Review on Research Progress of C$_6$F$_{12}$O as a Fire Extinguishing Agent

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Abstract: Clean gas fire suppressants with high efficiency are widely applied. This paper provides a systematic review of the research advances in the novel environmentally friendly suppressant, C$_6$F$_{12}$O. Considering the principle of screening fire suppressants, the physical and chemical properties of C$_6$F$_{12}$O are presented first. Specifically, research on the measurement of the thermodynamic parameters, toxicity, corrosion, environmental compatibility and dispersion characteristics are summarized, revealing that the poor dispersibility, corrosion of the hydrolysates (perfluoropropionic acid), corrosion and toxicity of thermal breakdown products such as HF and COF$_2$ and environmentally unfriendly products such as perfluorocarbons should be paid more attention. Three main synthesis routes of C$_6$F$_{12}$O are also introduced in view of its promising prospects for application. Furthermore, the fire extinguishing efficiency of C$_6$F$_{12}$O has been fully investigated in both a laboratory burner scale and full-scale fire extinguishing experiment, the results of which show that the minimum extinguishing volume concentration of C$_6$F$_{12}$O is lower than HFCs, but the mass concentration is much higher. Although C$_6$F$_{12}$O has shown satisfactory fire extinguishing performance in various fire protection scenarios, fire enhancement phenomenon and the large production of HF have been observed during fire extinguishment. Finally, the fire extinguishing mechanism of C$_6$F$_{12}$O has been discussed. The flame suppression effect of C$_6$F$_{12}$O, combustion enhancement phenomenon and the influence of water in the reaction zone have been revealed. This review fully evaluates C$_6$F$_{12}$O, in hope that it will provide a reference for follow-up research and the development of a halon replacement.

Keywords: fire suppressant; halon replacement; C$_6$F$_{12}$O; physical and chemical property; synthesis route; fire extinguishing mechanism

1. Introduction

Chemical gas fire suppressants are widely applied in fire protection systems due to their high fire extinguishing efficiency, stable, clean, convenient storage and transportation characteristics, and their easy installation and maintenance [1,2]. Among them, ozone-depleting substances (ODSs) [2] containing chlorine or bromine such as CF$_3$Br (Halon 1301), a kind of bromofluorocarbons (halon), once widely applied, have been phased out under the Montreal Protocol (1987), except for some specific applications in aircrafts and ships [3–5]. The search for proper fire suppressants with ozone depletion potential (ODP) close to 0 has become one of the key indicators for halon replacements.

Gas fire suppressants substituted for halon are mainly divided into inert gases (IGs) and hydrofluorocarbons (HFCs). IGs, such as CO$_2$, N$_2$, Ar and their mixtures, with their large storage space, low safety margin and poor fire extinguishing efficiency, have limited applications. HFCs including heptafluoropropane (HFC 227ea, FM200), pentafluoroethane (HFC 125, FE27), hexafluoro propane (HFC 236fa, FE36), trifluoromethane (HFC 23, FE13), etc., with no Cl, Br atoms (ODP is 0), and a fire extinguishing performance close to halon are widely used as halon substitutes at present. However, HFCs belong to greenhouse gases [3] and the global warming potential (GWP) is extremely high. Meanwhile, HFCs cannot
completely replace halon in aircrafts, ships and some other fields [4], so these substances can only be treated as transitional fire suppressants in the process of halon replacement. The Kyoto Protocol (1997) and the Kigali Amendment to the Montreal Protocol (2016) have set a deadline for the phasing out of HFCs [6]. Additionally, the signing of the Paris Agreement (2016), which is committed to maintaining the global temperature rise within 2 °C, will further accelerate the phasing out process of HFCs.

In order to cope with the problem that no gas fire suppressant can be used in the future, perfluoro-2-methyl-3-pentanone (C$_6$F$_{12}$O), 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. C$_6$F$_{12}$O belongs to fluorinated ketones which is different to HFCs. Its nontoxicity, noncombustibility, excellent insulation properties and fire suppression efficiency have attracted worldwide attention. It has been listed as an available substitute in the significant new alternatives policy (SNAP) program of the United States Environment Protection Agency (EPA) in 2003 and also listed in fire extinguishing system design standards including ISO 14520 and NFPA 2001. For now, C$_6$F$_{12}$O has been applied in many places such as electrical and electronic equipment, aircrafts, ships and libraries [7], and has shown great potential as a next generation halon substitute.

Table 1. Environmental characteristics of four typical fire suppressants (Halon 1301, HFC 125, HFC 227ea and C$_6$F$_{12}$O) [7].

| Fire Suppressants | ODP | GWP | ALT  |
|-------------------|-----|-----|------|
| Halon 1301        | 12  | 6290| 110y |
| HFC 125           | 0   | 3170| 41y  |
| HFC 227ea         | 0   | 3350| 36.5y|  
| C$_6$F$_{12}$O    | 0   | 1   | 5d   |

In this paper, progress in research on C$_6$F$_{12}$O in recent years is systematically described focusing on three aspects: fire suppressant characteristics, synthesis routes and fire extinguishing efficiency and mechanism, providing a reference for follow-up research and also the development and application of C$_6$F$_{12}$O in the fire protection system.

2. Properties and Characteristics of C$_6$F$_{12}$O

The thermophysical parameters, safety and environmental issues and other properties such as the dispersion characteristics of C$_6$F$_{12}$O 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.

2.1. 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$_6$F$_{12}$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$_6$F$_{12}$O presented by 3M Company, as shown in Table 2. McLinden et al. [8] measured the parameters of vapor pressure and $p\rho T$ properties of C$_6$F$_{12}$O (almost in liquid phase) and obtained more accurate calculation equations according to the experimental results. Then, Tanaka [9] measured the $p\rho T$ parameters in the near critical and supercritical range. Wen et al. [10] used vibrating string viscometer to measure the viscosity of C$_6$F$_{12}$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. [11] measured the dynamic viscosity and surface tension of C$_6$F$_{12}$O in the range of 303–433 K by surface light scattering (SLS). Furthermore, thermal conductivity was obtained by Perkins et al. [12] 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 2. Thermophysical parameters of C$_6$F$_{12}$O at 25 °C originated from technical data of 3M company [7].

| 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 (1 atm)   | 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, (1 atm, $n_2 = 1.0$) | 2.3 |

2.2. 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.

2.2.1. 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 [13]. 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 3 shows the toxicity index values of C$_6$F$_{12}$O and other typical gas fire extinguishing agents to the human body compared with the minimum fire extinguishing concentrations (MEC) tested by cup burners [2,14] (it will be detailed in Section 4.1.1). The designed fire extinguishing concentration of C$_6$F$_{12}$O is generally 4–6% [7], less than 10% and higher than NOAEL, which indicates that C$_6$F$_{12}$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. [15] studied the acute inhalation toxicity of C$_6$F$_{12}$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\textsubscript{6}F\textsubscript{12}O for a long time may damage the function of myocardium and liver.

Table 3. Toxic data and minimum extinguishing concentration of typical gas fire suppressants [2,14].

| Fire Suppressant | LC\textsubscript{50}/ALC (%) | NOAEL (%) | LOAEL (%) | MEC (%) |
|------------------|-----------------------------|-----------|-----------|---------|
| C\textsubscript{6}F\textsubscript{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\textsubscript{6}F\textsubscript{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\textsubscript{2}, C\textsubscript{4}F\textsubscript{8}, CO, C\textsubscript{3}F\textsubscript{6}, etc. [16–18]. Table 4 summarizes the toxicity data of the main thermal decomposition products detected in the experiments [19,20]. 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 4. Xing et al. [21] further examined the pyrolysis products and mechanism of C\textsubscript{6}F\textsubscript{12}O through the reactive molecular dynamics simulation (ReaxFF MD), as shown in Figure 1 [21], which identified not only the pyrolysis products including radicals and intermediates, but also the decomposition pathways of C\textsubscript{6}F\textsubscript{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 [22]. Since the final fire extinguishing products of fluorine-containing suppressants are mainly HF and COF\textsubscript{2} which are easier to monitor in the experiments, research on the fire extinguishing products of C\textsubscript{6}F\textsubscript{12}O mainly focuses on these two substances. However, COF\textsubscript{2} is unstable and easily reacts with water in the environment to generate HF and CO\textsubscript{2}, so the production of HF has attracted much more attention. Ditch [23] measured the products concentration of C\textsubscript{6}F\textsubscript{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\textsubscript{2} produced was about 1/7 of that of HF. Andersson et al. [24] compared the reaction products of typical fire suppressants including C\textsubscript{6}F\textsubscript{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\textsubscript{6}F\textsubscript{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\textsubscript{6}F\textsubscript{12}O is large, the actual production of HF of C\textsubscript{6}F\textsubscript{12}O is similar to HFC 227ea and HFC 125, far higher than Halon 1301. Therefore, as the fire extinguishing products of C\textsubscript{6}F\textsubscript{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.
Table 4. LC50 and GWP data of main decomposition products of C6F12O [19,20].

| By-Products | LC50          | GWP     |
|-------------|---------------|---------|
| HF          | 1276 ppm/1 h  | -       |
| CO          | 1807 ppm/4 h  | -       |
| COF2        | 360 ppm/1 h   | -       |
| CF4         | 895,000 ppm/15 min | 6630   |
| C2F6        | 20 pph/2 h    | 11,100  |
| C3F6        | 750 ppm/4 h   | 9200    |
| C3F8        | 6100 ppm/4 h  | 8900    |
| C4F8        | 81 ppm/4 h    | 9540    |
| C4F10       | -             | 9200    |
| C5F12       | -             | 8550    |

Figure 1. A reactive molecular dynamics study of the pyrolysis mechanism of C6F12O [21]: (a) simulation model, (b) Kinetic analysis of C6F12O pyrolysis, (c) evolution of the main pyrolysis products, (d) main generation pathway of COF2 observed from simulations.

2.2.2. Corrosion

The application scenarios and the design of fire protection systems need to consider the corrosiveness of the fire extinguishing agents. In terms of C6F12O, 3M company [7,25] 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 C6F12O 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 increase, especially under high exposure temperature that may have some negative impacts on its physical and mechanical properties. Li et al. [26] carried out the compatibility
research of C₆F₁₂O 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, C₆F₁₂O 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 C₆F₁₂O with silver is better than that of aluminum and copper. Zhang et al. [27] studied the compatibility between C₆F₁₂O-air gas mixture with copper and aluminum through experiments and the results showed that C₆F₁₂O-air is incompatible with heated copper, which leads to the decomposition reactions of C₆F₁₂O 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. [28]. Zhang et al. [29] further investigated the compatibility between C₆F₁₂O and sealing rubber materials, EPDM, in a 280-day experiment and molecular dynamic simulations. It was found that the chemical reactions between EPDM and C₆F₁₂O exist and C₆F₁₂O could dissolve EPDM and diffuse around and inside EPDM. Moreover, C₆F₁₂O can be hydrolyzed through a similar Haloform reaction to produce HFC 227ea and corrosive perfluoropropionic acid and the alkaline environment would accelerate this process [1,30] as shown in Figure 2.

![Figure 2. Hydrolysis reaction of C₆F₁₂O.](image)

Hence, impurity factors such as water in the fire suppressant or moisture in suppressant usage scenes will affect the actual application of C₆F₁₂O, but certain public reports are still lacking.

Meanwhile, corrosion is also related with the thermal decomposition products of C₆F₁₂O. The corrosive thermal breakdown products described in the previous section are mainly HF and COF₂, which would be threat to facilities in the fire protection area. Similar to HFCs, the corrosion of C₆F₁₂O in application is related to the number of acidic substances, environmental temperature and humidity, and equipment materials, etc. Ke et al. [31] investigated color change in the historic wooden remains after fire suppression by fluorinated chemical gases including C₆F₁₂O, HFC 227ea, Halon 1301, 2402 (C₂F₄Br₂) and 1323 (C₃H₂BrF₃) and found 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 H₂O, 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 [32], and the corrosion of the acid gases produced by the fire suppressant is much weaker than the smoke [33].

2.3. 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 [34,35], 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. C₆F₁₂O 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 [36,37]. Taniguchi et al. [38] 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. [39] 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. [30] explored the photolysis, hydrolysis and hydration of $C_6F_{12}O$ to find the source of perfluoropropanoic acid (CF$_3$CF$_2$(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. [40] 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 $C_6F_{12}O$.

2.4. 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. [41] 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 [7] 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 pressureing 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 boiling 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. [42] obtained that the storage performance of C₆F₁₂O 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 C₆F₁₂O 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/m³ and 1397 kg/m³, respectively. Furthermore, compared with hexafluoropropane (HFC 236fa), which is gaseous at room temperature, C₆F₁₂O 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 [43]. Fan et al. [44] investigated the flow characteristics of C₆F₁₂O compared with water and Halon 1301 through hydraulic calculation and experiments, which found that C₆F₁₂O 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 C₆F₁₂O. 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 C₆F₁₂O. Xing et al. [45] studied the method of improving the dispersibility of C₆F₁₂O 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 C₆F₁₂O 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.

Table 5. Dispersion properties of typical fire suppressants [45].

| Fire Suppressants | Molecular Weight | Boiling Point (°C, 1 atm) | Vapor Pressure (MPa, 25 °C) | Diffusion Coefficient (10⁻⁶ m²/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                    | 0.498                        | 5.68                            |
| C₆F₁₂O            | 316              | 49.2                     | 0.04                         | 4.17                            |

Figure 3. Device for improving the dispersibility of C₆F₁₂O by mixing inert gas [45]. Reprinted with permission from Ref. [45]. 2019, IEEE.
3. Synthesis Route

C₆F₁₂O is in great demand on the market with its excellent environmental performance and broad application prospects. It is of great significance to the development of a synthetic route for C₆F₁₂O, suitable for industrial production. There have been many reports on the synthesis of C₆F₁₂O, mainly in the following categories as shown in Figure 4.

The oxidation reaction of hexafluoropropene

\[
\begin{align*}
\text{F}_3\text{C} & \quad + \quad \text{F}_3\text{C} \\
\text{reaction conditions} & \quad \rightarrow \quad \text{CF}_3 \quad \text{C} \quad \text{C} \\
\end{align*}
\]

reaction conditions: yield of C₆F₁₂O

a. CsF as catalyst, R.T. 34.6% yield
b. KCN as catalyst, MeCN 53.4%-73.8% yield
c. CsF@activated carbon, in gas phase 90% yield

The oxidation rearrangement method of hexafluoropropylene-dimer

The reaction of hexafluoropropylene and pentafluoropropionyl fluoride

\[
\begin{align*}
\text{F}_3\text{C} & \quad + \quad \text{F}_5\text{C} \\
\text{KF, 70 °C, 1 MPa diglyme} & \quad \rightarrow \quad \text{CF}_3 \quad \text{C} \quad \text{C} \\
\end{align*}
\]

90.6% yield

Figure 4. Three main synthesis routes for C₆F₁₂O.

3.1. The Oxidation Reaction of Hexafluoropropene

Vilenchik et al. [46] proposed that hexafluoropropene is oxidized to prepare hexafluoropropylene epoxide. Hexafluoropropylene epoxide could react with hexafluoropropene under room temperature catalyzed by cesium fluoride. This method with high molecular utilization but low reactive selectivity could give C₆F₁₂O, accounting for approximately 35%. Furthermore, the yield could be enhanced to approximately 50–70% using halogen-like potassium salts (i.e., KOCN, KSCN, KCN) as a catalyst and the acetonitrile as a solvent (SU698289). Hexafluoropropylene epoxide and hexafluoropropene could react through a gas phase reaction under a catalysis of cesium fluoride with activated carbon as the carrier,
and the yield of C₆F₁₂O could be improved to more than 90% (RU2010150091A). However, the raw materials of this method are uncommon and the reaction yield in actual production is less than the theory. The by-product, hexafluoropropylene dimer, is difficult to separate and the reaction selectivity needs to be enhanced.

3.2. The Oxidation Rearrangement Method of Hexafluoropropylene Dimer

Zapevalov et al. [47] reported a method to prepare C₆F₁₂O through the oxidation rearrangement reaction for hexafluoropropylene dimer. Hexafluoropropylene dimer has two isomers including perfluoro-4-methyl-2-pentene and perfluoro-2-methyl-2-pentene. Additionally, two kinds of corresponding epoxides could be obtained from hexafluoropropylene dimer under the oxidation of sodium hypochlorite. The epoxides could be converted into C₆F₁₂O using cesium fluoride or trimethylamine, which is mild and could give 93% yield. This process includes multiple reactions, the yields of which need to be improved so that it could be practically used in the industry.

Compared with perfluoro-2,3-epoxy-4-methyl pentane, the epoxidation of perfluoro-2,3-epoxy-2-methyl pentane gives only one product, which is more suitable for the preparation of C₆F₁₂O. However, oligomerization of hexafluoropropylene mainly gives perfluoro-4-methyl-2-pentene. Additionally, it is now very significant in the industry to produce perfluoro-2-methyl-2-pentene through isomerization of perfluoro-4-methyl-2-pentene. The patent of 3M company (WO1995025082A1) disclosed a method for preparing C₆F₁₂O using perfluoro-2-methyl-2-pentene as a raw material through multi-step reactions, such as epoxidation by sodium hypochlorite and catalysis by cesium fluoride. Based on this, researchers (CN103508868B) have designed and optimized the reaction route: (1) isomerization from perfluoro-4-methyl-2-pentene to obtain perfluoro-2-methyl-2-pentene, (2) epoxidation to obtain perfluoro-2,3-epoxy-2-methyl pentane, and (3) catalysis to obtain C₆F₁₂O. In the optimization study of this method [48], the yield of C₆F₁₂O could reach more than 95%, which shows the prospective of the method. The patent (CN105198719B) disclosed a one-step preparation of C₆F₁₂O through the gas-phase reaction under the conditions of oxidizing gas and catalyst. This process requires only one step reaction with no solvent, reducing the pollution and cost.

3.3. The Reaction of Hexafluoropropylene and Perfluoropropionyl Fluoride

The reaction of hexafluoropropylene and perfluoropropionyl fluoride as raw materials under the conditions of alkali metal fluoride catalyst in aprotic polar solvent, diglyme or acetonitrile is also the main method for C₆F₁₂O synthesis [49]. 3M company (WO2001005468A2) disclosed the reaction conditions: diglyme as the solvent and active potassium fluoride as the catalyst, 70 °C, 1 MPa pressure in their patent. This reaction with high selectivity gives a C₆F₁₂O 90.6% yield. However, the raw material, perfluoropropionyl fluoride is highly corrosive, which is difficult to prepare and store. In addition, the reaction needs to be carried out under a higher pressure, and the entire process has high requirements on the material of the reactor. Fenichev et al. [50] proposed that perfluoropropionyl fluoride can be easily obtained by isomerization of hexafluoropropene oxide using alkali metal fluorides, KF and CsF, with the same conditions of C₆F₁₂O synthesis. They found that the water content in acetonitrile is the main factor resulting in the deactivation of the catalyst and the methods of isolating C₆F₁₂O from the reaction mixture by hydrolysis, and subsequent hydrogenation on the palladium catalyst supported on the activated carbon could lead the target product with a purity of 99.95 wt%. They also designed and created the pilot setup for production. Sha et al. [51] discussed the synthesis process of perfluoropropionyl fluoride. They produced hexafluoropropylene oxide through liquid phase oxidation of hexafluoropropylene as raw material using molecular oxygen, and then obtained the final product after isomerization using a bubbling reactor, which seems to be an ideal reaction route for industrial production.

All these three synthesis routes for C₆F₁₂O use hexafluoropropylene as the raw material. Some problems exist in these routes in that they all have certain side reactions, and
the by-products are difficult to separate from major products. Moreover, the purity of the product should be paid more attention. There are various kinds of fluoride involved in the synthesis of $\text{C}_6\text{F}_{12}\text{O}$, and the toxicity of different fluorides varies greatly. If these substances are not effectively separated, even very small amounts of toxic impurities exist in the final product, the toxicity for the product of $\text{C}_6\text{F}_{12}\text{O}$ will be totally different. It is urgent to optimize the synthesis routes and look for a safe, green, high yield, low in cost, less impurity and continuous synthesis routes for industrial production.

4. Fire Extinguishing Efficiency and Mechanism of $\text{C}_6\text{F}_{12}\text{O}$

4.1. Extinguishing Efficiency

The extinguishing efficiency of $\text{C}_6\text{F}_{12}\text{O}$ is evaluated mainly through two ways. One is measuring the flame minimum extinguishing concentration (MEC) at the laboratory scale, and the other is testing the actual fire extinguishing efficiency in a full-scale experiment.

4.1.1. Laboratory Scale Experiments

MEC is the key parameter to evaluate the efficiency of the fire suppressants and to design the fire extinguishing system. Due to the large amount of preparatory work, high cost, poor repeatability, safety issues and complexity, it is difficult to obtain accurate or even meaningful results of MEC through full-scale experiments [52,53]. However, the laboratory scale tests overcome these disadvantages and are widely used to test the MEC of various fire suppressants with different fuels.

The cup burner method is widely used to measure the MEC of gaseous fire suppressants. The laminar co-flow diffusion flame of the cup burner resembles real fire. Furthermore, the flame is more stable compared to real fire, leading to the higher MEC measured by the cup burner method. This method has been adopted as the standard procedure listed in ISO 14520 and NFPA 2001, since the first systematic introduction by Hirst [52]. However, the cup burner method is generally used to test the MEC of gaseous agents at room temperature. As for $\text{C}_6\text{F}_{12}\text{O}$ with the high boiling temperature of 49°C (1 atm), the method is modified so that the liquid agent is measured after vaporization by pre-heating.

Table 6 shows the MEC of $\text{C}_6\text{F}_{12}\text{O}$ tested by different researchers through the modified method, from which it can be concluded that the test results of MEC are highly consistent, and the extinguishing efficiency of $\text{C}_6\text{F}_{12}\text{O}$ is also very high. In terms of the synergistic effect of $\text{C}_6\text{F}_{12}\text{O}$ with nitrogen, carbon dioxide and Halon 1301, the extinguishing efficiency shows a negative synergistic effect of mutual inhibition, while when $\text{C}_6\text{F}_{12}\text{O}$ was combined with HFC 125, it shows a positive synergistic effect [54]. It could be speculated that the fire extinguishing mechanism of $\text{C}_6\text{F}_{12}\text{O}$ might be similar with HFC 125.

Table 6. Measurement of critical fire-extinguishing concentration of $\text{C}_6\text{F}_{12}\text{O}$ based on cup burner.

| Researcher             | Fuel                        | Test Result of MEC | Note                                                                 |
|------------------------|-----------------------------|--------------------|----------------------------------------------------------------------|
| Carnazza et al. [55]   | n-heptane, alcohol and other liquid fuels | n-heptane 4.5%, alcohol 5.6% | lower than HFC 125 and HFC 227ea under the same experimental conditions, higher than Halon 1301 |
| Andersson et al. [24,56]| propane                     | 6.4%               | lower than Halon 1301 and Halon 1211 under the same experimental conditions but the required mass for the same fire extinguishing efficiency is relatively high |
| Rivers et al. [14]     | propane                     | 3.5%               |                                                                                                                                 |
| Takahashi et al. [57]  | propane                     | 4.17%              | the calculated MEC is 4.12%                                         |
| Li [54]                | n-heptane                   | 4.5–5%             | under different gasification heating temperature, air temperature, heating coil and environment temperature |
The cup burner method is easily influenced by fuel type, fuel level, burner size, agent temperature, air and agent flow rate and pre-burn time [38], and the turbulence state in practical fire development is also neglected, leading to consistency problems between the laboratory scale and lager scale experiments [59]. In order to comprehensively evaluate the fire extinguishing concentration of the fire suppressants, researchers [60,61] have proposed the tubular burner method, in which the fuel and fire extinguishing mediums are mixed in a hot bath in advance before the fuel burns, and the flow rate of fire suppressants is adjusted until the flame is extinguished. This method determines the amount of needed fire suppressants by measuring the required extinguishing medium portion (REMP) value, which is defined as the ratio of the mass flow rate of the fire suppressant to the mass flow rate of the fuel. Andersson et al. [24] used this method to measure the REMP value of \( \text{C}_6\text{F}_{12}\text{O} \). The results showed that the REMP value of \( \text{C}_6\text{F}_{12}\text{O} \) (15) was much higher than that of Halon 1301 (1.5), HFC 125 (5.6) and HFC 227ea (6.8), which also verified that the fire extinguishing volume fraction of \( \text{C}_6\text{F}_{12}\text{O} \) is low, while the required mass concentration is high.

Although there are some differences between the two methods mentioned above in terms of the supply mode of the fire extinguishing agent and fuel and the calculation method of the fire extinguishing concentration and flame combustion state, these two methods have a common character in that when they are applied to measure \( \text{C}_6\text{F}_{12}\text{O} \) concentration, the fire suppressant vaporizes before reaching the flame, and what they measure is the fire extinguishing concentration of the agent in a gaseous state. For the high boiling point extinguishing agent, \( \text{C}_6\text{F}_{12}\text{O} \), partial evaporation occurs in the transport pipe of the fire extinguishing system, and the remaining part of the agent is sprayed in droplets. When the droplets approach the flame, phase change will happen under the high temperature of the fire, which will absorb the heat of the flame and reduce the temperature of the fire. The evaporative heat of this part has effects on the fire extinguishing, especially for water and polar molecules, while these two methods cannot take into account the extinguishing contribution of liquid phase transition of \( \text{C}_6\text{F}_{12}\text{O} \) [62].

Yang [63,64] proposed a dispersed liquid agent fire suppression screen apparatus (DLAFSS), a kind of counterflow cylindrical burner which can form a stable two-dimensional laminar non-premixed flame. It can accurately measure the fire extinguishing efficiency of solid, liquid and gaseous fire extinguishing mediums, and has been applied in when testing the fire extinguishing efficiency of some liquid suppressants [65]. However, research on the fire extinguishing efficiency of the high boiling point agent \( \text{C}_6\text{F}_{12}\text{O} \) is still lacking.

\( \text{C}_6\text{F}_{12}\text{O} \) can be used in a total flooding fire extinguishment system. 3M researchers [55] tested the minimum inert concentrations for methane and propane air mixtures according to ISO14520 standard and obtained minimum inert concentrations for methane and propane of 8–9%. Andersson et al. [56] also obtained similar experimental results. The inert concentration of \( \text{C}_6\text{F}_{12}\text{O} \) (7–9%) is similar to that of Halon 1301 (7.5–8.7%) and lower than that of HFC 125 (14–16%) and HFC 227ea (11–12%). However, in the FAA’s aerosol can test (FAA-ACT) [66–68], aiming at examining the feasibility of applying halon substitutes to aircraft, several halon substitutes including \( \text{C}_6\text{F}_{12}\text{O} \) were tested with concentrations lower than the minimum inert concentration. The results showed that these halon substitutes all lead to a pressure rise in the can to some degree, and with the addition of a low concentration of \( \text{C}_6\text{F}_{12}\text{O} \) (4.2%), the pressure increases nearly three times, indicating that \( \text{C}_6\text{F}_{12}\text{O} \) and other halon substitutes enhance flame combustion under some certain conditions.

4.1.2. Full-Scale Experiment

According to the problems found in previous studies, researchers carried out various kinds of fire suppression experiments in different fire scenes, as shown in Table 7. It could be concluded that \( \text{C}_6\text{F}_{12}\text{O} \) is similar to halon and other substitutes that have high fire extinguishing efficiency, but it also has some problems, such as the large amount of acid gas production, more agents required compared with other gas fire suppressants and combustion enhancement during fire extinguishment. As mentioned in the previous
section, the dispersion of C₆F₁₂O is relatively poor, and the fire extinguishing effect can be improved under the condition of increasing the charging pressure [23].

Table 7. Full-scale fire extinguishing experiments of FK-5112.

| Researcher       | Aim                                                                 | Fire Scene                                                                 | Result                                                                                                                                 |
|------------------|----------------------------------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| Hodges et al. [69]| Evaluate the fire extinguishing efficiency of C₆F₁₂O and the generation amount of acid gas in specific scenarios | Military vehicle, 7.36 m² chamber                                           | The fire extinguishing efficiency of C₆F₁₂O is similar to that of halon and its substitutes, which can extinguish 7.36 m² fire within 200 ms. However, the mass of fire extinguishing agent and the amount of acid gas in products cannot meet the application standard. |
| Bengtson et al. [70]| Fire extinguishing efficiency and re-burning of C₆F₁₂O in polymer fire ignited by different electric power | Polymer fire ignited by 192W electric power                                  | The fire extinguishing concentration is less than Halon 1301 and higher than the n-heptane test result given by NFPA 2001. When the fire suppressant concentration is higher than the test value of cup burner, the fire can be prevented from re-ignition. |
| Kim et al. [71]   | The fire extinguishing efficiency and acid gas generation of C₆F₁₂O | 3 kW cable fire, small oil pool and wood stack fire under the design concentration (6.5%) in 58 m³ space | It takes a long time for the extinguishing agent to reach the extinguishing concentration in the confined space. The cable fire is put out 72 s after combustion, while it is put out in 30 s in the open and ventilated environment. The wood stack and oil pool fire can be put out in 10 s. A large amount of acid gas is produced in a large flame. |
| Liu et al. [72]   | Fire extinguishing efficiency of C₆F₁₂O for lithium batteries       | 38 Ah prismatic ternary (Li(Ni₁/₃Co₁/₃Mn₁/₃)O₂/graphite) battery with the voltage of 4.2 V in 47.5 * 21.5 * 16 cm³ module box | With the increase in agent concentration, the fire extinguishing effect first decreases and then increases. No obvious cooling effect of C₆F₁₂O was found in the experiment |
| FAA et al. [73]   | Feasibility of fire extinguishing application of C₆F₁₂O in aviation application | Jet A fuel in the inclined-plane fire tests, 16- and 30-ft pan tests and the simulated engine nacelle fire tests | It is similar to halotron I (CF₃CHCl₂/Ar/CF₄ mixture), but the volume and mass of C₆F₁₂O are larger than halotron I |

4.2. Fire Extinguishing Mechanism

C₆F₁₂O has a high fire extinguishing efficiency in different fire scenes, and its fire extinguishing mechanism can be divided into a physical and chemical mechanism.

4.2.1. Physical Mechanism

The physical mechanism can be divided into the cooling effect on combustion and the dilution and isolation effect on combustion components.

Due to its high boiling point, C₆F₁₂O is stored in liquid phase at room temperature and ejected in the form of a gas–liquid mixture. Liquid C₆F₁₂O rapidly vaporizes when it approaches the flame and removes a part of heat from the fire. After vaporization, C₆F₁₂O and air will form a gaseous mixture with a high heat capacity which could absorb more heat from the fire. According to the report of 3M Company [7], C₆F₁₂O mainly absorbs the heat of the fire through this way to cool down and further extinguish the fire. Compared with other commercial halon substitutes, C₆F₁₂O has the higher heat capacity, resulting in the lower MEC, as shown in Figure 5, and it could be found that chemical effect would also play an important role in fire extinguishment for the chemical gas agents, especially for
Halon 1301. At the same time, when C₆F₁₂O contacts the flame, the heat of the fire will also be taken up by some breaking and formation of chemical bond processes in the thermal decomposition of C₆F₁₂O. Moreover, C₆F₁₂O is easier to decompose than HFC 227ea, which leads to better cooling effect during pyrolysis. The decrease in temperature will reduce the reaction rate and destroy the conditions of the combustion.

The dilution and isolation effects of C₆F₁₂O play an important role in the total flooding system. These effects can reduce the oxygen concentration in the fire and prevent oxygen from contacting the active radicals, and thus inhibit the free radical chain reactions in the combustion.

4.2.2. Chemical Mechanism

Chemical Extinguishing Process of C₆F₁₂O

The chemical mechanism of the fire suppressant refers to the decomposition products or radicals of C₆F₁₂O capturing the combustion radicals generated from the fuel, which would inhibit the combustion chain reactions to extinguish fire.

To obtain the reaction mechanism of C₆F₁₂O with the hydrocarbon flame, Linteris et al. [74] established the reaction kinetics model of C₆F₁₂O with hydrocarbon flame by modifying the analogy of similar substances with the existing decomposition model. Four sub-mechanisms were obtained including: (1) hydrocarbon combustion; (2) decomposition products of C₆F₁₂O containing fluorinated C1-C3; (3) C3 reactions related to HFC 227ea reaction in the flame; and (4) flame inhibition of C1-C2 fluorocarbon. They concluded that owing to the rapid decomposition of C₆F₁₂O, the heat absorption in this process has a limited effect on flame inhibition, and the critical effect on flame inhibition is the reaction of C1–C2 fluorocarbons with free radicals produced in fuel combustion. Moreover, the major breakdown products of C₆F₁₂O can form C₅F₇ and C₂F₅, and the Fourier transform infrared spectroscopy (FTIR) quantitative analysis of the products from the reaction of C₆F₁₂O with the flame shows that the decomposition products have a strong absorption peak at the wave number of 1027.2 cm⁻¹, which is similar to those of HFC 125 and HFC 227ea [24]. It can be inferred that the flame inhibition mechanism of C₆F₁₂O is the combination of HFC 125 and HFC 227ea. Takahashi et al. [57] studied the extinguishment of cup burner flames by C₆F₁₂O and found that the flame-anchoring reaction kernel weakens as the concentration...
of C₆F₁₂O increases gradually, which leads to the extinguishment of the flame. Xu et al. [75] obtained the specific reaction path of C₆F₁₂O in methane-air premixed flame through the numerical simulation and counterflow flame experiment, as shown in Figure 6. In total, 74.1% of C₆F₁₂O will directly decompose into C₂F₅CO and C₃F₇, and C₂F₅CO will further decompose into C₂F₅. The remaining C₆F₁₂O will react with free radicals OH (12.6%), H (8.3%) and O (5%). The inhibition mechanism of methane-air premix flame is realized by the direct capture of free radicals in the chain termination reaction to generate stable HF and CF₂O. Because the formation of HF releases heat, the inhibition effect of the agent will be weakened when the exothermic reaction is dominant.

![Figure 6. Reaction path of FK-5112 in methane/air premixed flame [75]. Adapted with permission from Ref. [75]. 2016, SAGE.](image)

Influence of H Content in Reaction Environment on Fire Extinguishing Process

Previous studies have speculated that the fire extinguishing mechanism of C₆F₁₂O is the combination of HFC 125 and HFC 227ea. However, compared with the latter two agents, C₆F₁₂O does not contain H in the molecule, and the level of H in the reaction zone would have a greater impact on fire extinguishment. Linteris et al. [74] found that when the concentration of C₆F₁₂O is high while H is inadequate in the reaction zone, HF cannot be formed and COF₂ is formed instead through the simulation method. The heat release rate of the system and the flame temperature would all decrease. Andersson [24] analyzed the thermal breakdown products of HF and COF₂ of C₆F₁₂O experimentally and found that the production of HF decreases with the increase in C₆F₁₂O concentration, while COF₂ demonstrated the contrary. Hence, the relation between the production of HF and COF₂ and concentration of C₆F₁₂O obtained by Linteris et al. [74] in the simulation study was verified from the view of decomposition products. However, the presence of water in the reaction zone can provide H and OH. Pagliaro et al. [76] studied the environmental humidity on the fire extinguishment of C₆F₁₂O and concluded that the inhibition effect of the fire suppressant on the combustion depends on the ratio of F/H of the reaction zone. When the concentration of C₆F₁₂O is high, that is, the ratio of F/H is large, water vapor can provide H and OH for combustion, resulting in combustion enhancement, and the combustion inhibition will occur provided the ratio is low.

Flame Enhancement Mechanism during the Fire Extinguishment

The aforementioned FAA-ACT showed that C₆F₁₂O can cause the overpressure similar to HFCs because of the combustion enhancement by the suppressant. This phenomenon was observed in the changes in flame temperature, speed and system pressure [4,74–77] and CO and CO₂ production before and after the addition of the agent [24]. The combustion enhancement of C₆F₁₂O is of great concern in its application.

Some researchers have revealed that the inhibition effect of C₆F₁₂O on the flame depends on the combustion state of the fuel and the addition amount of the suppressant. Under the condition of the rich combustion, the reaction rate of the system can always be
reduced by adding a fire suppressant. Additionally, under the condition of lean combustion, the effect of adding the agent on the reaction rate of the system first increases and then decreases with the increase in the volume fraction of the fire suppressant [4,74–77]. In addition, the concentration of C₆F₁₂O also has a key effect on combustion enhancement. Liu et al. [78] found that the inhibition effect of C₆F₁₂O on the flame is not sensitive to the type of hydrocarbon fuel. When the volume fraction of C₆F₁₂O exceeds a certain value, laminar flame velocity can be inhibited regardless of the chemical equivalent ratio between the fuel and air. Thermodynamic equilibrium and perfectly stirred-reactor calculations showed that the overpressures in FAA test may be caused by high heat release from the reaction of the agent itself [74,79,80]. It has been considered that the highly exothermic reactions between fluorine-containing groups and combustion radicals is the main reason resulting in combustion enhancement, and when the fire suppressant is insufficient enough to capture the combustion radicals, it would accelerate the release of heat enhancing the combustion [31,81]. Takahashi et al. [57] found that exothermic reactions to form HF and CF₂O in the two-zone trailing flame results in unwanted combustion enhancement and the total heat release increases up to three times for a large number of carbon and fluorine atoms in the molecules. They further concluded that unwanted combustion enhancement occurs because of the agent reacts exothermically in the air before approaching the main flame zone to inhibit combustion. Physical and chemical effects of C₆F₁₂O are coupled in the fire extinguishment, which should be distinguished to study the combustion enhancement and fire extinguishing mechanism. Ren et al. [82] used the numerical simulation method to decouple the contribution of physical and chemical extinguishing effects. It was concluded that the chemical action of C₆F₁₂O can enhance combustion under the poor combustion condition of the fuel, while its physical action always inhibits the combustion. A similar method was adopted by Takahashi et al. [57], and they found that the blow-off extinguishment occurs at ≈1700 K with the addition of the inert C₆F₁₂O, which is identical to that of inert gases. From the perspective of combustion products, the thermal decomposition of C₆F₁₂O would produce combustible substances such as C₂F₄, C₄F₆ and CO, which can become involved in combustion [21].

Due to the combustion enhancement of C₆F₁₂O, it is necessary to further analyze the occurrence conditions of the flame enhancement phenomenon and the combustible decomposition products of C₆F₁₂O in subsequent research to prevent the occurrence of the phenomenon in fire extinguishment.

5. Summary

This paper summarizes recent advances in research regarding the novel environmentally friendly suppressant, C₆F₁₂O, by focusing on physical and chemical properties, synthetic routes, and fire extinguishing efficiency and mechanisms. The main points derived from this study are as follows:

1. C₆F₁₂O is an environmentally friendly fire suppressant, but thermal breakdown products such as perfluorocarbons (PFCs) have significant greenhouse effects, similar to HFCs.

2. C₆F₁₂O can be considered as a non-toxic and non-corrosive agent, but it can be hydrolyzed in the presence of water to produce HFC 227ea and corrosive perfluoropropanoic acid, especially in an alkaline environment. Further investigation on the reaction characteristics and compatibility of C₆F₁₂O with other substances is needed. Toxic and strong corrosive thermal decomposition substances such as HF and COF₂ can be produced during fire extinguishment, and it is necessary to reasonably design a fire extinguishment system to control the generation of toxic and corrosive products in the acceptable range.

3. C₆F₁₂O is a high boiling point fire suppressant, and its dispersibility is relatively poor, which has non-negligible impacts on the transportation of the agent and fire extinguishing efficiency.
(4) The synthesis route of \( \text{C}_6\text{F}_{12}\text{O} \) mainly falls into three categories. The impurity of \( \text{C}_6\text{F}_{12}\text{O} \) produced by different routes should receive special attention. Even the presence of tiny toxic impurities may lead to a significant change in the safety of \( \text{C}_6\text{F}_{12}\text{O} \) products.

(5) The MEC test methods of \( \text{C}_6\text{F}_{12}\text{O} \) mainly test the fire extinguishing concentration of the vapor state without considering the effect of heat absorption in the phase change process of \( \text{C}_6\text{F}_{12}\text{O} \). Although \( \text{C}_6\text{F}_{12}\text{O} \) has high fire extinguishing efficiency compared with other halon substitutes, the required mass fire extinguishing concentration is larger and would also produce considerable acid gases. Combustion enhancement would therefore occur in fire extinguishment.

(6) Research on the extinguishing mechanism of \( \text{C}_6\text{F}_{12}\text{O} \) mainly focuses on the typical hydrocarbon flame. The concentration of \( \text{C}_6\text{F}_{12}\text{O} \) and the combustion state of the fuel will affect the extinguishing effect. Furthermore, environmental humidity has a significant influence on the generation of HF and COF\(_2\) and the combustion enhancement phenomenon, which needs to be further investigated in its application.

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