Research on Leakage and Fire Accidents of the Heating and Refrigerating Systems Charging with the Flammable Working Fluids

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Abstract: Working fluids have been considered as the vital factor in the aspects of environmental protection and energy conservation for all the heating and refrigerating systems. The mainly on using hydrochlorofluorocarbons and hydrofluorocarbon working fluids as well as their substitutes in the transitional period are not environmentally friendly, which possess the ozone depletion potential and larger global warming potential. Mounting evidences have been indicated that most of the considerable candidates of the next generation working fluids have the disadvantage of flammability. It is increasingly important to research the combustion and leakage characteristics of the flammable working fluids. This paper contributes to analyze their flammable properties and typical leakage and fire accidents concerning the heating and refrigerating systems world widely. Some technical reasons have been concluded and available strategies have been proposed. And also it focuses the leakage characteristics of the equipment from the view of their whole life periods, beginning manufactured then transported, stored, used, repaired and scrapped. The possibilities of ignition sources for different segments have also been discussed. In addition, the prevention measures have been suggested on the associated consideration of both the hominine and technological factors.

Keywords: flammability, refrigerant, heat pump, leakage, ignition sources

1. INTRODUCTION

Currently, the mainly on using working fluids (WFs) for refrigerating and heating systems are the HCFCs, which make negative influences to the climate change. It is becoming urgent and vital to search new sustainable WFs which possess the characteristics of environmentally friendly, non-hypertoxic, acceptable system energy efficiency, chemical stability, suitable operating pressures, and lower cost. However there is “no fluid is ideal in all regards” [1]. Presently, HFC-32, HFC-152a, HFC-161, HFO-1234ze (E), HFO-1234yf, HC-290, HC-600a, HC-1150, HC-1270, ammonia and their blends have been attracting plenty of attention, and considered as the candidates of the next generation WFs. While it is a pity that most of them are flammable. Therefore, it is necessary to research the leakage and combustion characteristics of the WFs to ensure the safety and optimal operation. There are six typical combustion characteristics, which are lower flammable limit (LFL), upper flammable limit (UFL), minimum ignition energy (MIE), flame propagation velocity, heat of combustion and the production of combustion. Among them, LFL and UFL are mentioned frequently, concerning the dangerous concentrations range of gaseous WFs in air [3-4] and the WFs charge limitation in each system. Scholars have made plenty of contributions in the aspects of the combustible characteristics as well as relevant systems.

McLinden et al [1] explored the possibilities of 1,200 candidate fluids from more than 56,000 small molecules for refrigerants by applying screening criteria of estimating GWP, flammability, stability, toxicity, and critical temperature. Kondo, Takizawa and partners researched the effects of temperature and humidity on the flammable limits of 2L refrigerants NH_3, R32, R143a, R1234yf and R1234ze with the ASHRAE 34 method [5], and they also tested the burning velocity of fluorinated compounds (HFC-32, HFC-143, HFC-152a) by spherical-vessel method [6]. Gharagheizi [7] estimated the LFLs of pure compounds based on a combination of the group contribution method and neural networks. Eckhoff and Olsen [8] considered that the ASTM E 582 method for determination of MIEs of gases provided little guidance as to the exact way in which ignition tests should be performed, and no guidance at all as to the statistical procedure that should be applied for deriving MIE from the raw data, after determining MIE of propane/air. Colbourne et al. [9] researched the variation of gas concentrations at floor level when release 400 g propane in a 20 m^2 room over 3 min. Sequentially they made the quantitative risk assessment for propane in ice cream cabinets, resulting that the ignition frequency was less than one ignition event in a per 10 million[10]. The author and her partners have been researched the leakage and flammability characteristics of refrigerants since 1990s, and the flame suppression efficiencies of inhibitors R13I1, R227ea, R125, R134a, R245fa on the fuels R290, R600a, RE170, R32, R600, R152a, R1150, R142b etc. have already been tested, and some available evaluation theories (the new flame-retarding coefficient index, new LFL estimation method, district of initial charge for inflammable concentration etc.) have been proposed one after another [2, 11-14].

Although several distinguished publications in the field could be found in the open literature, in fact, few of them contributed to the leakage and fire accidents concerning the working fluids and the related heating and refrigerating systems from the view of their whole life periods. In addition the prevention measures on the associated consideration of both the hominine and technological factors are needed.

2. ACCIDENT INVESTIGATION CONCERNING WFs

2.1. Ammonia

Ammonia (R717) has been widely used in refrigerating systems of fruits, vegetables, sea-food, daily-food, wine, ice-cream storage and manufacture for more than 100 years, covering vapor compression refrigeration cycle, absorption and adsorption refrigeration cycles. R717 is considered as an attractive refrigerant from many technical perspectives, illustrated in Fig.1, and Table 1 summarized the flammable characteristic parameters of R717.

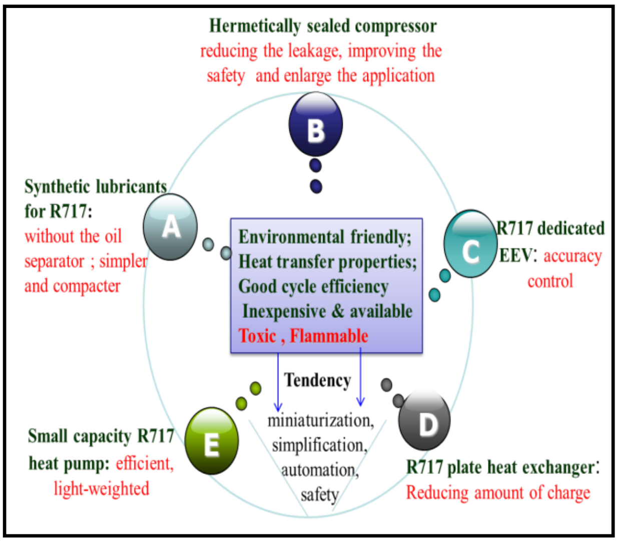

Fig.1 R717 characteristics and technology developing directions

Table 1 the flammable characteristic parameters and concentration limitation of R717

Items	Value	Unit
Lower flammable limits	16.7	%
Upper flammable limits	28	%
Minimum ignition energy	100-300	mJ
Heat of combustion	22.5	MJ/kg
Burning velocity	7.2	cm/s
Immediately Dangerous To Life And Health	320	ppm
Permissible Exposure Limit	50	ppm
Occupational Exposure Limit	25	ppm

However two successive R717 accidents occurred last year in China aroused demotic panics. On June 4, 2013, a poultry processing plant using R171 refrigeration system in Jilin province was burnt, leading to about one hundred workers injured or killed, which may result from the short circuit of electric wires and then fire the nearby combustible materials, and the heated air with high temperature caused the physical explosion of tubes with R717 inside. Two months later August 31, another calamity happened in an aquatic products processing company of Shanghai city. Fifteen people were dead and 30 others injured on account of a cap on pipe carrying liquid ammonia fell off and then the liquid ammonia leaked. Statistical data on the thirty-six hazardous substances from ex-Ministry of Chemical Industry of China indicated that there are sixty-ninth accidents concerning R171 among the total two hundred and forty-three [15]. R717 accidents occurs world widely. French Ministry of Environment [16] analyzed more than 400 accidents (109 involving ammonia) between 1992 and 2001, and concluded that most (but not all) of the accidents involving “other refrigerants” actually were the consequence of a fire, rather than a leakage. Fig.2-3 summarized the ammonia accidents in U.S. and Japan. It can be seen the number of ammonia accidents in U.S. tends to drop off and the number of workers who injured in R717 accidents in Japan is not exceed 4 from beginning to end. Table 2 reviewed some other recent R717 accidents as well as the reason analysis. It can be seen that many accidents are due to equipment failure, poor maintenance or human misoperation.

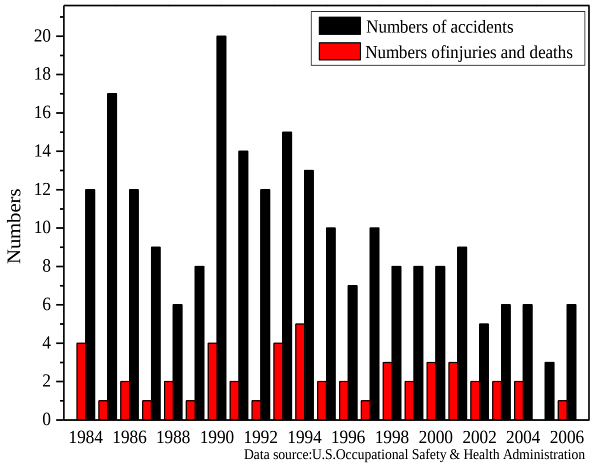

Fig.2 R717 accidents in U.S.

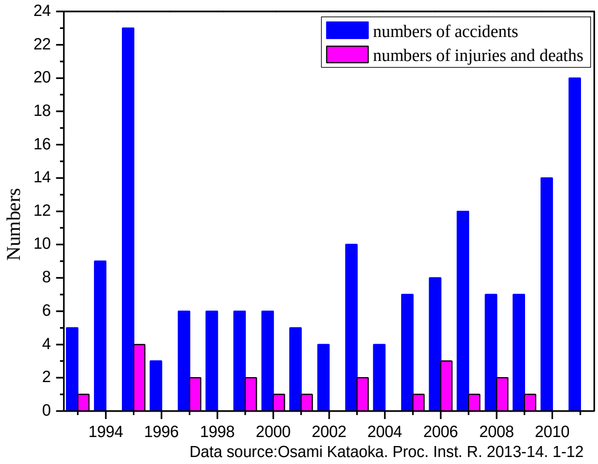

Fig.3 R717 accidents in Japan

Table 2: Some recent R717 accidents

Time	**incident description**	**NO. of injury**	**reason analysis**
2011 -3-16	Ammonia leaked from the workshop of a wholesale vegetable market , leading to wide influence by the white fog.	None	The tube has not been welded tightly, leading to fracture suddenly.
2011 -7-3	A R717 leakage accident occurred in a county-level fisheries frozen company at nightfall.	24 Injured	A boost valve was broken when conveying gaseous ammonia
2012 -3-28	A R717 leakage accident occurred in a dumped refrigeration house that belonged to a textile mill, which reported by the people who smelled the pungent odour	None	It is long neglected and in disrepair
2012 -1-19	Workers were wept by the leaked ammonia from the workshop of a frozen foodstuffs factory. Even ice layer can be seen on the protective cloth surface of the firefighters.	unknown	The R717 refrigerating equipment is too old, and it engenders crack in the welding point of valve.
2013 -6-9	R717 leaked from a refrigeration storage in the process of maintenance	None	The valve, used for a long time, was not been shut down perfectly
2013 -7-16	A machine room of a suburban factory got fired, and both the flame and the odour of ammonia can be detected around the plant.	None	A sudden fire occurred in the machine room, and then it burnt the seal ring of the ammonia pipeline, leading to R717 leakage.
2013 -9-16	A R717 leakage accident occurred in an ice-making factory	4 Injured	the tube was burst by the high pressure of ammonia when the worker charging it into the refrigeration system
2013 -10-1	Ammonia leaked from a tube of auxiliary unit in a water treatment plant	1 Injured	The worker was operating a controlling valve, and suddenly the tube was broken.
2013 -10-9	A dry red pepper storage using R717 refrigeration system was burnt	None	When wedding, the generated spark fired the foaming heat insulation board
2013 -11-15	A mass of ammonia ejected from the hole of tube of a cold storage, causing injury accident.	3 Injured	When the workers were loading productions, the forklift suddenly broke the calandria that was filled with ammonia.

2.2 hydrocarbons (HCs)

Many HCs have been researched to replace the halogen refrigerants, such as R600a (Isobutane), R290 (Propane), R170(ethane), R1270 (Propylene) and R1150 (Ethylene) [1-2,12], which are miscible with both the mineral oils and synthetic lubricants in compressors, holding the advantage on without changing the lubricants in the existing systems using HCFC and HFC refrigerants. HCs are fairly low in cost and possess considered properties, which can used in the equipment of air conditioning, heat pumps, chillers, industrial refrigeration. But the disadvantage of high flammability raises the significant safety concerns. Table 3 summarizes some typical HC refrigerants accidents. It can be seen that the hydrocarbon WFs are more dangerous than the ammonia in the aspect of flammability, not only which are easier to be burnt, but also the accident effects are more severe. The accidents of hydrocarbon WFs covered the process of production, storage, using, and transportation, even for the factories which got in touch with them for many years.

Table 3: Some typical hydrocarbon WFs as refrigerants accidents

Time	incident description	NO. of injury	reason analysis
Jar.1997	R600a leaked from the tank of vehicle, then it was burnt by the driver when he lighted up a cigarette.	Death 1	Incidental leakage of chemicals, came across the man-made ignition source.
Jar-2001	An explosion accident occurred in a refrigerator producing factory	Injury 11	The leaked R600a got together in the low-lying area, then burnt.
Jul.-2001	A fire accident happened, when sellers were disseminating that the flammable refrigerants can be used in automotive air conditioning	Injury 2	Maybe, it due to the inappropriate handing for some emergency accidents
Jun.-2003	A truck that carried 140 refrigerators fell into the reservoir, leading to the drinking water pollution.	Death 1 Injury 2	Traffic accident
Apr.-2008	An explosion accident occurred in a refrigeration storage which using R290 and R170 blends as the refrigerant.	Death 1 Injury 6	Incidental leakage of R290 and R170 were burnt by the unknown ignition source.
Mar.-2013	An big explosion tore the wall and roof of a hydrocarbon working fluids bottling plant that operating for 16 years	Injury 4	The production line of gaseous production got breakdown, then came across the fire.

2.3 Fluoride WFs (Freon)

Freon refrigerants have been used in the heating and refrigerating systems since 1960s, including CFCs (chlorofluorocarbons), HCFCs (hydrochlorofluorocarbons), HFCs (hydrofluorocarbons), HFEs (Hydrofluoroethers), and hydrofluoro-olefins (HFOs). Table 4 summarized some accidents concerning Freon, it covered the WFs production plant, automobile/submarine transportation, industrial refrigerating factory, and maintenance process etc. Many accidents were not caused by the working fluids directly but the sudden failure of other factors. The number of accidents concerning fluoride chemical leakage was larger than that of combustion in this statistics, because that the previous Freon WFs widely used were uninflammable, such as HCFC-22 and HFC-134a. However under the compulsive requirement world-widely of the environmental friendly characteristics for new generation WFs, scientists and engineers have no choose but to accept some flammable Freon and their blends, such as HFC-32, HFC-161, HFC-152a, HFO-1234yf etc., which would motivate the research on the leakage characteristic and fire accidents of the WFs and the related heating and refrigerating systems.

Table 4: Some typical hydrocarbon WFs as refrigerants accidents

Time	incident description	NO. of injury	reason analysis
2001-11-8	A nuclear-powered submarine was out of order on its trial trip. The fire extinguishing system launched suddenly.	Injury 22 Death 20	Maybe, the Freon WFs leaked after violation operation
2004-1-29	A hydrofluoric acid leakage accident happened in a chemical plant. A mass of fluoride smoke ejected from the plastic tank, and the near road was painted to purple.	Injury 1	The valve was failure, then the plastic buffer tank was blocked, broke the related pipes.
2005-8-27	The chlorine-fluoride chemical leakage accident occurred in a chemical plant, causing the rice field withered and yellow.	Injury 30	The sight glass located in the rectification column of No.2 workshop suddenly burst, then leakage occurred
2007-5-16	Freon oozed out of the refrigerating systems that running in a casting factory, leading to the workers coma.	Injury 9 Death 2	unknown
2009-6-20	A city bus was seen the Freon escaping with white fog, when it was passing the intersection.	None	The pipeline of vehicle air conditioner was broken within 10 min after turned on.
2009-8-11	Blend of 133A, HF, trichloroethylene, and impurities uncorked from a chemical factory	Injury 3	A bucket of reaction vessel was broken, then hundreds kilogram intermediate product poured out.
2009-8-25	A dangerous cargo transport semi-trailer rolled over at 4:33 A.M., two bottle of dichloromethane leaked.	None	It is the fatigue driving that result in traffic accident.
2011-8-28	A tank truck that carrying $34m^3$ Freon rolled over when taking a sudden turn, then leakage happened.	Injury 1 Death 1	A gap was detected out near the flange of tank, resulting from the traffic accident
2011-9-22	The antimony pentachloride (a raw material of producing $CHClF_2$) escaped out.	None	The valve of a section of pipeline malfunctioned, during the period of maintenance
2011-12-27	A semi-trailer delivering 10 tons Freon cargo overturned at midnight, one of the bottles came out small hole.	None	The semi-trailer hit the highway guardrail since the fatigue driving, result in traffic accident.
2013-1-28	A semiconductor production factory suffered hydrofluoric acid leakage. The affected tube was fused firstly, then a mass of hazarding gas uncorked out.	Injury 4 Death 1	The diluted gaseous hydrofluoric acid leaked out during the period of supply system maintenance.
2013-7-31	A minibus was exploded suddenly from the inside, and the window glass was shattered	Unknown	Untrained worker covered the steel bottles of Freon in the minibus, then which were super-heated, and exploded.
2013-7-18	A warehouse of a consulate was burnt since the combustion accident of the air conditioning	Injury 5 Death 1	The servicemen broke the air conditioning system and leading to the Freon leakage when maintaining

2.4 Security strategies

From the above presented investigation results on the leakage and fire accidents on the working fluids and the relevant heating and refrigerating systems, some security strategies and suggestions have been proposed and already illustrated in Fig.4, covering the processes of production, operation, transport and maintenance. The maintenance process must be attached great cares. For governments, policies about the standardization management of the customer service center and the maintenance company

Should be promulgated. And grading system for the mechanic should be established, and only the qualified worker is allowed to maintain the devices charged with the flammable WFs. For companies, on one hand, the training course on the special requirements of the equipment is indispensable; on the other hand it is forbidden for approving or compelling the maintenance worker to operate at tired status.

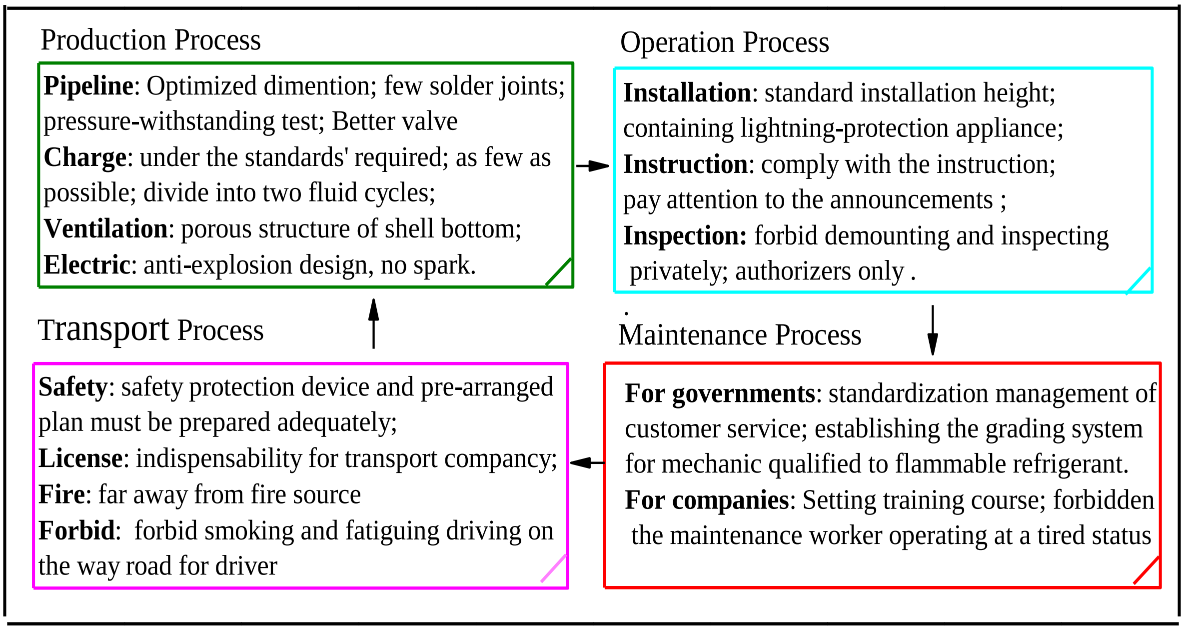

Fig.4 Security strategy and suggestion for ACs and HPs charged with hazardous WFs

3. LEAKAGE AND FLAMMABLE CHARACTERISTICS OF WFs

There are three necessary factors for the combustion accidents of WFs occurring: (1) WFs leaks out of the vessel; (2) The concentrations of escaped WFs in air are larger than LFLs but smaller than UFLs; (3) Getting in touch with the available ignition sources. Therefore, the following section will discuss the possibility of preventing fire accidents from these three factors.

3.1 Leakage assessment

Leakage may occur in the whole life periods of WFs (Fig.5) due to the following reasons:

[1] In factory: ① the rack of fusion can lead to gas, slag inclusion, pore, undercut, overlap, burn-through, segregation, unfilled etc.② material quality of tubes and vessel; ③ tightness of connections; ④ the extremely mini hole that cannot be detected out by the common instrumentation. All of them may bury the hidden troubles.

[2] In storage and carriage: ① Big hole may be generated when the container hit others or fell down. ②Traffic accident ; ③ surface corrosion of the bottle; ④ the warehouse get fired by other factors

[3] Operating and running: ① The unit is installed unqualifiedly ; ② “Buckets effect”, local damage; ③ The valve failure; ④ Too old; ⑤ misoperation by works ⑥Strange reason, e.g. thunderstruck.

[4] Maintenance and abandonment: ① low recyclability rate of direct emission; ② the un-tight resealing after maintenance; ③ some other WFs with higher vapor pressure were charged into the primary system; ④ The tube line was broken incautiously by workers.

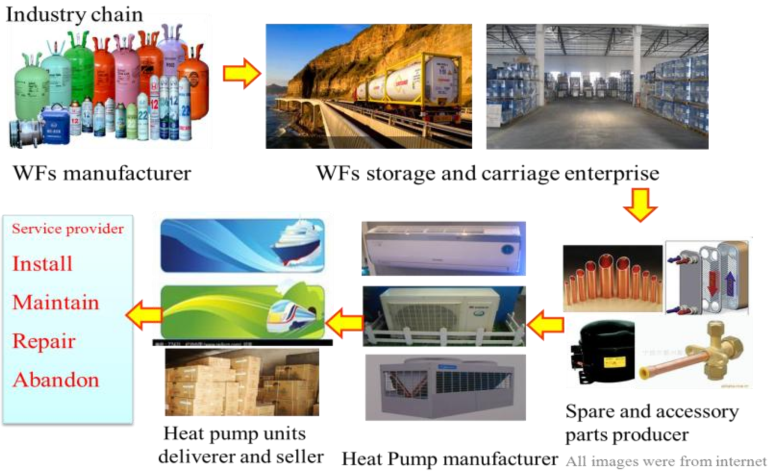

Fig.5 The whole life periods of WFs

3.2. Ignition sources

The following section may get in touch the ignition sources:

[1] In Compressor: ① The short circuit of electrical motor may generate spark; ② When start or stop the compressor, it momentary high current may make the electric line overloaded; ③ Electric arc may generated in socket. ④ Blockages to the outlet can cause overheating or explosion.

[2] In storage and carriage: ① The lighter, match, furnace of the driver or administrator ; ②vehicle-mounted electric equipment malfunction; ③ the warehouse get fired by other ignition sources

[3] Domestic ignition source when using: ① In kitchen, stove, oven, electric kettle, water heater, ② In office, lighter, match, cigarette, launcher, socket, computer switch; ③ Living room, TV, AC, High-power electrical appliances and all kinds of electrical switch;

[4] Maintenance and recovery: ① The lighter, match, cigarette of the serviceman; ② Welding, incision; ③ metal crash spark

3.3 WFs concentration in air

As mentioned in the first section, LFLs and UFLs concern the dangerous concentrations range of gaseous WFs in air. Fig.6 summarizes the LFLs and UFLs of some typical flammable refrigerants. The flammability can be suppressed by R13I1, R227ea, R125, R134a and R245fa. Fig.6 shows the flames of R245fa/R142b of the test carrying on a self-built test rig according to Standard GB/T 12474-2008. The critical concentration ratio of flammability suppression completely for R245fa to R142b is 0.24:1.

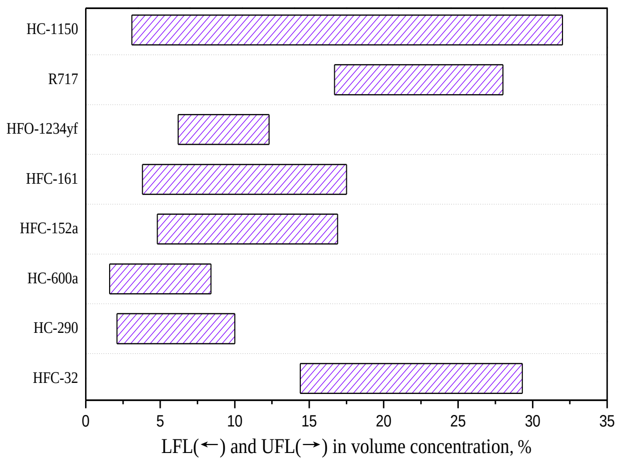

Fig.5 LFLs and UFLs of some typical WFs

Fig.6 Flame of R245fa/R142b for LFL and UFL(0.1:1)

There are some other measures to reduce the WFs concentration in air, such as ① optimizing the whole system to decrease the amount of required WFs; ② using the secondary fluid that are incombustible, such as CO2; ③ the WFs charge should be restrained by EN 378 or ISO 5149.

5. CONCLUSION

[1] The possibilities of leakage and fire accidents concerning the working fluids and the related heating and refrigerating systems exist in their whole life periods.

[2] Many accidents are due to equipment failure, poor maintenance or human misoperation. The faults on manage and operation are more severe than technical failure.

[3] It is possible to reducing the leakage and combustion accidents by analyzing the risks and enhance the precautionary measures in each process.

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