Experimental Study of Explosion Limits of Refrigerants and Lubricants' Mixture

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ABSTRACT

The explosion limits of refrigerants and lubricants' mixture were studied. The refrigerants like R161, R1234yf and R152a are combustible. Lubricants, to a certain extent, are combustion-supporting. In many actual conditions, lubricants and refrigerants are mixed together. In this paper, a test device which can be run automatically was established according to ASTM E681-09, and the explosive experimental of refrigerants and lubricants' mixture in some ratio was studied. By altering the proportions of refrigerants and lubricants, we got curve and scope of explosions. In some certain ratio, refrigerants and lubricants' mixture has different explosion limits compared to refrigerants with no lubricants in it.

1. INTRODUCTION

CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, Halon-1211, Halon-1301 and Halon-2402 are being completely phased out according to "Montreal Protocol on Substances that Deplete the Ozone Layer". Expect that, global warming potential gases should be used carefully. GWP is also taken into consideration. The global environmental problem makes it urgent to search for new environmentally friendly refrigerant alternatives in the field of refrigeration and air-conditioning industry. Mixed-refrigerants are widely applied; however, many mixed-refrigerants have one or more component that is combustible. Such as HFC-410A and HFC-407C respectively contains 50 percent and 25 percent HFC-32 in mass fraction. Some mixed refrigerant like HFC-134a/HFC-290/HFC-600a is used to take a major share in the automobile air-conditioning sector. Synthetic PAG oil is usually used along with HFC-134a. As lubricant oil with a flash point above 200℃，its combustible character should be taken into consideration. The flammability limit is one of the most important indices to access the fire and explosion hazards of flammable gases.

$$\frac{1}{L} = \frac{c_1}{L_1} + \frac{c_2}{L_2} + \frac{c_3}{L_3} \dots \dots \qquad (1)$$

In the formula, $c_1, c_2, c_3 \dots$ are moles fractions of component gases whose lower flammability limits are $L_1,\ L_2,$ $L_3 \dots$

The upper flammability limit of blended gases U can also be estimated:

$$\frac{1}{U} = \frac{c_1}{U_1} + \frac{c_2}{U_2} + \frac{c_3}{U_3} \dots \dots \qquad (2)$$

$$c_1 + c_2 + c_3 \dots \dots = 1 \qquad (3)$$

It is found that as to the lower flammability limit of blended gases or vapors, the Le Chatelier's rule works quite well, though the upper flammability limit does not fit accurately.
Experimental study on flammability limit of refrigerant mixture has been studied. Measurements were made in an ASHRAE style apparatus, as set forth in Appendix A of ASTM E681-09. (See figure 1)

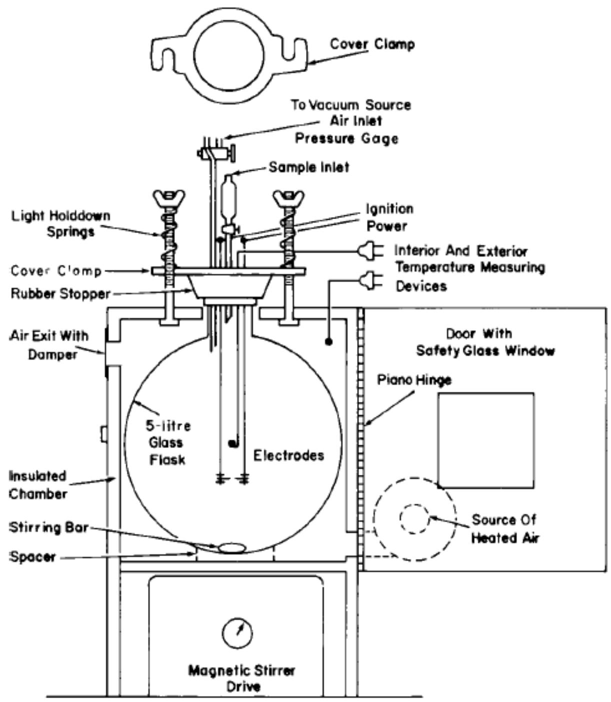

Fig 1: Apparatus for testing combustive gases or vapors

By remaking the ASTM 681-09 apparatus, we eject lubricant in the flask. After mixed together, blends are ignited, to determine the limits of refrigerants and lubricants' mixture. In an actual catastrophe situation, ignition sources energy are often not much larger than 20mJ, which means surface temperature is 460℃. Thus, the lubricants often exist as phase of liquid.

2. Experimental Apparatus

Standard GB/T 12474-90 provides a method which is applied in testing various kinds of combustive gases under pressure of atmosphere. However, this kind of method doesn't fit for halo hydrocarbons, for its long quenching distance. For this reason, we applied the ASHRAE style apparatus. According to ASTM E681-09, we manufacture a vessel. The explosion proceeds in a twelve liter spherical glass flask with 5~6 millimeter thickness, 300 millimeter inner diameter, bottleneck inner diameter 57 millimeter, and 400 millimeter height. A rubber plug jams at the bottleneck. A pair of tungsten electrodes impales the rubber plug, placed at upper 1/3 position of the vessel. High voltage potential transformer is connected to the pair of tungsten electrodes, which provides 15 kilovolt alternating current. After the circuit is closed, sparks generates. In less than half a second, the electricity should be cut off. By observing the angle of flame, judge whether the mixture is ignited or not.

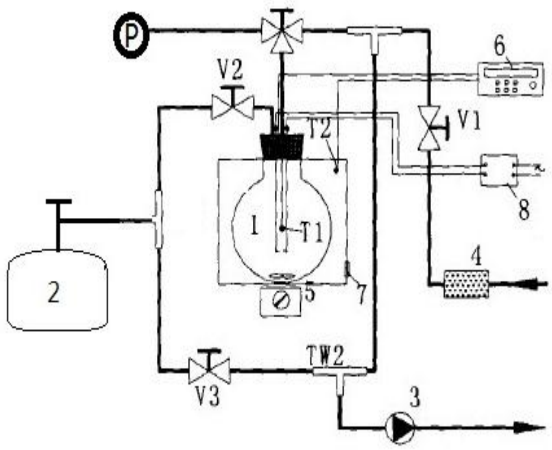

Fig 2: Experimental apparatus system

As is known that the ratio of each gas is determined by Dalton partial pressure law, in order to get more accurate ratio relations, we develop a LabVIEW program to control the electronic valve. Through general-purpose interface bus, personal computer is connected to the Keithley2002, who has eight and a half precision. By means of pressure's accurately measuring and controlling, we can get accurate data for each component. Before introduce any gases in to the flask, vessel must be evacuated. The electrical valve responds to the pressure of gas in the vessel. After the vessel evacuated, valve to vacuum pump is cut off, and gas valve is open. Pressure arriving at setting value, valve switches to another channel, and let another gas to enter the vessel. Air must be dewatered before entering the vessel. And finally inject some synthetic PAG oil, before mixing with the refrigerants the lubricant should be fully atomized. By atomization, the PAG oil can be blended as uniformly as possible. Ignite the blends, and observe flame's transmission angle. At the point of flame achieving rectangular, we judge that the blends' flammability is coming. To get atomizing lubricant, disintegrating nozzle is fixed in the bottom of the flask.

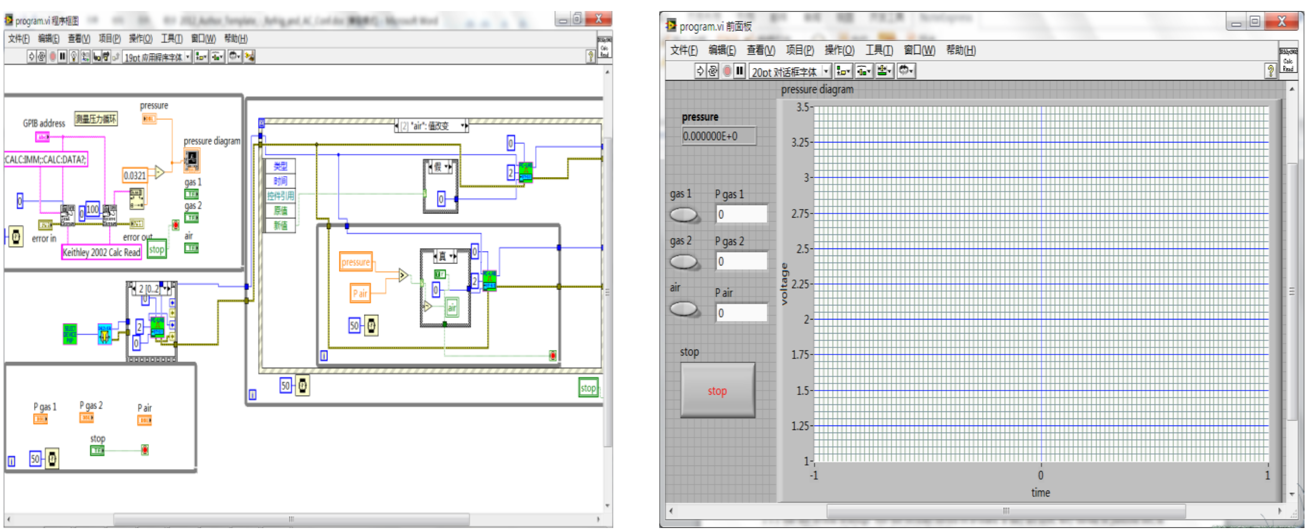

Fig 3: LabVIEW program for controlling valve through the pressure

3. Theoretical analysis of flammability limits

3.1 Estimate of flammability limit of two mixed refrigerants

Assume the combustive component in the whole blends occupies φ, and the flame retardant component does β, thus, $\beta + \varphi = 1$. In the process of ignition, if the two components do not produce chemical reaction with each other, one of the incombustible gas or vapor is considered to be inert gas. After the refrigeration's complete combustion, according to combustion theory, we have the following equation equilibrium of chemical reaction:

$$\varphi C_n H_m Cl_a F_b + \varphi\left(\mathrm{n} + \frac{m-a-b}{4}\right) O_2 + \mathrm{c} N_2 + \gamma \mathrm{RX} \rightarrow \mathrm{n}\varphi \mathrm{CO}_2 + \varphi \frac{m-a-b}{2} H_2 O + a\varphi \mathrm{HCl} + \mathrm{b}\varphi \mathrm{HF} + \gamma \mathrm{RX} \quad (4)$$

In this chemical equilibrium, RX is the incombustible component, and γ is its volume ratio in the blends. So the blends' stoichiometric concentration in volume C_s:

$$C_s = \frac{100}{1+4.773\left(1+a(n-1)+\frac{m-\beta a-\gamma b}{4}\right)+\frac{\gamma}{\varphi}} \quad (5)$$

When the blends reach up to the lower flammability limit, the percentage of the flammable component in the blends is φ_L=0.7C_s. For the reason that the ratio of flammable component in blends is φ, the lower flammability limit of blends LFL:

$$LFL_m = \frac{\varphi_L}{\varphi} = \frac{0.7C_s}{\varphi} \quad (6)$$

So, the lower flammable limit of blends is:

$$LFL_m = \frac{70\mathrm{LFL}}{70\varphi + \mathrm{LFL}(1-\varphi)} \quad (7)$$

As for the upper flammability limit, the accurate estimate has not been generally accepted. We can calculate it to be the weighted average as the upper flammability of the blends. Weight of each component is its volume fraction.

$$UFL_m = \sum (x_i UFL_i) \quad (8)$$

UFL_i and x_i represent the component i's upper flammability limit and fraction in blends respectively. If one of the component in blends is combustive, this product of this term equal to zero.
This estimate leaves a huge margin for error. But for this method, experiments have to be done more times.

4. Results and discussion

Experiment on flammability limit of mixed refirgerants were done. The critical supperession ratio can be easily drawn from Fig 4. The figure show that HFC-134a's critical supperession ratio to HFC-32 is about 0.55, which means if the volume ratio of HFC-134a and HFC-32 is more than that point, the combusion is not able to occure. When the lubricant is added in, the curve is not what it looks like without PAG. If the PAG oil's amount is larger than the blends, it is hard to ignite the mixure. In consideration of the synthetic PAG oil's combustibility, it is hard to study quantitatively. Through many times to try, combustion restores stability, so that make it possible to observe. As is show in the Fig 5, at lower ratio of HFC-134a in blends, the addition of lubricatant makes it hard to ignite, but as the critical supperession ratio is bigger than that without lubricant, which means that addition of oil play a combustion-supporting role.

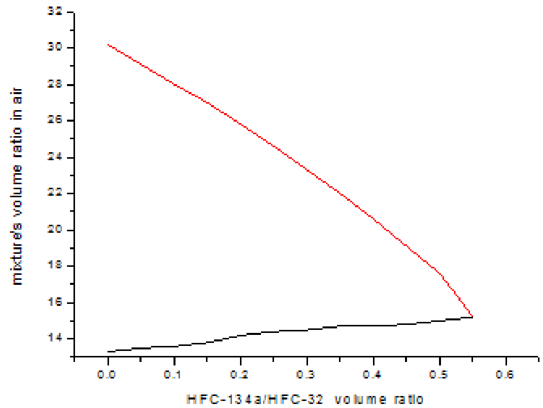

Fig 4: Flammability limit of HFC-134a/HFC-32

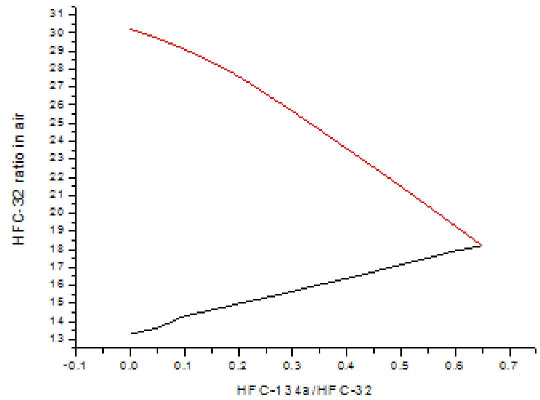

Fig 5: Flammability limit of HFC-134a/HFC-32 with PAG

5. Assessment of risk

The refrigerant's charge has the major impact on the performance of refrigeration and heat pump system. For each flammable refrigerant, there exists a maximum charge of flammable refrigerants for safety, which are showed in the EN 378-1:2008 standard. The maximum charge in a room shall be in accordance with the following rules:
If the charge size is larger than $4m^3 \times LFL$, the maximum charge is

$$m_{max} = 2.5 \times LFL^{5/4} \times h_0 \times A^{1/2} \tag{9}$$

h_0 is the height of installation, 0.6 m for floor location, 1.8 m for wall mounted, 1.0 m for window mounted, 2.2 m for ceiling mounted. LFL is in kg/m^3 and molecular mass of refrigerant is greater than 42. Take a room with 25 m^2, floor installation as an example, the maximum charge for a HFC-32 refrigerant is 2.09 kg, which means cooling capacity is only about 1kW. Blends of HFC-32 mixed and HFC-134a, with the same cooling capacity, only have less than half of the pure HFC-32, which means in the safety charge amount, cooling capacity is much larger. However, after lubricants mixed together, the risk of flammability increases.

6. CONCLUSIONS

The experiment of HFC-32 and other flammable refrigerants' flammability limit were studied. Just like Fig 4 and Fig 5 showed, refrigerants mixed with lubricants no longer have the same combustive character as the lubricants' combustive property.

- Blends of refrigerants were mixed and ignited automatically; achieving the goal that gases and vapor are precisely measured. To guarantee the datas' accuracy, the method of chromatography has been used of.
- The experiments were done at standard method accordance with ASTM standard, so results showed that the method is simple and rapid with good precision and reproducibility.
- Results showed that lubricants increased combustion to a certain extent. After chain reaction of combustive refrigerants, the lubricants were heated and ignited. Thus, if a leak of refrigerants happens, the vapor of lubricants can be a danger to increase the combustion.
- Various kinds of mixture were studied, and HFC-32 has the most safe appliance range, however, the lubricants give another aspect risk.

NOMENCLATURE

L/LFL	lower flammability limit
UFL	upper flammability limit
c	mole fraction of gases or vapor
C	concentration
m	mass
h	installation height
A	area
φ	ratio of flammable component
β	ratio of flame retardant component

Subscripts

i	participants
s	stoichiometric
max	maximum

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