Insights on decomposition process of c-C₄F₈ and c-C₄F₈/N₂ mixture as substitutes for SF₆

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In recent years, many scholars have carried out studies on c-C₄F₈ and its gas mixture and found it has potential to be used as an environment-friendly insulating medium to replace SF₆ in medium-voltage equipment. In this paper, the c-C₄F₈ and c-C₄F₈/N₂ gas mixture models were built to study its decomposition process by the combination of reactive molecular dynamics method and density functional theory. The yield of the main decomposition products, the reaction pathways and enthalpy under different temperatures were explored. It was found that the decomposition of c-C₄F₈/N₂ mainly produces CF₂,F, CF₃, CF, C, CF₄ and C₂F₄, c-C₄F₈ can decompose to C₂F₄ by absorbing 43.28 kcal/mol, which is the main decomposition path and this process easily occurs under high temperature. There is a dynamic equilibrium process among the various produced radicals, which ensures the insulation performance of system to a certain extent. The decomposition performance of c-C₄F₈/N₂ mixture is better than that of pure c-C₄F₈ at the same temperature. Relevant results provide guidance for engineering application of the c-C₄F₈/N₂ gas mixture.

1. Introduction

Nowadays, electrical equipment using SF₆ as the insulation medium occupies a dominant position in the field of medium-voltage (MV) and high-voltage (HV) application. About 80% of the SF₆ gas produced worldwide is used in HV circuit breakers (GCB) and in gas-insulated switchgear [1]. However, the atmospheric lifetime of SF₆ is up to 3200 years and its global warming potential (GWP) is...
23,500 times than that of CO₂. Over the past 5 years, the global atmospheric content of SF₆ has increased by 20% and its atmospheric mole fraction reaches to 7.28 ppq (parts per quadrillion) currently corresponding to a radiative forcing of 0.0041 W m⁻² [2,3]. In addition, SF₆, SO₂F₂, SO₂, SOF₂ and other products produced by the decomposition of SF₆ under long-term operating conditions are toxic substances, which pose a threat to equipment maintenance personnel [4]. With the increasing demand in environmental protection around the world, the carbon emission of power industry has also been strictly limited. Therefore, it is urgent to seek for an environmentally friendly gas as insulation medium for power industry.

At present, scholars have made some achievements on environmentally friendly insulation medium such as perfluorocarbons (PFCs), trifluoroiodomethane (CF₃I), fluoro ketones (FKs), fluoronitriles and their gas mixture [5–8]. Among them, CF₃I is a moderately toxic gas and can precipitate iodine element after discharges. Particulate iodine may cause corrosion to the equipment to a certain extent, which limits the application of CF₃I [9,10]. FKS have a crude formula of the form CₓF₂ₙ₋₁O. C₄F₁₀O and C₃F₁₀O are the two main FKS with the liquefaction temperatures of 26.9°C and 49°C under normal pressure and thus need to be used with other gases with lower liquefaction temperature [11]. Fluoronitriles contain CN group in their molecular structure and may produce toxic substances. PFCs mainly include c-C₄F₈, C₃F₆, C₂F₆, and C₂F₄. The insulation performance of c-C₄F₈ reaches 1.1 times than that of SF₆, and its GWP value is 8700 [12]. Many scholars have carried out experimental and theoretical research on c-C₄F₈ and its gas mixture. It was found that the insulation performance of c-C₄F₈/N₂ is great, indicating that c-C₄F₈ gas mixture has immense potential for use in MV equipment [12–14].

The internal insulation of the electrical equipment is ageing under normal operating conditions. And it is inevitable to produce a variety of insulation defects, leading to partial discharge (PD) or flashover and decomposition of insulating medium. Thus, the evaluation of the decomposition characteristics of gas-insulated medium is of great significance. Several achievements have been made in the research on the decomposition characteristics of c-C₄F₈ under a discharge and local overheating faults. Li et al. tested the decomposition products of c-C₄F₈/N₂ gas mixture under PD, spark discharge and arc discharge. They found that CF₄, C₂F₆, C₃F₈, C₄F₆, and C₂F₆ are the main decomposition products [15]. Hayashi et al. explored the reaction mechanism of CF₂ particles produced by c-C₄F₈ based on density functional theory (DFT) and revealed the dissociation properties of c-C₄F₈ molecules comprehensively [16]. Cobos et al. investigated the thermal decomposition characteristics of c-C₄F₈ at 1150–2300 K. It is found the decomposition of c-C₄F₈ firstly produces two C₂F₄ molecules, and C₂F₄ can further dissociate producing CF₂ particles [17].

In this paper, the decomposition mechanism of c-C₄F₈ and c-C₄F₈/N₂ gas mixture was investigated by the combination of reactive molecular dynamics method and DFT. We built the c-C₄F₈ and c-C₄F₈/N₂ models to explore the decomposition process of c-C₄F₈ gas mixture under different temperatures. The yield of the main decomposition products, the reaction pathways and enthalpy under different temperatures were also obtained. Relevant results provide guidance for engineering application of c-C₄F₈/N₂ gas mixture.

2. Methods

The development of reactive molecular dynamics method provides an effective way to study the physical and chemical properties of large-scale system (millions of atoms). Reactive force field (ReaxFF) describes bond cleavage and formation based on the bond level, which originates from the distance between two atoms. ReaxFF has been widely used in the field of pyrolysis, combustion and catalysis [18–22]. The terms of total energy in ReaxFF can be described as the following equation [23]:

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{con}} + E_{\text{vdW}} + E_{\text{Coulomb}}
\]

where \(E_{\text{bond}}\) denotes the bond energy; \(E_{\text{over}}\) and \(E_{\text{under}}\) correspond to the over and under coordinated atom in the energy contribution, respectively; and \(E_{\text{val}}\), \(E_{\text{pen}}\), \(E_{\text{tors}}\), \(E_{\text{con}}\), \(E_{\text{vdW}}\) and \(E_{\text{Coulomb}}\) represent the valence angle term, penalty energy, torsion energy, conjugation effects to energy, non-bonded van der Waals interaction and Coulomb interaction, respectively.

In order to explore the decomposition mechanism of c-C₄F₈ and c-C₄F₈/N₂ gas mixture, two periodic cubic models were built (as shown in figure 1). It is reported that the highest allowable pressure of 20% c-C₄F₈/80% N₂ gas mixture at −20°C and −30°C is about 0.35 and 0.2 MPa, respectively [24]. And most MV equipment working at 0.15–0.3 MPa. In order to explore the decomposition mechanism of c-C₄F₈/N₂ mixture at this scale, we built models with 20% c-C₄F₈ and 80% N₂. The
The width of the c-C₄F₈ system is 155 Å, which contains 100 c-C₄F₈ molecules with the density about 0.008918 g cm⁻³. The width of c-C₄F₈/N₂ system is 265 Å, which contains 100 c-C₄F₈ molecules and 400 N₂ molecules with the density about 0.00274 g cm⁻³. The above parameters correspond to the actual density of the gas mixture at 0.1 MPa, 25 °C.

The system was minimized for 5 ps at 5 K using the NVE (keep the number of atoms, volume and potential energy constant) ensemble and then equilibrated with the NVT (keep the number of atoms, volume and temperature constant) ensemble for 10 ps at 1000 K using a time step of 0.1 fs [22]. Then the NVT (keep the number of atoms, volume and temperature constant) molecule dynamics simulations were performed at different temperatures for 1000 ps with the time step of 0.1 fs. The Berendsen thermostat method with a 0.1 ps damping constant was used to control the temperature [25]. All the ReaxFF-MD simulations were carried out using the Amsterdam density functional package, and the force field file is given in the data availability section [26].

In addition, quantum chemistry DFT calculation was performed to obtain the reaction enthalpy of the main decomposition paths at different temperatures [27]. The geometry optimization of the reactants and products for each path is performed using the double numerical atomic orbital augmented by d-polarization (DNP) as the basis set. The exchange–correlation energy is described using the meta-generalized approximation (mGGA-M06 L) function [28]. Geometry optimizations of all the particles were performed using the convergence threshold of 1.0 × 10⁻⁵ Ha on energy, 0.005 Å on displacement and 0.002 Ha Å⁻¹ on gradients. We also did zero-point energy (ZPE) correction and enthalpy correction based on the frequency analysis to obtain more accurate results. All the DFT calculations in this paper were conducted using DMol³ package of the Materials studio.

3. Results and discussion

3.1. Decomposition rate of c-C₄F₈ and c-C₄F₈/N₂ gas mixture

Local overheating, PD and arc discharge are the common failures in electrical equipment [29]. PD and arc discharge are mostly caused by insulation defects in the devices. And the temperature in the central region of the PD and arc discharge is about 1000 K and 3000–12 000 K, respectively [30,31]. High temperature will lead to the decomposition of insulating medium, producing various free radicals or decomposition products. The generation of decomposition products may affect the insulation performance of the gas-insulated medium and cause threat to the equipment. In this paper, we carried out the reactive molecular dynamics simulations of c-C₄F₈ and c-C₄F₈/N₂ system at different temperature conditions to explore its decomposition mechanism.

Figures 2 and 3 describe time evolution of c-C₄F₈ decomposition in pure c-C₄F₈ and c-C₄F₈/N₂ systems and the maximum number of decomposed c-C₄F₈ at 2600–3400 K, respectively. It should be noted that in order to allow chemical reactions to be observed on the computational affordable time scale, we enhanced the temperatures to accelerate the simulation process. We have tested and found that c-C₄F₈ and c-C₄F₈/N₂ mixture begin to decompose largely at 2600 K (figure 2). The decomposition rate of c-C₄F₈ shows an increasing trend with the increase of temperature. The
decomposition rate of c-C_{4}F_{8} in the pure c-C_{4}F_{8} system is significantly accelerated above 3000 K. The final decomposition amount and the decomposition rate of c-C_{4}F_{8} in c-C_{4}F_{8}/N_{2} system are lower than that of pure c-C_{4}F_{8} system at the same temperature, which indicates that the decomposition characteristics of c-C_{4}F_{8}/N_{2} gas mixture is great. For example, only 49 c-C_{4}F_{8} decomposed in c-C_{4}F_{8}/N_{2} system at 3400 K, whereas 59 c-C_{4}F_{8} molecules decomposed in c-C_{4}F_{8} system under the same condition. In addition, the density of c-C_{4}F_{8} system (0.008918 g cm^{-3}) is higher than that of c-C_{4}F_{8}/N_{2} system (0.00274 g cm^{-3}). Thus the molecules of c-C_{4}F_{8} in the unit volume increase, resulting in the increase of the effective collision number and the intensity of reactions. And the decomposition amount of c-C_{4}F_{8} in the c-C_{4}F_{8} system is higher than that of c-C_{4}F_{8}/N_{2} system at the same temperature.

Figure 4 shows time evolution of potential energy at 2400–3400 K in c-C_{4}F_{8} and c-C_{4}F_{8}/N_{2} system. It can be seen that the potential energy shows an increasing trend in the whole simulation process, indicating that the decomposition process of c-C_{4}F_{8} and c-C_{4}F_{8}/N_{2} gas mixture is endothermic. The total potential energy and its growth rate increases with the increase of temperature. The potential energy of c-C_{4}F_{8} system has no obvious change when the ambient temperature is at 2600 K, which is due to the insufficient occurrence of various reactions at this temperature. When the ambient temperature reaches above 3200 K, the potential energy of the system increases rapidly in the time range of 0–400 ps, and exhibits a saturated growth trend after 400 ps. This means the decomposition of c-C_{4}F_{8} is concentrated at 0–400 ps. The time evolution of potential energy in c-C_{4}F_{8}/N_{2} system is basically the same as that of c-C_{4}F_{8} system.

Figure 2. Time evolution of c-C_{4}F_{8} decomposition at 2600–3400 K.

On the whole, the decomposition performance of c-C_{4}F_{8}/N_{2} mixture is better than that of pure c-C_{4}F_{8} at the same temperature, which is suitable to use as a gas-insulated medium in the field of MV equipment.
3.2. Distribution of decomposition products

The distribution of the main decomposition products in the c-C₄F₈ and c-C₄F₈/N₂ system is shown in figure 5. It can be found that decomposition of c-C₄F₈ mainly produces CF₂, CF₃, CF, F, C, C₂F₄ and CF₄.

For the c-C₄F₈ system, the yields of CF, F and C show a linear increase trend with the increase of temperature. The two groups of free radicals, CF₂ and CF₃ show a saturated growth trend at temperatures below 3200 K. When the temperature is higher than 3200 K, the yield of CF₂ decreased in the range of 400–1000 ps and the yield of CF₃ decreased in the range of 600–1000 ps, which is relative to the re-decomposition of CF₂ and CF₃ particles at high temperature. The yield of CF₄ increased significantly at temperatures above 3200 K. The generation of CF₄ requires the participation of CF₃, thus the decrease of CF₃ content is related to the formation of CF₄. The yield of C₂F₄ reached its peak at the beginning of the simulation at 3200 and 3400 K, and then began to decrease. In addition, C atoms are also found during the simulation. It should be noted that particulate carbon is detrimental to the insulation properties of the system.

The yields of the main decomposition particles in the c-C₄F₈/N₂ system are lower than that of pure c-C₄F₈ system at the same temperature. The content of CF₂ shows a saturated growth trend when the temperature is above 3200 K. The generation of CF₃ begins at 3000 K and its content is relatively low. The time evolution of CF and F radicals is similar to that of c-C₄F₈ system. In
addition, the yields of C2F4 and C are much lower than those of pure c-C4F8 system at the same temperature.

The maximum number of produced decomposition products of c-C4F8 and c-C4F8/N2 system is shown in figures 6 and 7, respectively. It can be found that the content of F in the C4F8 system is the highest among all the decomposition products, followed by CF2, CF and C. The content of F
and CF$_2$ is the highest in the c-C$_4$F$_8$/N$_2$ system and the content of CF$_3$ is relatively low among all the decomposition products.

### 3.3. Decomposition mechanism of c-C$_4$F$_8$

The proposed decomposition mechanism and reaction enthalpy of c-C$_4$F$_8$ molecule based on the ReaxFF-MD simulation results are shown in table 1 and the relative energy change of c-C$_4$F$_8$ decomposition process is shown in figure 8. It can be found that the generation of C$_2$F$_4$ needs to absorb 43.28 kcal mol$^{-1}$, which is more prone to occur than the formation of C$_3$F$_6$ and CF$_2$. C$_3$F$_6$ can further decompose to two CF$_2$ radicals, which needs to absorb 77.93 kcal mol$^{-1}$. As the main decomposition product of c-C$_4$F$_8$, CF$_2$ can also dissociate to produce CF and F or combine with F to generate CF$_3$, and these processes need to absorb 97.23 kcal mol$^{-1}$ or release 79.80 kcal mol$^{-1}$, respectively. In addition, the formation of CF$_4$ and C$_2$F$_6$ releases 116.8 and 98.67 kcal mol$^{-1}$, respectively. And the decomposition of CF requires to absorb 111.49 kcal mol$^{-1}$. 

![Figure 6. Maximum number of produced decomposition products of c-C$_4$F$_8$ at 2600 – 3400 K (c-C$_4$F$_8$ system).](image)

![Figure 7. Maximum number of produced decomposition products of c-C$_4$F$_8$ at 2600 – 3400 K (c-C$_4$F$_8$/N$_2$ system).](image)
As shown in figure 8, the various free radicals produced by c-C₄F₈ reacting stepwise to form CF₄ and C₂F₆ need to absorb 1.47 and 19.6 kcal mol⁻¹, respectively, and the generation of C and F requires to absorb 406.79 kcal mol⁻¹. From the thermodynamic point of view, there is a dynamic equilibrium process between the various produced radicals, which ensures the insulation performance of the system to a certain extent.

In order to further analyse the influence of temperature on the main reaction, the enthalpy of each path at 300–3400 K is also calculated (as shown in figure 9). It can be found that the enthalpy of path 1 and path 3 shows a decrease trend with the increase of temperature, which means the decomposition of c-C₄F₈ is more likely to occur under high-temperature conditions. The enthalpy of path 2, 4, 5 and 8 does not change with the increase of temperature, thus the ambient temperature has no obvious effect on these reactions. The reaction enthalpy of path 6 and path 9 decreases with the increasing temperature, indicating that the generation of CF₃ and C₂F₆ occurs with more difficulty at high temperature.

![Relative energy change of c-C₄F₈ decomposition process.](image)

**Table 1.** Proposed decomposition mechanism and reaction enthalpy of c-C₄F₈.

| no. | reaction | enthalpy (kcal mol⁻¹) a |
|-----|----------|------------------------|
| 1   | c-C₄F₈ → 4CF₂       | 198.07                 |
| 2   | c-C₄F₈ → 2C₂F₄      | 43.28                  |
| 3   | c-C₄F₈ → C₃F₆ + CF₂ | 74.34                  |
| 4   | CF₂ → CF + F        | 97.23                  |
| 5   | CF → C + F          | 111.49                 |
| 6   | CF₂ + F → CF₃       | 79.80                  |
| 7   | CF₃ + F → CF₄       | −116.80                |
| 8   | 2CF₂ → C₂F₆         | −77.93                 |
| 9   | 2CF₃ → C₂F₆         | −98.67                 |

aT = 300 K, at mGGA-M06 L level with ZPE correction and enthalpy correction.
4. Conclusion

In this paper, the decomposition process of c-C4F8 and c-C4F8/N2 gas mixture were explored based on the ReaxFF molecular dynamics method and DFT. It is found that the decomposition of c-C4F8 mainly produces CF2, F, CF3, C2F4, and C2F4. c-C4F8 can decompose to C2F4 by absorbing 43.28 kcal mol⁻¹, which is the main decomposition path and this process occurs easily under high temperature. There is a dynamic equilibrium process between the various produced radicals, which ensures the insulation performance of system to a certain extent. The decomposition performance of c-C4F8/N2 gas mixture is better than that of pure c-C4F8 at the same condition, which is suitable to use as a gas-insulated medium in the field of medium voltage (MV) equipment.

Data accessibility. Our data are deposited at Dryad Digital Repository; http://dx.doi.org/10.5061/dryad.2zp984j6 [32].

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