Alternative Environmentally Friendly Insulating Gases for SF$_6$

Yong Wang, Danqing Huang, Jing Liu *, Yaru Zhang and Lian Zeng

Electric Power Test and Research Institute, Guangzhou Power Supply Co. Ltd., Guangzhou 510410, China; wangy@guangzhou.csg.cn (Y.W.); xujie@guangzhou.csg.cn (D.H.); zhangyaru1989@163.com (Y.Z.); whu282070193@live.com (L.Z.)
* Correspondence: greengasguangzhou@163.com

Received: 12 March 2019; Accepted: 8 April 2019; Published: 15 April 2019

Abstract: Sulfur hexafluoride (SF$_6$) shows excellent insulation performance as an insulating gas. It is suitable for various climate conditions due to its low boiling point (−64 °C). Therefore, it has been widely used in power grid equipment. However, its global warming potential (GWP) is 23,500 times higher than that of CO$_2$. Thus, it is imperative to find an environmentally friendly insulating gas with excellent insulation performance, lower GWP, and which is harmless to equipment and workers to replace SF$_6$. In this review, four possible alternatives, including perfluorocarbons, trifluoroiodomethane, perfluorinated ketones, and fluoronitrile are reviewed in terms of basic physicochemical properties, insulation properties, decomposition properties, and compatibility with metals. The influences of trace H$_2$O or O$_2$ on their insulation performances are also discussed. The insulation strengths of these insulating gases were comparable to or higher than that of SF$_6$. The GWPs of these insulating gases were lower than that of SF$_6$. Due to their relatively high boiling point, they should be used as a mixture with buffering gases with low boiling points. Based on these four characteristics, perfluorinated ketones (C$_5$F$_{10}$O and C$_6$F$_{12}$O) and fluoronitrile (C$_4$F$_7$N) could partially substitute SF$_6$ in some electrical equipment. Finally, some future needs and perspectives of environmentally friendly insulating gases are addressed for further studies.

Keywords: SF$_6$; environmentally friendly insulating gas; perfluorocarbon; trifluoroiodomethane; perfluorinated ketone; fluoronitrile

1. Introduction

In high-voltage transmission systems, gas insulation has the advantages of being light weight, cost-effective, having simple manufacturing construction, and recyclability when compared with liquid or solid insulation. Thus, it has been widely applied in power grids all over the world. At first, a mixture of CCl$_4$ vapor and air was used as insulating gas. Herb and Rodine found that CCl$_4$ vapor and air can synergize and enhance the dielectric strength, especially with a lower CCl$_4$ concentration [1]. Charlton and Cooper found that CCl$_2$F$_2$ and CF$_4$ also showed better dielectric strength than N$_2$ [2,3]. SF$_6$ was first patented as an insulating gas by Cooper in 1938 (Figure 1). Since then, it has been studied systematically. It has been noted for its arc quenching capability and insulating properties. The excellent arc quenching capability is because of its high heat capacity, dissociation, and reassembly properties. The high dielectric strength can be attributed to its large molecular weight, complexity, and electron affinity, which affects the reaction between gas molecules and free electrons [4]. The decomposed products of SF$_6$ can recompose again when the temperature decreases, which ensures that the insulation strength is maintained well. As a result, it decomposes by only about 5% after working at 140 °C for 25 years [5]. Besides, it is non-poisonous, chemically stable, and non-flammable, which provides security for operation in practical applications. Considering the dielectric strength, cost, stability,
toxicity, and liquefaction temperature, SF₆ stands out as the best insulating gas. It has been widely used in air-insulated switchgear (AIS) and gas-insulated switchgear (GIS) since the 1960s [6].

![Figure 1. Development of insulating gases [7].](image1)

However, SF₆ has also caused serious environmental problems. It was identified as one of the seven greenhouse gases in the Kyoto Protocol. It shows a remarkable absorption at infrared frequency and absorbs upward radiance 42,000 times more effectively than CO₂, thus causing a great greenhouse effect [7]. The global warming potential (GWP) of SF₆ is 23,500 times higher than that of CO₂ over a 100 year integration time horizon according to the report of Intergovernmental Panel on Climate Change (IPCC) in 2013, and its lifetime in the atmosphere reached to 850 years with an uncertainty range of 580–1400 years [8]. With the rapid development of electrical insulation media, large amounts of SF₆ have been leaking or discharged into the atmosphere. In fact, the concentration of SF₆ in the atmosphere since 1995.

![Figure 2. The concentration of SF₆ in the atmosphere since 1995.](image2)
Therefore, an environmental alternative to completely replace SF₆ is necessary and urgent. It should meet the features of low GWP, no ozone depletion potential (ODP), it should be non-toxic or hypotoxic, and have high dielectric strength, good thermal conductivity, low boiling point, good compatibility with switchgear materials, etc. [5,9]. Herein, we have reviewed the pioneered studies about environmentally friendly insulating gases, including perfluorocarbon, trifluoroiodomethane, perfluorinated ketones, and fluoronitrile (Table 1). For each alternative, its basic physicochemical properties, insulation properties, decomposition properties, metal compatibility, and influence of trace H₂O or O₂ on its insulation performance are reviewed in detail in order to provide a better understanding of these compounds’ insulation performances.

Table 1. Basic properties of compounds used in electrical insulation. GWP: global warming potential; ODP: ozone depletion potential.

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>GWP/100-Years</th>
<th>Lifetime/ Years</th>
<th>Dielectric Strength Relative to SF₆</th>
<th>Boiling Point/ °C</th>
<th>Toxicity</th>
<th>ODP</th>
<th>Flammability</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₆</td>
<td>22,800</td>
<td>850</td>
<td>1</td>
<td>−64</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>CF₄</td>
<td>9200</td>
<td>50,000</td>
<td>0.4</td>
<td>−128</td>
<td>Low-toxicity</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>C₂F₆</td>
<td>12,200</td>
<td>10,000</td>
<td>0.76</td>
<td>−78.1</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>C₃F₈</td>
<td>8830</td>
<td>2600</td>
<td>1.01</td>
<td>−36.7</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>c-C₃F₈</td>
<td>8700</td>
<td>3200</td>
<td>1.3</td>
<td>−8</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>CF₃I</td>
<td>0.4</td>
<td>0.0055</td>
<td>1.23</td>
<td>−22</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>C₃F₁₀O</td>
<td>1</td>
<td>0.044</td>
<td>1.5–2</td>
<td>27</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>C₄F₁₂O</td>
<td>1</td>
<td>0.014</td>
<td>2.7</td>
<td>49</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>C₅F₁₄N</td>
<td>2100</td>
<td>22</td>
<td>2</td>
<td>−47</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>CF₆</td>
<td>6630</td>
<td>50,000</td>
<td>0.4</td>
<td>−128</td>
<td>-</td>
<td>Non-flammable</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>-</td>
<td>0.32–0.37</td>
<td>−79</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>N₂</td>
<td>-</td>
<td>-</td>
<td>0.34–0.43</td>
<td>−196</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>air</td>
<td>-</td>
<td>-</td>
<td>0.37–0.40</td>
<td>−193</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>He</td>
<td>-</td>
<td>-</td>
<td>0.02–0.06</td>
<td>−268.9</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>Ar</td>
<td>-</td>
<td>-</td>
<td>0.04–0.10</td>
<td>−186</td>
<td>Non-toxic</td>
<td>0</td>
<td>Non-flammable</td>
</tr>
</tbody>
</table>

2. Perfluorocarbons

Due to the electronegativity of fluorine, it is believed that perfluorocarbon has good insulation performance. Therefore, perfluorocarbons have attracted a great deal of attention as new insulation gases. The mainly proposed perfluorocarbons are CF₄, C₂F₆, C₃F₈, and C₄F₈. Their basic properties are listed in Table 1. Their GWP’s are all lower than that of SF₆, they show no ozone depletion potential, comparable dielectric strength, and relatively lower GWPs relative to SF₆.

2.1. Perfluoromethane (CF₄), Perfluoroethane (C₂F₆), and Perfluoropropane (C₃F₈)

CF₄, C₂F₆, and C₃F₈ have the potential to be used in gas insulation equipment because of their strong electronegative property. However, the lifetimes of CF₄ and C₂F₆ are as long as 50,000 and 10,000 years, respectively. Their dielectric strengths are both lower than that of SF₆. Further, CF₄ may cause choking disease. Therefore, CF₄ and C₂F₆ are unsuitable for gas insulation.

Meanwhile, C₃F₈ is harmless to O₃ in the stratosphere. It also has low toxicity, good thermal stability, relatively low boiling point, and comparable dielectric strength to SF₆. The GWP of C₃F₈ is 8830, which is 58.7% that of SF₆. The breakdown voltages of C₃F₈/N₂ or C₃F₈/CO₂ have a significant linear correlation with the ratio of C₃F₈. The GWPs of C₃F₈ (12%)/N₂ (2736) and C₃F₈ (12%)/CO₂ (6612) were found to be 12% and 29% of that of SF₆ (22,800), respectively [12]. The C₃F₈/N₂ mixture exhibited higher dielectric strength than that of C₃F₈/CO₂. When the ratio of C₃F₈ was 20%, the insulation strength of C₃F₈/N₂ reached 60% of that of pure C₃F₈. The insulation strength under 0.79 MPa was comparable to that of SF₆ at 0.5 MPa. Besides, the liquefaction temperature decreased to −30 °C and the GWP also decreased greatly [13]. Thus, it is feasible to apply C₃F₈/N₂ or C₃F₈/CO₂ in practical insulation equipment.
2.2. Perfluorocyclobutane (c-C\textsubscript{4}F\textsubscript{8})

Among CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, C\textsubscript{3}F\textsubscript{8}, and c-C\textsubscript{4}F\textsubscript{8}, c-C\textsubscript{4}F\textsubscript{8} exhibits the highest dielectric strength [14]. The insulation strength is about 1.3 times higher than that of SF\textsubscript{6}. The GWP of c-C\textsubscript{4}F\textsubscript{8} is 8700, which is 38.2\% of that of SF\textsubscript{6}. Moreover, c-C\textsubscript{4}F\textsubscript{8} also has the features of non-toxicity, no O\textsubscript{3} destruction, and high thermal stability. Thus, it has the potential to replace SF\textsubscript{6} as an environmentally friendly insulating gas [15]. However, due to its high boiling point (−8 °C), it should be used by mixing with CF\textsubscript{4}, N\textsubscript{2}, CO\textsubscript{2}, or air. The dielectric strength of c-C\textsubscript{4}F\textsubscript{8}/CO\textsubscript{2} is higher than that of SF\textsubscript{6}/CO\textsubscript{2}, and the GWP of c-C\textsubscript{4}F\textsubscript{8}/CO\textsubscript{2} is much lower than that of SF\textsubscript{6}/CO\textsubscript{2} [16]. Li et al. [17] studied the dielectric strength of c-C\textsubscript{4}F\textsubscript{8} with CF\textsubscript{4}, CO\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, and air mixture by Boltzmann equation. They found that c-C\textsubscript{4}F\textsubscript{8}/N\textsubscript{2} and c-C\textsubscript{4}F\textsubscript{8}/air mixtures showed comparable dielectric strength, which were higher than those of c-C\textsubscript{4}F\textsubscript{8}/CF\textsubscript{4}, c-C\textsubscript{4}F\textsubscript{8}/CO\textsubscript{2}, and c-C\textsubscript{4}F\textsubscript{8}/O\textsubscript{2}. When the concentration of c-C\textsubscript{4}F\textsubscript{8} exceeded 80\%, the dielectric strengths of c-C\textsubscript{4}F\textsubscript{8}/N\textsubscript{2} and c-C\textsubscript{4}F\textsubscript{8}/air were comparable to that of pure SF\textsubscript{6}. After 30 experimental breakdown tests, the breakdown voltage of the c-C\textsubscript{4}F\textsubscript{8}/N\textsubscript{2} decreased by only 0.76\%, indicating a good self-recovery characteristic. It was also reported that the decomposition rate of c-C\textsubscript{4}F\textsubscript{8}/N\textsubscript{2} was lower than that of pure c-C\textsubscript{4}F\textsubscript{8} at the same temperature, which is more suitable in practical gas insulation systems. The main decomposition path of c-C\textsubscript{4}F\textsubscript{8} was from c-C\textsubscript{4}F\textsubscript{8} to C\textsubscript{2}F\textsubscript{3}I, and it further decomposed into CF\textsubscript{2}I, F\textsubscript{3}I, CF\textsubscript{3}I, C, CF\textsubscript{4}, and C\textsubscript{2}F\textsubscript{4} [18]. However, when a certain amount of O\textsubscript{2} was added into the mixture gas of c-C\textsubscript{4}F\textsubscript{8}/N\textsubscript{2}, the breakdown voltage decreased more and more observably with the O\textsubscript{2} content increase from 0\% to 1\%. Then, the breakdown voltage decreased slightly when further increase of the O\textsubscript{2} content. The breakdown voltage decreased by 4.47\% after 30 breakdown tests in the presence of 3\% O\textsubscript{2}. This was mainly attributed to the relatively lower dielectric strength of O\textsubscript{2} and the new produced products [19]. O\textsubscript{2} promotes the decomposition of c-C\textsubscript{4}F\textsubscript{8} and generates the very toxic and corrosive COF\textsubscript{2}. Thus c-C\textsubscript{4}F\textsubscript{8} should be used without O\textsubscript{2} [20].

3. Trifluoriodomethane (CF\textsubscript{3}I)

CF\textsubscript{3}I is a colorless, odorless, incombustible, and stable gas. Because of the excellent electronegative property of CF\textsubscript{3}I, its dielectric strength is 1.2 times higher than that of SF\textsubscript{6}. Besides, the GWP of CF\textsubscript{3}I is 1–5, which is far less than that of SF\textsubscript{6}. The C–I bond can be easily cracked under UV irradiation. Therefore, its lifetime in atmosphere is less than 2 days, and it does not cause O\textsubscript{3} destruction [21,22]. According to these characteristics, CF\textsubscript{3}I has been a potential alternative to SF\textsubscript{6} as a new insulating gas.

Due to its high boiling point of −22.5 °C and the formation of I\textsubscript{2} in pure CF\textsubscript{3}I, CF\textsubscript{3}I should be mixed with other gases with low boiling point, such as N\textsubscript{2}, CO\textsubscript{2}, O\textsubscript{2}, air, CF\textsubscript{4}, Ar, Xe, and He. Among the mixtures, CF\textsubscript{3}I/N\textsubscript{2} showed the best insulating strength [22,23]. Li et al. [22] found that the saturated vapor pressure of CF\textsubscript{3}I/N\textsubscript{2} was higher than that of c-C\textsubscript{4}F\textsubscript{8}/N\textsubscript{2}, indicating that CF\textsubscript{3}I/N\textsubscript{2} can be used under higher pressure. Besides, the dielectric strength of CF\textsubscript{3}I/N\textsubscript{2} was higher than that of c-C\textsubscript{4}F\textsubscript{8}/N\textsubscript{2}, and they were both higher than that of SF\textsubscript{6}/N\textsubscript{2} [24]. The dielectric strength of CF\textsubscript{3}I (20\%)/N\textsubscript{2} at 0.79 MPa was 102\% of SF\textsubscript{6} at 0.5 MPa at −10 °C. When the CF\textsubscript{3}I concentration exceeded 65\%, the insulation strength of CF\textsubscript{3}I/N\textsubscript{2} was higher than that of SF\textsubscript{6}/N\textsubscript{2}. It was even higher than that of SF\textsubscript{6} when CF\textsubscript{3}I concentration exceeded 70\% [23]. Regarding CF\textsubscript{3}I/CO\textsubscript{2}, the CF\textsubscript{3}I and CO\textsubscript{2} can act synergestically and enhance the physicochemical properties of CF\textsubscript{3}I. When the ratio of CF\textsubscript{3}I or SF\textsubscript{6} was 10\%–30\% at 0.1–0.3 MPa, the partial discharge inception voltage of CF\textsubscript{3}I/CO\textsubscript{2} was 0\%–20\% higher than that of SF\textsubscript{6}/CO\textsubscript{2}. The insulation strength of CF\textsubscript{3}I/CO\textsubscript{2} was comparable or even higher than that of SF\textsubscript{6}/CO\textsubscript{2} [25]. In this case, both the boiling point and insulation strength could satisfy the practical requirements. The breakdown performance of CF\textsubscript{3}I/CO\textsubscript{2} was also superior to that of CF\textsubscript{3}I/N\textsubscript{2}. In quasi-uniform and highly non-uniform electric fields, the breakdown voltages of CF\textsubscript{3}I/CO\textsubscript{2} were 84\% and 65\% of pure SF\textsubscript{6}, which were both higher than that of CF\textsubscript{3}I/N\textsubscript{2} [26,27]. The 50\% breakdown voltages of CF\textsubscript{3}I (30\%)/CO\textsubscript{2} and CF\textsubscript{3}I (20\%)/CO\textsubscript{2} under 0.1 MPa were 67.1 and 66.6 kV, respectively. For CF\textsubscript{3}I (30\%)/N\textsubscript{2} and CF\textsubscript{3}I (20\%)/N\textsubscript{2}, they were 60.5 and 50.1 kV, respectively [28]. After 20 breakdown experiments, less CF\textsubscript{3}I decomposed in CF\textsubscript{3}I/CO\textsubscript{2} mixture than that in CF\textsubscript{3}I/N\textsubscript{2} mixture. It was explained that CO\textsubscript{2} could
provide an additional C source for the reaction system to maintain the C balance, which suppressed the decomposition of CF$_3$I [26].

According to density functional theory (DFT), the reactions of CF$_3$I to CF$_4$, C$_2$F$_6$, C$_2$F$_4$, and C$_2$F$_5$I were more energetically favorable than that to C$_3$F$_8$, C$_3$F$_6$, and I$_2$. Thus, the decomposition products were mainly C$_2$F$_6$, C$_2$F$_4$, and I$_2$. It can be clearly seen that the transparent glass changed to tawny after several experiments, indicating the formation of I$_2$. The products in partial discharge were stable after 20 h test [29]. Although the products cannot reassemble to CF$_3$I completely after discharge, there is a dynamic equilibrium among CF$_3$, CF$_2$, I, F, and CF$_3$I. Thus, the insulating strength can be maintained well for pure CF$_3$I [30].

However, in the presence of O$_2$, the O· from O$_2$ consumes free radicals (CF$_3$, CF$_2$·) from CF$_3$I and generates COF$_2$ (Figure 3), which is a highly toxic irritant for respiratory mucosa and skin. What is more, it destroys the dynamic equilibrium among CF$_3$, CF$_2$, I, F, and CF$_3$I, hindering the regeneration of CF$_3$I. As a result, the CF$_3$I content and insulation performance decreased with the extension of discharge time [31]. In order to ensure the insulation strength and safety, the O$_2$ content in CF$_3$I cannot exceed 7% and 20%, respectively [32]. Therefore, it is impracticable to use O$_2$ and air as buffer gases with CF$_3$I in GIS.

![Figure 3. Decomposition mechanism of CH$_3$I with O$_2$ during discharge.](image)

Moreover, the free radicals H· and HO produced from H$_2$O destroy the balance between CF$_3$I and free radicals, which aggravates the decomposition of CF$_3$I and generated C$_2$F$_6$, I$_2$, C$_2$F$_4$, C$_2$F$_3$I, C$_3$F$_8$, HF, H$_2$, COF$_2$, CF$_3$I, CF$_3$I. As a result, the partial discharge initial voltage and insulating strength decrease gradually [33,34]. So, it is vital to control the content of H$_2$O in insulating systems.

Zhang et al. [35] studied the influence of metal particles (Cu, Al, and Fe) on the insulation property of CF$_3$I. They found the metal particles—especially Cu and Al—could increase the electrical conductivity and decrease the insulation strength of CF$_3$I. The breakdown voltages decreased with the increase of metal particles. Therefore, the metal particles in insulation equipment should be well-covered by an insulating varnish or sleeve to avoid the interaction between CF$_3$I and metal particles.

Zhang et al. [36] studied the feasibility of CF$_3$I/N$_2$ in gas insulating equipment. They concluded that CF$_3$I (30%)/N$_2$ at 0.3 MPa could be applied in some low-pressure insulating equipment. By increasing
the total pressure or the partial pressure of CF$_3$I, the CF$_3$I/N$_2$ can also be applied in apparatuses requiring high insulation strength. Tan et al. [37] applied a CF$_3$I (20%)/N$_2$ mixture in 126 kV GIL (gas-insulated line). The insulation performance was 83% of that of SF$_6$ (20%)/N$_2$ and 59% of that of pure SF$_6$. When the pressure of CF$_3$I (20%)/N$_2$ exceeded 0.7 MPa, it could meet the insulating and safety requirements. However, authors did not consider the safety and feasibility over a long time period.

4. Perfluorinated Ketones (C$_5$F$_{10}$O and C$_6$F$_{12}$O)

Recently, it was found that perfluorinated ketones (C$_n$F$_{2n}$O; C$_5$F$_{10}$O and C$_6$F$_{12}$O) can act as new eco-friendly and promising insulating gases. They were initially applied in fire extinguishing applications due to their incombustibility [38,39]. Their physical property parameters can be seen in Table 1. C$_n$F$_{2n}$O shows high insulation capacity and its dielectric strength is 1–3 times higher than that of SF$_6$. Moreover, the atmospheric lifetime is just 7 days because of its instability under UV radiation, and it does not cause any damage to O$_3$. Therefore, it causes low greenhouse effect and other atmospheric environmental damage. However, the boiling point of C$_n$F$_{2n}$O (n = 5, 6) is above 27 °C, making it easy to liquify under natural conditions. Therefore, it is infeasible to apply pure fluoroketones as insulating gases, but only as additives to other buffer gases with low boiling points, such as N$_2$, air, and CO$_2$.

4.1. Perfluoropentanone (C$_5$F$_{10}$O)

Zhang et al. [40,41] studied the decomposition mechanism of C$_5$F$_{10}$O products by gas chromatography-mass spectrometry (GC-MS) and density functional theory (DFT). The reaction paths of C$_5$F$_{10}$O are shown in Figure 4. According to the relative energy change, the breakage of the C–C bond between carbonyl carbon and α-carbon atom was more likely to occur and generate CF$_3$CO· and C$_3$F$_7$ (Reaction A1) or C$_3$F$_7$CO and CF$_3$ (Reaction B1). They reacted further to generate CF$_4$, C$_2$F$_6$, C$_3$F$_8$, C$_5$F$_{10}$, C$_3$F$_{12}$, and C$_6$F$_{14}$. The decomposition rate increased with the increase of breakdown tests, generating more products with weaker dielectric strength relative to C$_5$F$_{10}$O. The products cannot reassemble into C$_5$F$_{10}$O when the environment temperature cools down [42]. As a result, the breakdown voltage decreased gradually. Besides, they also found that when the temperature was over 625 K and 825 K, the decomposition of C$_3$F$_7$CO· and CF$_3$CO· was enhanced. Reactions A1 and B1 would change to spontaneous. Among the products, C$_2$F$_6$, C$_3$F$_8$, and C$_4$F$_8$ have choking, bronchitis, anesthetic, and pneumonia effect. However, the content of C$_5$F$_{10}$O in practical application is below 20% and the concentration of products is extremely low. It has been reported that during arc discharge, the product of C$_3$F$_6$ was 50 ppm and just 6.5 ppb may have leaked into the air, which was far less than the exposure threshold of 0.1 ppm [43]. Although the GWPs of CF$_4$, C$_2$F$_6$, C$_3$F$_8$, C$_4$F$_{10}$, and C$_6$F$_{14}$ are 7390, 12,200, 8830, 8860, and 9300 (much higher than that of C$_5$F$_{10}$O), it should be noted that the concentration of deposited products is extremely low under normal working conditions [44]. Therefore, C$_5$F$_{10}$O is safe as an insulating gas. The application in GIS does not pose a threat to the environment or human health.
As an additive, the ratio of C₅F₁₀O in mixtures is usually less than 20%. For C₅F₁₀O/N₂ mixtures, the GWPs are lower than 0.7. However, these mixtures generate some CO and CF₃CN with high toxicity. For C₅F₁₀O/air mixtures, less CO was generated and more oxygenated chemicals were generated, decreasing the toxicity of the products. However, more C₅F₁₀O would decompose in C₅F₁₀O/air mixtures than that in C₅F₁₀O/N₂ mixtures [45]. For C₅F₁₀O/CO₂ mixtures, the breakdown voltages of C₅F₁₀O (10%)/CO₂ mixtures can reach to 62% of SF₆ under 200 kPa. When the percentage of C₅F₁₀O increased to 20%, the breakdown voltage increased by 32.5% [46].

Zhang et al. [47] studied the compatibility between C₅F₁₀O and Cu by theoretical calculation. Due to the high activity of the carbonyl group in C₅F₁₀O, it could be strongly absorbed on Cu (1 1 1) surfaces by chemical bonding. However, the interaction between the F atom and Cu is weak, which contributed to physical adsorption. Besides, they studied the compatibility between C₅F₁₀O and Al or Ag. The strong interaction between C₅F₁₀O and Al (1 1 1) was chemical adsorption. The weak adsorption on Ag (1 1 1) resulted from van der Waals force. Thus, they considered that Ag is more compatible with C₅F₁₀O than Cu and Al [48].

4.2. Perfluorohexanone (C₆F₁₂O)

When adding 3% C₆F₁₂O into N₂, the liquefaction temperature was ~26 °C. The breakdown voltage of the mixture gas was 1.7 times higher than that of the pure N₂, which was equal to that of SF₆ (10%)/N₂. The decomposed products of C₆F₁₂O/N₂ were mainly CO, CO₂, CF₄, C₂F₆, C₂F₄, C₃F₈, C₃F₆, CF₃CN, C₂HF₅, C₄F₁₀, C₅F₁₂, and C₆F₁₄. Similar to C₅F₁₀O/N₂, the reaction generated CF₃CN, which causes mortal danger [49]. Besides, the products (e.g., C₂F₆, C₃F₈, and C₄F₁₀) showed high insulation strength. Thus, the breakdown voltage of C₆F₁₂O (3%)/N₂ was maintained even after 100 voltage breakdown tests. With the increase of total pressure, the breakdown voltage of the mixture gas decreased gradually [50,51]. For the mixture of C₆F₁₂O and air, the generation of CF₃CN is avoided. The products are mainly CO₂, CF₆, C₂F₆, C₃F₈, and C₂O₃F₆, among which the content of CO₂ is the highest [49]. When the temperature exceeded 475 °C, the decomposition of C₆F₁₂O/CO₂ was enhanced. The possible decomposition paths are shown in Figure 5. The strength of the C–C bond is weaker than that of C–F and C=O bonds. Thus, C₆F₁₂O firstly decomposed into C₅F₇COCF₂ and C₂F₅COCF₂CF₃. Then, they further decomposed into fragments such as F, CF₃, CF₂, CF, CF₃, CO, COF₂, and C. These free radicals cannot recombine to C₆F₁₂O. The final products were mainly CF₄, C₂F₆, C₃F₈, C₃F₆, and C₅F₁₂ and their contents decreased as follows: C₂F₆ > C₃F₈ > C₃F₆ > CF₄ [52].
Figure 5. The proposed decomposition mechanisms of C₆F₁₂O/CO₂ [52].

In the presence of trace water, the produced HO and H aggravate the decomposition of C₅F₁₀O and produce more new products, such as C₃F₇COH, C₃F₇OH, HF, and CF₂O. The ionization parameters of
the new formed products are lower than that of C$_5$F$_{10}$O, thus resulting in decreased dielectric strength. Furthermore, the newly formed CF$_2$O has an irritative effect on the skin and respiratory mucosa. HF can cause aggressive corrosion to equipment and irritation to humans [53]. Therefore, the presence of water negatively impacts the insulation performance of C$_5$F$_{10}$O.

During practical application, the insulating gas and equipment must have good compatibility to maintain security. Zhang et al. [54] systematically studied the compatibility between C$_6$F$_{12}$O and metal materials by combining experimental tests and theoretical calculation. C$_6$F$_{12}$O can be absorbed on the surface of Cu and Al due to chemical adsorption between C=O and C$_6$F$_{12}$O, generating metal oxide. The interaction between C$_6$F$_{12}$O and Ag is attributed to physical adsorption, and thus less C$_6$F$_{12}$O was absorbed. Overall, from their SEM images, it was seen that C$_6$F$_{12}$O did not cause serious corrosion to the surface of Cu, Al, or Ag even after reaction for 125 days. Thus, the compatibilities between C$_6$F$_{12}$O and Cu, Al, and Ag were excellent.

5. Fluoronitrile (C$_4$F$_7$N)

Heptafluoro-iso-butynitrile (C$_4$F$_7$N), one kind of fluoronitrile, was firstly prepared and commercialized by the 3M$^{\text{TM}}$ Company. It has the features of low toxicity and high thermal conduction. Its lifetime in the atmosphere is 22 years. The GWP is 2100, and its insulation strength is about one-fold higher than that of SF$_6$ under normal pressure. Its insulation property makes it a promising alternative to SF$_6$ in electrical insulation systems.

However, C$_4$F$_7$N cannot be applied alone due to its relatively high boiling point of $-4.7^\circ$ C. Thus, it is necessary to add other buffer gases to decrease the boiling point of insulating gas mixtures in practical applications. The breakdown voltage of C$_4$F$_7$N (12%)/N$_2$ at 0.4 MPa was comparable to pure SF$_6$ at 0.2 MPa. Increasing the ratio of C$_4$F$_7$N in gas mixtures can effectively enhance the insulation strength. Considering the minimum temperature of $-25^\circ$ C in practical application, the breakdown voltages of C$_4$F$_7$N (5%)/N$_2$ at 0.3, 0.4, 0.5, and 0.6 MPa were 63.4%, 54.6%, 49%, and 56.4% of that of pure SF$_6$, respectively. Moreover, the negative partial discharge inception voltages reached 80.4%, 66.9%, 62.8%, and 68.8% of that of pure SF$_6$, respectively. The insulation strength of C$_4$F$_7$N/N$_2$ in a uniform electric field was higher than that in a non-uniform electric field [55]. The insulation strength and breakdown voltage of C$_4$F$_7$N (5%)/N$_2$ were 83.34% of that of pure SF$_6$. The breakdown voltage was maintained at 33.6 kV after 30 breakdown tests, indicating an excellent self-recovery property. The GWP of C$_4$F$_7$N (5%)/N$_2$ was less than 600, which was far less than that of SF$_6$ (22,800). The probable decomposition pathways are shown in Figure 6. C$_4$F$_7$N mainly decomposed to four free radicals (CF$_3$, CN, F, and C$_3$F$_7$) and the path from C$_4$F$_7$N to C$_3$F$_4$N and CF$_3$ was the most energy favorable. The free radicals react with each other form different products. CF$_3$ can react with CN, F, and other free radicals to generate products. Among the products, C$_2$F$_6$, CF$_4$, and CF$_3$CN are dominant. Although the products (e.g., CF$_3$CN and C$_2$F$_5$CN) were toxic, their concentrations were extremely low. Overall, the toxicity of the products was lower than that of the products of SF$_6$ decomposition, and was acceptable. Besides, N$_2$ was more likely to decompose than C$_4$F$_7$N. Thus, it acted as buffer gas and avoided the excess decomposition of C$_4$F$_7$N, which ensured the insulation performance [56]. For C$_4$F$_7$N, the decomposed products were mainly C$_3$F$_7$, CN, CNF, CF$_3$, CF$_2$, CF, CF$_3$CFCN(C$_2$NF$_4$), F, other free radicals, and CF$_4$. Their amounts increased with the increase of temperature. The free radicals recombined with each other and generated products such as CF$_4$, C$_2$F$_6$, C$_3$F$_8$, CF$_3$CN, CO, and so on. However, less C$_4$F$_7$N decomposed and less products were generated in C$_4$F$_7$N/CO$_2$ mixture due to the buffer action of CO$_2$. At 2400 K, the amount of products in pure C$_4$F$_7$N was 96%, while that in C$_4$F$_7$N/CO$_2$ was 58%. Besides, the amount of CF$_4$ and C decreased after introducing CO$_2$, thus avoiding the formation of precipitate carbon and other products with relatively inferior insulation performance [57,58].
The H· and HO· radicals generated from H₂O decomposition are active in reacting with free radicals decomposed from C₄F₇N during discharge (Figure 7). The activation energy in all possible paths with H₂O is lower than that without H₂O. Thus, the decomposition of C₄F₇N was accelerated, and the insulation performance was weakened. With the catalysis of H, the reactions generating HF, HCN, CF₃H, and other small molecules were more likely to occur. In the presence of HO·, the reaction generating CF₃OH occurred easily. The products, including CF₂O, HF, HCN CF₃CH₂CN, CF₂HCN, and CH₂FCN, are toxic, which would cause damage to operation personnel. HF and HCN would also cause severe corrosion to the equipment [59].

Zhang et al. [60] studied the compatibility of C₄F₇N with Cu (1 1 1) and Al (1 1 1). They found that the interaction between C₄F₇N and Cu (1 1 1) or Al (1 1 1) was weak. The N atom was more likely than the F atom to react with Cu (1 1 1) or Al (1 1 1) and form a weak chemical bond. So, the compatibility of C₄F₇N with Cu (1 1 1) or Al (1 1 1) was good. They also studied the compatibility of decomposition products of C₄F₇N with Cu (1 1 1) and Ag (1 1 1). C₂F₅CN, CF₃CN, COF₂, and CF₄ could be adsorbed on Cu (1 1 1) and Ag (1 1 1) surfaces by van der Waals force. The adsorption energies of products...
Processes 2019, 7, 216

on Ag (1 1 1) surface were weaker than those on Cu (1 1 1) surface. Overall, the compatibility of decomposition products of C$_4$F$_7$N with Cu and Ag were excellent [61].

6. Challenges and Perspectives

Most of the related studies were conducted based on theoretical calculation (e.g., DFT), and few experimental studies have been done to investigate the insulation performance in practical application—especially with the existence of trace H$_2$O or O$_2$, which is more close to reality. A certain amount of H$_2$O or O$_2$ may lead to the severe deterioration of insulation performance.

The compatibilities between the insulating gases or their decomposed products and metals were simulated and studied based only on a certain crystal face of metals. In electrical equipment, every crystal face can be exposed to the insulating gas. Thus, the actual compatibility between the insulating gases or their decomposed products and the insulation equipment may be very complex. It is significant to consider the compatibility through systematic experiments.

Common adsorbents such as γ-Al$_2$O$_3$ can not only absorb the hazardous products, but also the insulating gas. It would be interesting to design a novel adsorbent which could absorb the harmful products exclusively. This could ensure the safety of employees and equipment and maintain the insulation performance.

7. Conclusions

The GWPs of C$_2$F$_6$, C$_3$F$_8$, and c-C$_4$F$_8$ are still too high to show significant advantages compared with SF$_6$. CF$_3$I shows distinguished low GWPs and dielectric strength, however, it has been identified as a cancerogenic substance, and its stability and compatibility with the materials of electric equipment should be further studied. The GWPs of perfluorinated ketones (C$_5$F$_{10}$O and C$_6$F$_{12}$O) and fluoronitrile (C$_4$F$_7$N) are low, and they show high dielectric strengths and low toxicity, and therefore they have the potential to partially replace SF$_6$ in some electric insulation equipment. However, the compatibility of these insulating gases with the equipment materials, and the leaking rate obtained by using the conventional sealing materials should also be well studied. The adsorbents used to eliminate H$_2$O and O$_2$, which can accelerate the decomposition of the insulating gas, should also be screened or developed to ensure the safe operation of the equipment.

Author Contributions: Conceptualization, J.L.; investigation, L.Z. and Y.Z.; writing-original draft preparation, Y.W.; writing-review and editing, J.L.; project administration, D.H.

Funding: This research was funded by the project 'Study on Physical, Chemical and Insulation Properties, and Engineering Demonstration of Environmental Insulating gas (I)-Project 3-Applied Feasibility Study of New Insulating Gas in Guangzhou Power Grid', numbered as GZJKJXM20170330.

Conflicts of Interest: The authors declare no conflict of interest.

References
4. Pollock, H.C.; Cooper, F.S. The effect of pressure on the positive point-to-plane discharge in N$_2$, O$_2$, CO$_2$, SO$_2$, SF$_6$, CCl$_2$F$_2$, A, He, and H$_2$. *Phys. Rev.* 1939, 56, 170–175. [CrossRef]
5. Beroual, A.; Haddad, A. Recent advances in the quest for a new insulation gas with a low impact on the environment to replace sulfur hexafluoride (SF$_6$) gas in high-voltage power network applications. *Energies* 2017, 10, 1216. [CrossRef]


42. Zhong, L.; Rong, M.; Wang, X.; Wu, J.; Han, G.; Han, G.; Lu, Y.; Yang, A.; Wu, Y. Compositions, thermodynamic properties, and transport coefficients of high-temperature C$_6$F$_{12}$O mixed with CO$_2$ and O$_2$ as substitutes for SF$_6$ to reduce global warming potential. *AIP Adv.* 2017, 7, 075003. [CrossRef]


44. Li, Y.; Zhang, X.; Xiao, S.; Chen, Q.; Wang, D. Decomposition characteristics of C$_6$F$_{12}$O/air mixture as substitutes for SF$_6$ to reduce global warming. *J. Fluor. Chem.* 2018, 208, 65–72. [CrossRef]

45. Tatarinov, A.V.; Bilera, I.V.; Avtavaea, S.V.; Shakhatov, V.A.; Solomakhin, P.V.; Maladen, R.; Prévé, C.; Piccoz, D. Dielectric barrier discharge processing of trans-CF$_3$CH=CHF and CF$_3$C(O)CF(CF$_3$)$_2$, their mixtures with Air, N$_2$, CO$_2$ and analysis of their decomposition products. *Plasma Chem. Plasma Process.* 2015, 35, 845–862. [CrossRef]


61. Li, Y.; Zhang, X.; Xiao, S.; Chen, D.; Liu, C.; Shi, Y. Insights into the interaction between C4F7N decomposition products and Cu (1 1 1), Ag (1 1 1) surface. J. Fluor. Chem. 2018, 213, 24–30. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).