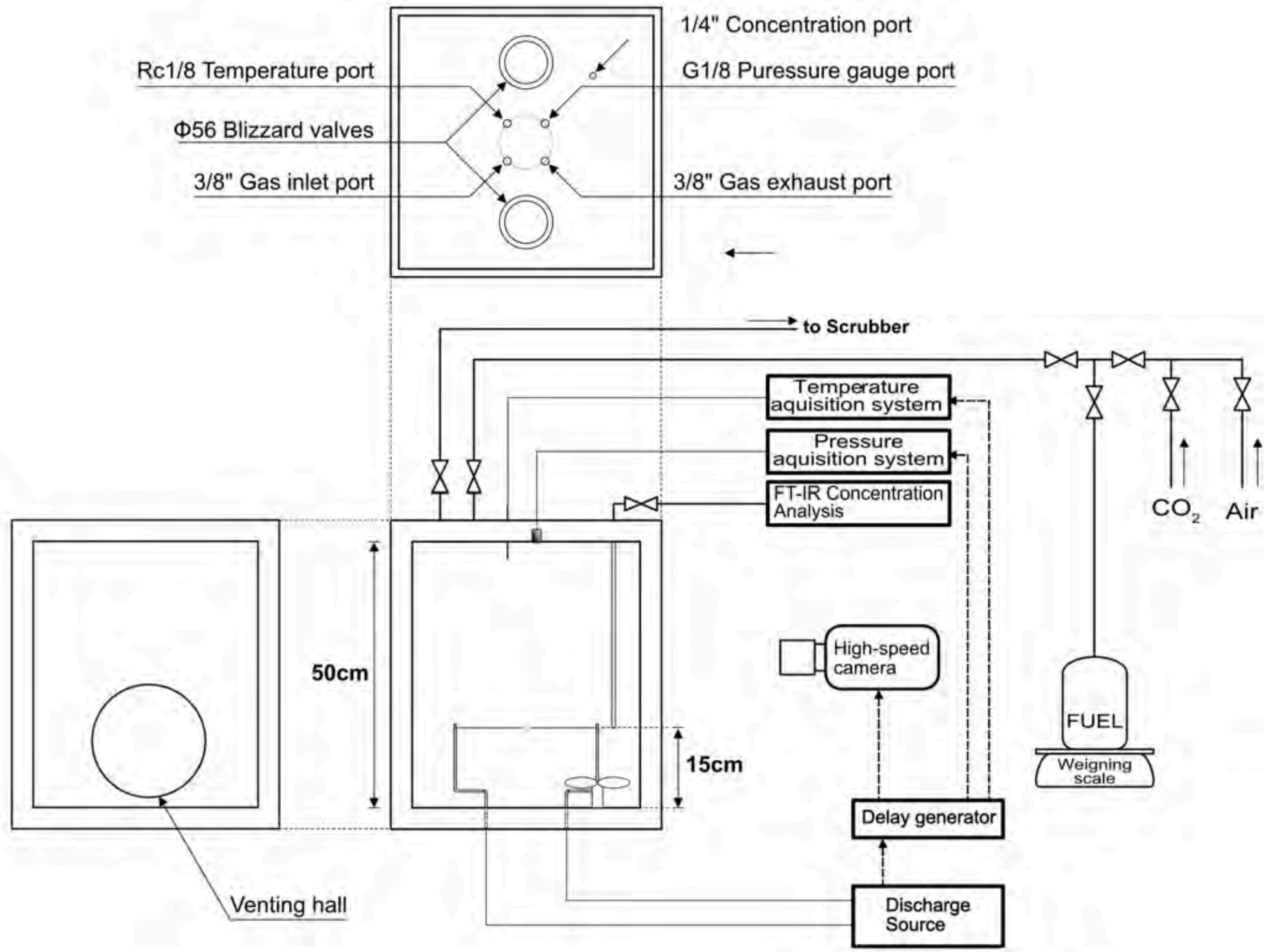
- Mixing condition of A2L gases
  - **1st: premixed**
  - 2nd: concentration gradient

Measurements

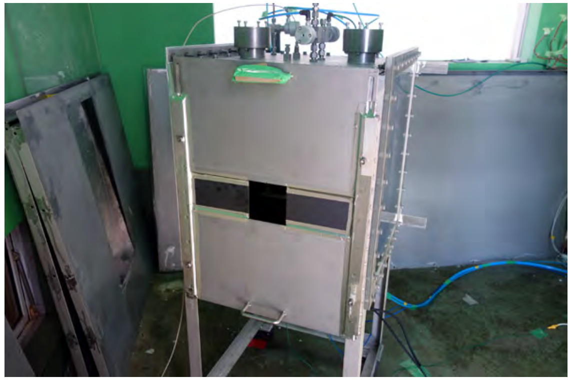
- pressure measurement ：reduce effect of pressure by venting through slit
- high-speed video observation: flammable behavior
- temperature measurement ：achieving temperature evaluation



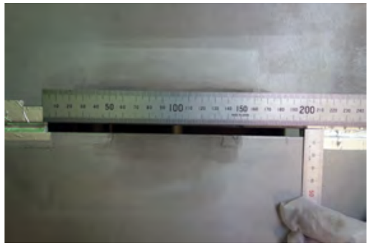
Experimental setup



Schematic illustrate of experimental apparatus

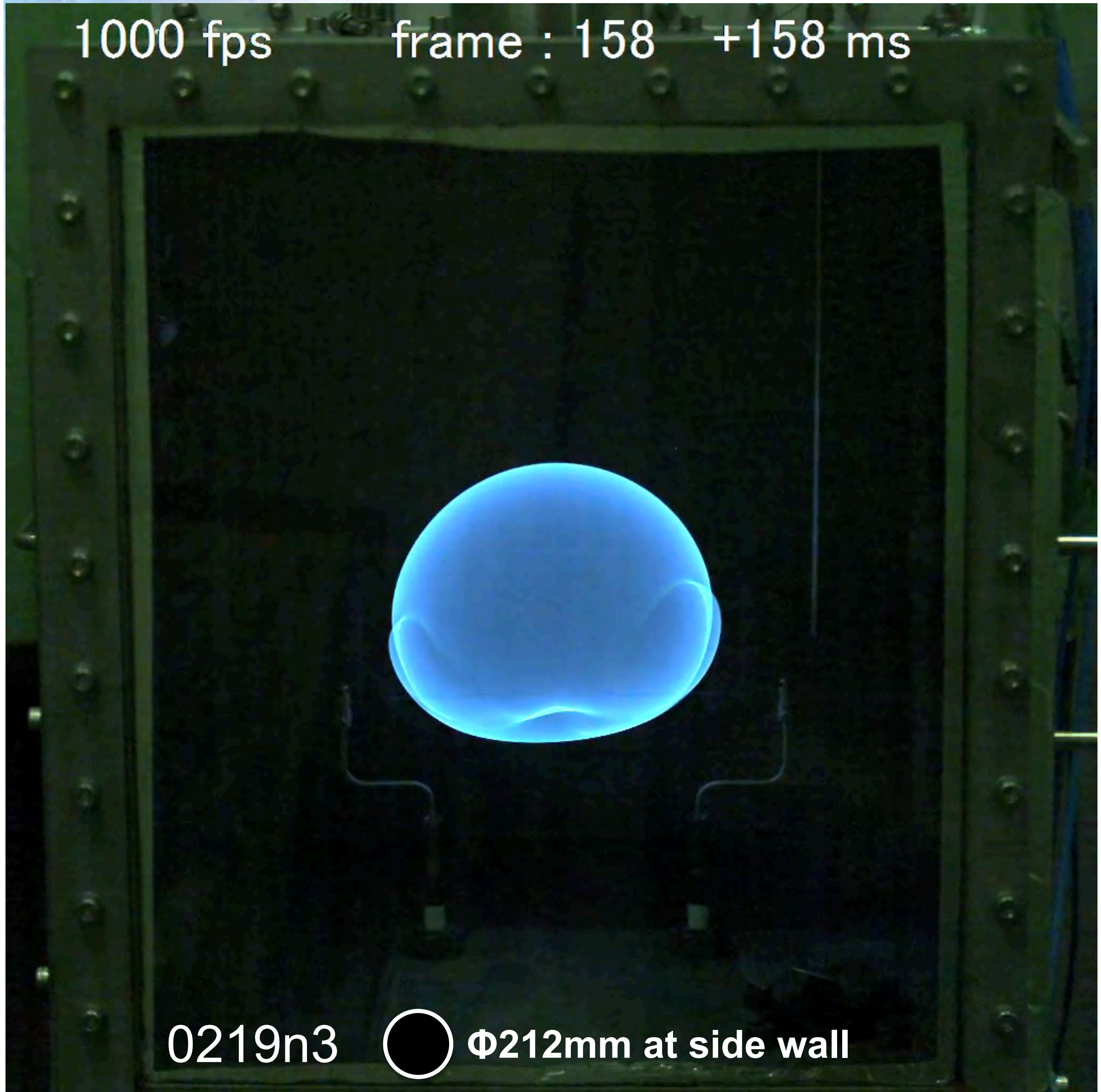


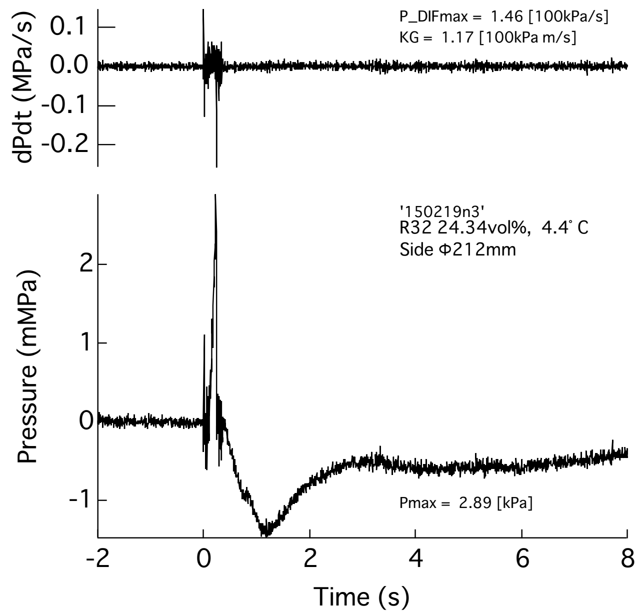
a rectangular vessel



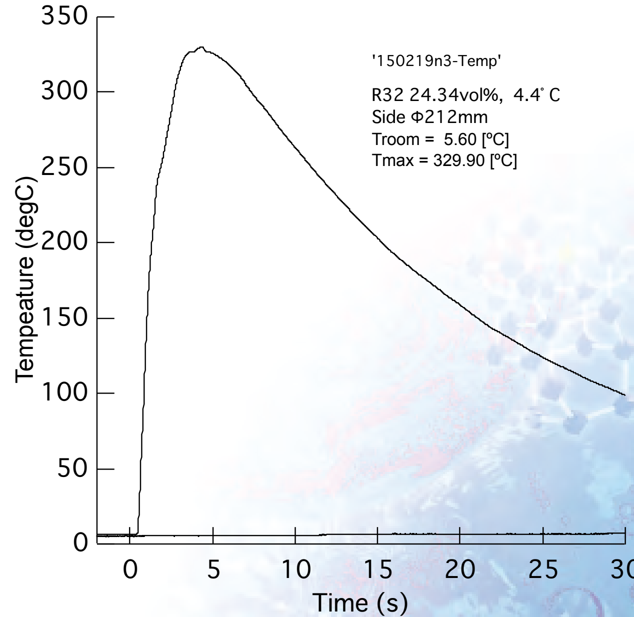
an example of opening

risk assessment experimental facility in Tokyo University of Science at Suwa





Pressure profile



Temperature profile

Contents list

Summary

To promote A2L refrigerants effectively and safely, the flammable behaviour of A2L refrigerants in the presence of moisture and elevated temperatures was experimentally investigated using a large volume combustion vessel to see the scale and buoyancy effects.

Frame fronts of A2L refrigerants were smooth and wrinkled front was not seen in large volume vessel even under moisture and elevated temperature conditions.

Deflagration index K_G is used for estimating effect of deflagration in closed space.

There is no significant potential of increase in K_G value at present.

Judging from K_G value, R32, R1234yf and R1234ze remain nearly same risk as or less than Ammonia even under moisture and elevated temperature conditions.
It should be noted that we should directly compare Ammonia with A2L refrigerants under the same experimental setup conditions.

To address the potential risk of combustion and explosion in actual situations, the reduced pressure effect by an existence of opening was examined according to the explosion venting technology based on deflagration index K_G.

Thank you

The result of this work contributes to publish the Progress report 2014 of 「the Risk Assessment of Mildly Flammable Refrigerants」

http://www.jsrae.or.jp/jsrae/committee/binensei/risk_e.html