Properties and Characteristics of C6F12O

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In order to cope with the problem that no gas fire suppressant can be used in the future, perfluoro-2-methyl-3-pentanone (C6F12O), also known as FK-5112, Novec 1230 or Novec 649, with its environmentally friendly performance, zero ODP, GWP of approximately one and atmospheric lifetime of up to two weeks (as shown in Table 1), has been considered as the next generation of halon alternatives. C6F12O belongs to fluorinated ketones which is different to HFCs. Its nontoxicity, noncombustibility, excellent insulation properties and fire suppression efficiency have attracted worldwide attention. The thermophysical parameters, safety and environmental issues and other properties such as the dispersion characteristics of C6F12O are important indexes to evaluate whether it is appropriate to replace the halon. Meanwhile, these properties and parameters are critical to determine the application scenes of fire suppressant, the selection of fire extinguishment facilities and the engineering calculation of the fire extinguishment system.

C6F12O Novec 1230 Thermophysical Parameters Toxicity Corrosion Environment diffusion Dispersion Performance

1. Thermophysical Parameters

The storage, transportation and application of fire suppressants involve heat transfer and flow processes. Accurate measurement and calculation of thermal physical parameters of $C_6F_{12}O$ are the basis for the design of a fire extinguishment system.

Some basic thermophysical parameters measured at 25 °C can be found in the technical data of $C_6F_{12}O$ presented by 3M Company, as shown in **Table 1**. McLinden et al. [1] measured the parameters of vapor pressure and ***ppT*** properties of $C_6F_{12}O$ (almost in liquid phase) and obtained more accurate calculation equations according to the experimental results. Then, Tanaka [2] measured the ***ppT*** parameters in the near critical and supercritical range. Wen et al. [3] used vibrating string viscometer to measure the viscosity of $C_6F_{12}O$ in 243–373 K range and established the viscosity relation which can be used in a wide range of temperatures and pressures. Cui et al. [4] measured the dynamic viscosity and surface tension of $C_6F_{12}O$ in the range of 303–433 K by surface light scattering (SLS). Furthermore, thermal conductivity was obtained by Perkins et al. [5] through the transient hot wire device under the temperature range of 183–501 K and pressure range of 0.02–69 MPa, and the corresponding equations were also proposed. The measurement of these thermal physical parameters and the establishment of accurate calculated equations provide useful references for the engineering application.

Table 1. Thermophysical parameters of $C_6F_{12}O$ at 25 °C originated from technical data of 3M company [6].

Properties	Data
Boiling point (1 atm)	49.2 °C
Freezing point	−108.0 °C
Critical temperature	168.7 °C
Critical pressure	18.65 bar
Critical density	639.1 kg/m^3
Density, sat. Liquid	1.6 g/ml
Density, gas (1 atm)	0.0136 g/mL
Specific volume, gas (1 atm)	0.0733 m^3/kg
Specific heat, liquid	1.103 kJ/(kg °C)
Specific heat, vapor (1atm)	0.891 kJ/(kg °C)
Heat of vaporization (boiling point)	88 kJ/kg
Liquid viscosity (0 °C/25 °C)	0.56/0.39 centistokes
Relative dielectric strength, (1atm, n_2 = 1.0)	2.3

2. Safety

The safety of fire suppressants can be divided into the toxicity and corrosiveness of the agent itself, and the toxicity and corrosiveness of the thermal breakdown products of the agent exposed to fire.

2.1. Toxicity

The effect of fire suppressants on human health is the key index to determine whether it can be applied in manned places. The harm of gas fire suppressants to human health includes its own toxicity, cardiac sensitization effect, oxygen consumption and the toxicity of fire extinguishing products [7]. The toxicity of the agent refers to the concentration of substances that can cause casualties, which is mainly measured by the half lethal concentration (LC_{50}) or approximate lethal concentration (ALC). Chemical gas fire suppressants belong to volatile halogen-containing substances, which can cause a cardiac sensitization effect which determines the level of no-obvious-adverse-effect-level (NOAEL) and lowest-observed-adverse-effect-level (LOAEL). It is worth noting that the so-called non-toxic and low toxic effects of fire extinguishing agent on human health are relative to the residence time of people in the agent application space and the release amount of the agent in the space. That is, the NOAEL value is higher than the designed concentration value of the fire extinguishing agent, which can be considered as safe. At the same time, the cardiac sensitization effect can also obtain the limited use conditions of the fire extinguishing agent under a different evacuation time. **Table 2** shows the toxicity index values of $C_6F_{12}O$ and other typical gas fire extinguishing agents to the human body compared with the minimum fire extinguishing concentrations (MEC) tested by cup burners [8][9]. The designed fire extinguishing concentration of $C_6F_{12}O$ is generally 4–6% [6], less than 10% and higher than NOAEL, which indicates that $C_6F_{12}O$ has a high safety margin and can be used in manned places. However, the designed fire extinguishing concentration for HFC 227ea and Halon 1301 is same as the values of NOAEL, which means the safety margin is low. Additionally, the value of NOAEL of HFC 125 is even lower than fire extinguishing concentration, hence the use of these substances is forbidden in manned places. Xu et al. [10] studied the acute inhalation toxicity of $C_6F_{12}O$ and obtained the volume fraction of LC_{50} is 28.2% (acute inhalation in mice). When exposed to 5%, 10% and 15% concentration of fire suppressant gas for 2 h, the activity of serum alkaline phosphatase in mice decreased, and the activities of alanine aminotransferase, aspartate aminotransferase and creatine kinase increased, which indicated that inhaling a high concentration of $C_6F_{12}O$ for a long time may damage the function of myocardium and liver.

Table 2. Toxic data and minimum extinguishing concentration of typical gas fire suppressants [8][9].

Fire Suppressant	LC_{50}/ALC (%)	NOAEL (%)	LOAEL (%)	MEC (%)
$C_6F_{12}O$	>10	10	>10	3.5–6.4
HFC 227ea	>80	9	10.5	5.8–6.6
HFC 125	>70	7.5	10	8.1–9.4
Halon1301	>80	5	7.5	2.9–4.0

The toxicity of fire suppressants is also reflected in the toxicity of thermal breakdown products during fire extinguishment. $C_6F_{12}O$ would decompose swiftly due to the high temperature of the flame as soon as it releases into the fire, and the main toxic gases are HF, COF_2, C_4F_8, CO, C_3F_6, etc. [11][12][13]. **Table 3** summarizes the toxicity data of the main thermal decomposition products detected in the experiments [14][15]. It should be noted that toxic decomposition intermediates will also be produced as the suppressant is exposed to the flame. Because these intermediates only exist for a short time, which makes them difficult to capture in the experiment, they are not listed in **Table 3**. Xing et al. [16] further examined the pyrolysis products and mechanism of $C_6F_{12}O$ through the reactive molecular dynamics simulation (ReaxFF MD), as shown in **Figure 1** [16], which identified not only the pyrolysis products including radicals and intermediates, but also the decomposition pathways of $C_6F_{12}O$, showing the promising perspective of the molecular dynamic simulation method. Moreover, the production of toxic substances is also related to the power of the fire source, release time of the agent, fire extinguishing time, temperature of the fire, concentration of the agent and other factors [17]. Since the final fire extinguishing products of fluorine-containing suppressants are mainly HF and COF_2 which are easier to monitor in the experiments, research on the fire extinguishing products of $C_6F_{12}O$ mainly focuses on these two substances. However, COF_2 is unstable and easily reacts with water in the environment to generate HF and CO_2, so the production of HF has attracted much more attention. Ditch [18] measured the products concentration of $C_6F_{12}O$ during fire extinguishment and found that more HF gas would be produced in the extinguishment of class B fire. In a specific n-heptane fire extinguishment experiment, HF concentration reached a maximum of nearly 5000 ppm, while the amount of COF_2 produced was about 1/7 of that of HF. Andersson et al. [19] compared the reaction products of typical fire suppressants including $C_6F_{12}O$, Halon 1301, HFC 227ea and HFC 125 with the diffusion flame of propane. The number of products is related to the amount of fire suppressants discharged. Under low release quantity of fire suppressants, HF (0.3 g/g) generated per unit of $C_6F_{12}O$ is lower than that of HFC 227ea and HFC 125 (0.7 g/g), and halon 1301 (0.4 g/g). Considering that the required mass concentration of $C_6F_{12}O$ is large, the actual production of HF of $C_6F_{12}O$ is similar to HFC 227ea and HFC 125, far higher than Halon 1301. Therefore, as the fire extinguishing products of $C_6F_{12}O$ contain toxic substances that are extremely harmful to humans, it is necessary to design the fire extinguishment system reasonably in order to put out the fire as soon as possible, which could reduce the contact time of fire suppressant with the flame, and thereby decrease the generation of toxic by-products in the fire extinguishment to the greatest extent.

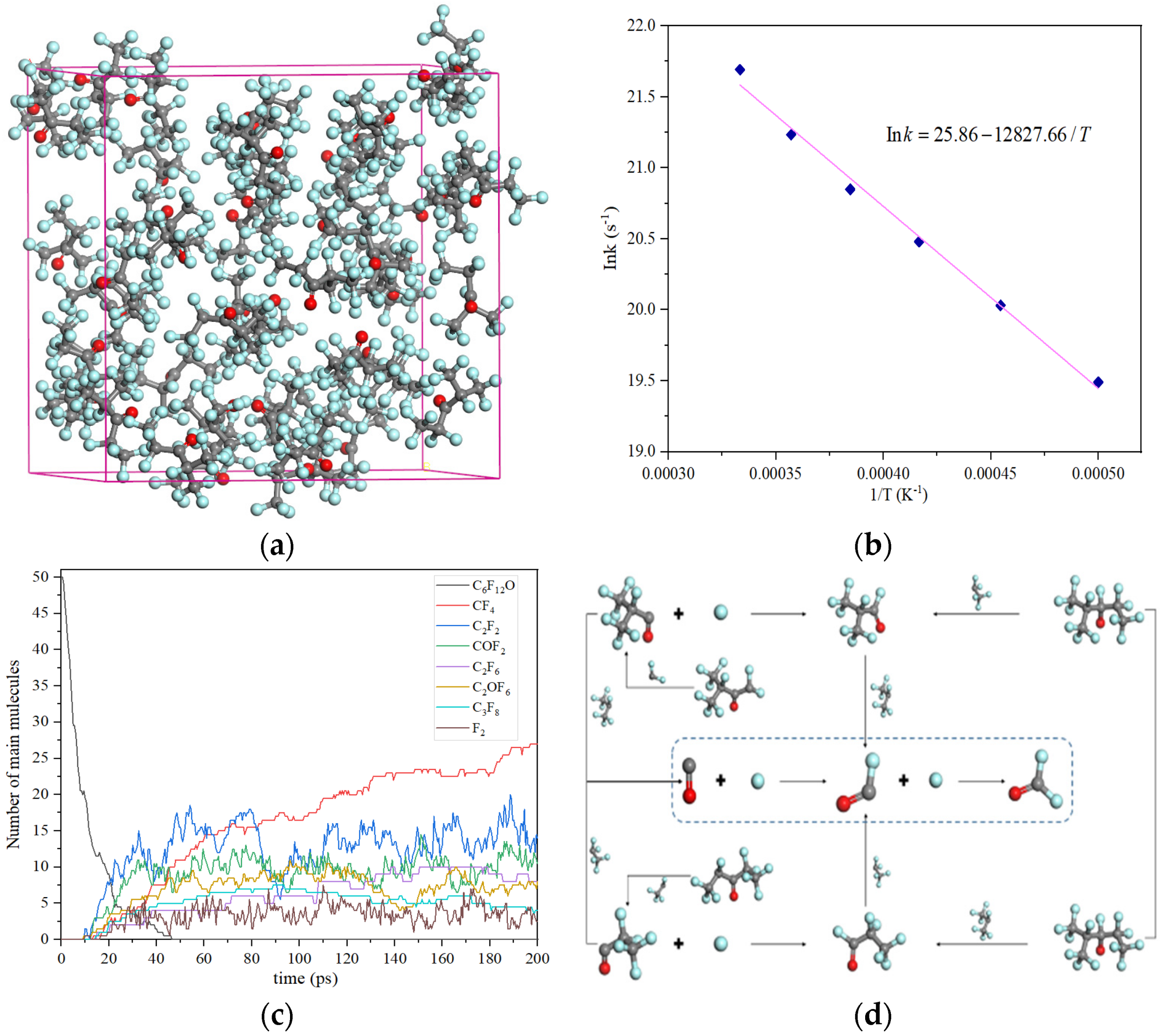

Figure 1. A reactive molecular dynamics study of the pyrolysis mechanism of $C_6F_{12}O$ [16]: (**a**) simulation model, (**b**) Kinetic analysis of $C_6F_{12}O$ pyrolysis, (**c**) evolution of the main pyrolysis products, (**d**) main generation pathway of

COF_2 observed from simulations.

Table 3. LC_{50} and GWP data of main decomposition products of $C_6F_{12}O$ [14][15].

By-Products	LC_{50}	GWP
HF	1276 ppm/1 h	-
CO	1807 ppm/4 h	-
COF_2	360 ppm/1 h	-
CF_4	895,000 ppm/15 min	6630
C_2F_6	20 pph/2 h	11,100
C_3F_6	750 ppm/4 h	9200
C_3F_8	6100 ppm/4 h	8900
C_4F_8	81 ppm/4 h	9540
C_4F_{10}	-	9200
C_5F_{12}	-	8550

2.2. Corrosion

The application scenarios and the design of fire protection systems need to consider the corrosiveness of the fire extinguishing agents. In terms of $C_6F_{12}O$, 3M company [6][20] tested a large number of materials, such as neoprene, butyl rubber, fluororubber, ethylene propylene diene monomer (EPDM), silicone rubber, nitrile, aluminum alloy, brass alloy, 304 and 316 stainless steel, copper, carbon steel, etc., and found that $C_6F_{12}O$ has good compatibility with these materials. No obvious corrosion could be seen, even in the presence of oxygen, except that some elastomers might absorb the agent resulting in weight increasement, especially under high exposure temperature that may have some negative impacts on its physical and mechanical properties. Li et al. [21] carried out the compatibility research of $C_6F_{12}O$ with aluminum, copper and silver. In the 125-day experiment, no obvious corrosion was observed in the scanning electron microscope images. According to the X-ray photoelectron spectroscopy analysis, $C_6F_{12}O$ would introduce fluorine into the surface of aluminum and copper, and form some metal oxides, while the surface of silver had no obvious change, indicating that the compatibility of $C_6F_{12}O$ with silver is better than that of aluminum and copper. Zhang et al. [22] studied the compatibility between $C_6F_{12}O$-air gas mixture with copper and aluminum through experiments and the results showed that $C_6F_{12}O$-air is incompatible with heated copper, which leads to the decomposition reactions of $C_6F_{12}O$ and the corrosion of copper, but the interaction cannot lead to the corrosion of aluminum, a phenomenon that was also shown in a study by Zhuo et al. [23]. Zhang et al. [24] further investigated the compatibility between $C_6F_{12}O$ and sealing rubber materials, EPDM, in a 280-day experiment and molecular dynamic simulations. It was found that the chemical reactions between EPDM and $C_6F_{12}O$ exist and $C_6F_{12}O$ could dissolve EPDM and diffuse around and inside EPDM. Moreover, $C_6F_{12}O$ can be hydrolyzed through a similar Haloform reaction to produce HFC 227ea and corrosive perfluoropropionic acid and the alkaline environment would accelerate this process [25][26] as shown in **Figure 2**.

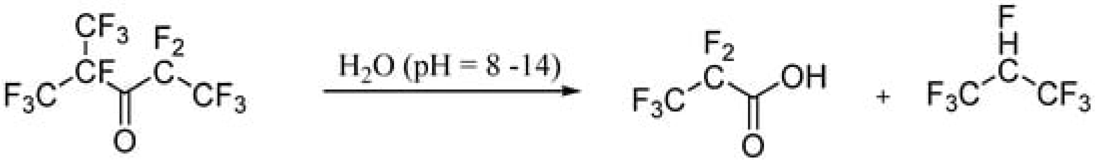

Figure 2. Hydrolysis reaction of $C_6F_{12}O$.

Hence, impurity factors such as water in the fire suppressant or moisture in suppressant usage scenes will affect the actual application of $C_6F_{12}O$, but certain public reports are still lacking.

Meanwhile, corrosion is also related with the thermal decomposition products of $C_6F_{12}O$. The corrosive thermal breakdown products described in the previous section are mainly HF and COF_2, which would be threat to facilities in the fire protection area. Similar to HFCs, the corrosion of $C_6F_{12}O$ in application is related to the number of acidic substances, environmental temperature and humidity, and equipment materials, etc. Ke et al. [27] investigated color change in the historic wooden remains after fire suppression by fluorinated chemical gases including $C_6F_{12}O$, HFC 227ea, Halon 1301, 2402 ($C_2F_4Br_2$) and 1323 ($C_3H_2BrF_3$) and found that that the amount of HF (the main fire extinguishing product) not only affects the F-deposited on the wooden surface, but also the color change mechanism with H_2O, which would highly improve its ability to change color. However, some reports have found that the threat to the facilities in the firefighting place is relatively low under the reasonable design conditions of the fire extinguishing system [28], and the corrosion of the acid gases produced by the fire suppressant is much weaker than the smoke [29].

3. Environment

As mentioned above, the reason behind the search for halon alternatives is the destruction of the ozone layer by bromine and chlorine in halon-type fire suppressants. Although HFCs mostly used as halon substitutes do not contain these two elements, these substances belong to greenhouse gases with a high GWP value. In recent years, a large increase in HFCs has been observed in the atmosphere [30][31], leading to significant negative impacts on the climate.

The level of GWP is related to the absorption spectral capacity and atmospheric residence time of the substances. Generally, substances containing carbon fluorine bonds have a strong spectral absorption capacity, and the level of GWP mainly depends on atmospheric residence time. $C_6F_{12}O$ as an environmentally friendly substitute for halon; its impact on the climate, including its atmospheric lifetime and environmental degradation characteristics, has attracted extensive attention from researchers.

Volatile organic compounds are degraded in the atmosphere, mainly by photolysis and gas phase chemical reactions. As for $C_6F_{12}O$, the C-F bond is more stable than the C-C bond, and the reaction activity with OH radical is weak. Therefore, $C_6F_{12}O$ can hardly react with OH radical and other oxides in the troposphere [32][33]. Taniguchi et al. [34] studied the atmospheric chemical reaction characteristics of $C_6F_{12}O$ for the first time and obtained that it cannot react with OH radical, chlorine and ozone. The shape and size of the ultraviolet absorption spectrum are close to the acetaldehyde molecule. Due to photolysis, the retention time of $C_6F_{12}O$ in the atmosphere is about 1–2 weeks. The degradation products are environmentally friendly, and the influence of greenhouse effect can be ignored in practical application. D'Anna et al. [35] investigated the photolysis of $C_6F_{12}O$ under natural light, which further determined that the atmospheric survival time is about one week. Jackson et al. [26] explored the photolysis, hydrolysis and hydration of $C_6F_{12}O$ to find the source of perfluoropropanoic acid (CF_3CF_2C (O) OH) detected in rainwater. It was found that the photolysis of $C_6F_{12}O$ could produce a small amount of perfluoropropanoic acid. The atmospheric lifetime of $C_6F_{12}O$ is 4–14 days affected by latitude and age, and there is almost no hydrolysis and hydration in the atmosphere. Ren et al. [36] conducted a comparative study on the photolysis of $C_6F_{12}O$, perfluoropentanone and 2-methyl-3-pentanone, and concluded that the atmospheric retention time of $C_6F_{12}O$ is 3–11 days, and the 100-year global warming potential (GWP_{100}) is lower than 0.21, the greenhouse effect of which could be ignored. Therefore, $C_6F_{12}O$ can be considered as an environmentally friendly substitute for halon.

Furthermore, in order to comprehensively evaluate the environmental characteristics of $C_6F_{12}O$ applied as the fire extinguishing agent, it is also necessary to consider whether the thermal breakdown products of $C_6F_{12}O$ are environmentally friendly. In the previous section, the fire extinguishing products of $C_6F_{12}O$ were analyzed, and the GWP of the main thermal breakdown products of $C_6F_{12}O$ was given in **Table 4**. It can be seen that although $C_6F_{12}O$ itself is an environmentally friendly substance, most fire extinguishing products are perfluorocarbons (PFCs) with strong greenhouse effects, similar to HFC 227ea and HFC 125. In practical application, the environmental characteristics of fire extinguishing products and the amount of these substances need to be fully considered to comprehensively evaluate the environmental effects of $C_6F_{12}O$.

4. Dispersion Performance

The dispersion performance is one of the most important factors that affects the extinguishing efficiency and application range of fire suppressants. **Table 5** shows the comparison of dispersion parameters of some typical fire extinguishing agents and the diffusion coefficient of the agents in air is calculated by the commonly used Fuller et al. [37] method. The main difference between $C_6F_{12}O$ and other kinds of suppressants is that $C_6F_{12}O$ has a boiling point of 49.2 °C (1 atm), which is liquid at room temperature (25 °C) and could be considered a high boiling point suppressant. Compared to other gaseous fire extinguishing agents, the vapor pressure of $C_6F_{12}O$ is the lowest and the dispersion performance is relatively poor, which would have a certain impact on the flow and spread of the fire suppressant after discharging, and further influence the fire extinguishing efficiency. There are relatively few studies on the dispersion characteristics of $C_6F_{12}O$. 3M company pointed out in their technical report [6] that the evaporation rate of $C_6F_{12}O$ is nearly 50-times faster than that of water, and it can be gasified and dispersed rapidly after releasing. The concentration of $C_6F_{12}O$ vapor can reach 39% before its saturation, while the typical design concentration of $C_6F_{12}O$ is less than 10%, which can meet the demand of the total flooding system. In addition, the vapor of $C_6F_{12}O$ will not condense during fire extinguishing except pressuring or cooling below its dew point temperature (the vapor pressure of $C_6F_{12}O$ can maintain 5% of the suppressant concentration at −16 °C). It is worth noting that due to its high boiling point, the storage pressure of $C_6F_{12}O$ in a pressurized nitrogen atmosphere will not change largely with the temperature. In the temperature range of −40–80 °C, the maximum filling density of $C_6F_{12}O$ is 1.8-times than that of other fire extinguishing agents with a low boing point (such as HFC 227ea). Hence, it is easy to store and transport, and has important application prospects in the fields of aerospace, oil exploration drilling platform, ocean-going ships and other fields with large working temperature difference ranges. Chen et al. [38] obtained that the storage performance of $C_6F_{12}O$ is better than Halon 1301 and HFC 227ea. Only when the filling density and initial filling pressure of the system are higher does the storage pressure of the system change obviously with the temperature. Meanwhile, the solubility of nitrogen in $C_6F_{12}O$ is very low, which is related to the system temperature and initial filling pressure, indicating that nitrogen is appropriate to use as the driving gas, and the maximum filling density of 2.5 MPa and 4.2 MPa fire extinguishing systems are 1419 kg/m^3 and 1397 kg/m^3, respectively. Furthermore, compared with hexafluoropropane (HFC 236fa), which is gaseous at room temperature, $C_6F_{12}O$ is in a two-phase flow state in the tube, with larger frictional resistance loss and the actual participation amount in cooling the fire after releasing is far less than the filling amount. Under the condition of high pressure, the cooling effect is better than HFC 227ea [39]. Fan et al. [40] investigated the flow characteristics of $C_6F_{12}O$ compared with water and Halon 1301 through hydraulic calculation and experiments, which found that $C_6F_{12}O$ conforms to single-phase flow in the more upstream sections of the pipeline and two-phase flow state in the main pipe, and the density of the mixture is only 1/26 that of liquid $C_6F_{12}O$. However, computational fluid dynamics (CFD) is a powerful method to investigate the flow of the medium, which is still lacking in the study of the flow characteristics of $C_6F_{12}O$. Xing et al. [41] studied the method of improving the dispersibility of $C_6F_{12}O$ by mixing with low boiling point inert gas (as shown in **Figure 3**) and found the droplets diameter, the mixing ratio and the type of mixed inert gases would affect the dispersibility of binary agents. The method develops the binary agents with a lower boiling point and realizes that $C_6F_{12}O$ is stored in liquid and released in gas, which could improve the dispersion performance of the high boiling point fire suppressant in its actual application.

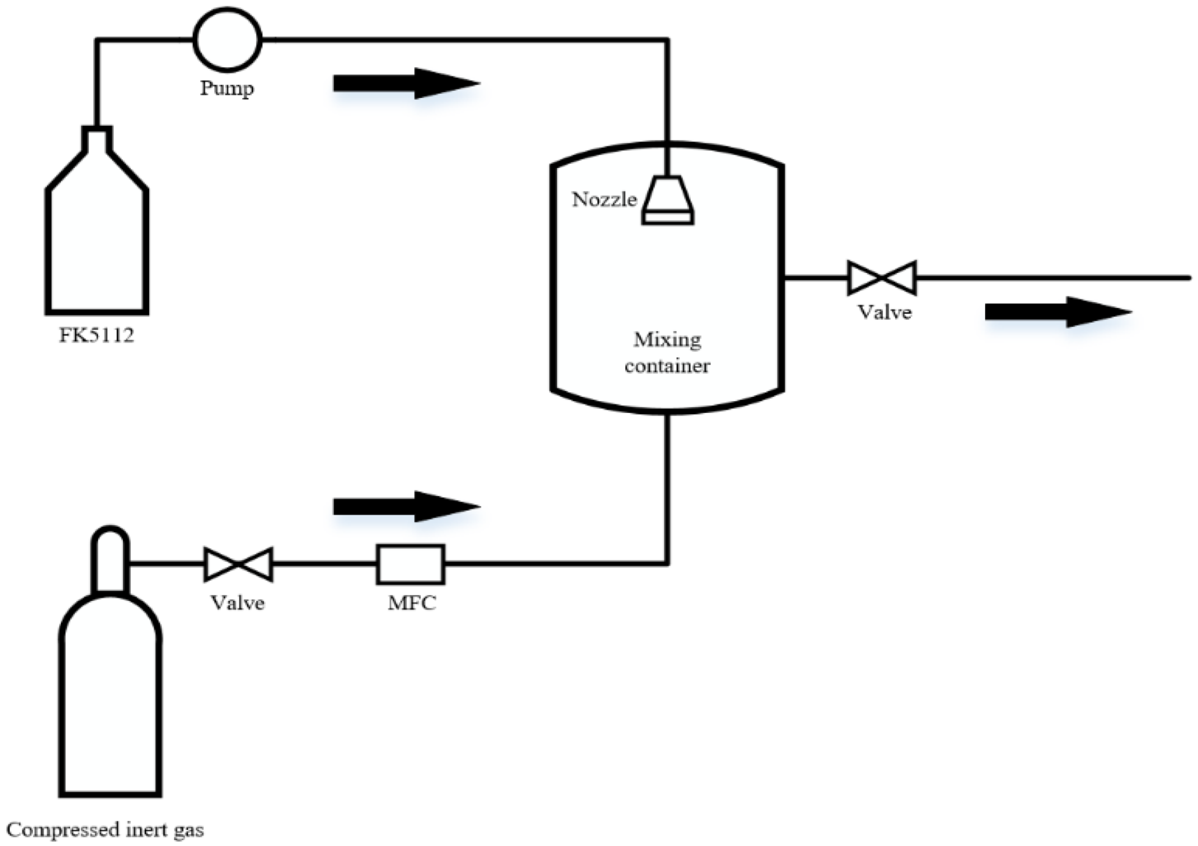

Figure 3. Device for improving the dispersibility of $C_6F_{12}O$ by mixing inert gas.

Table 4. Dispersion properties of typical fire suppressants [41].

Fire Suppressants	Molecular Weight	Boiling Point (°C, 1 atm)	Vapor Pressure (MPa, 25 °C)	Diffusion Coefficient (10^{-6} m^2/s, 1 atm, 0 °C)
Halon 1301	149	−57.9	1.62	7.49
HFC 125	120	−48.5	1.37	6.81
HFC 227ea	170	−16.4	0.458	5.68
$C_6F_{12}O$	316	49.2	0.04	4.17

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