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

Abderrahmane Beroual [1,*] (iD) **and Abderrahmane (Manu) Haddad** [2]

[1] Ecole Centrale de Lyon, University of Lyon, Ampere CNRS UMR 5005, 36 Avenue Guy Collongue, 69134 Ecully, France

[2] Advanced High Voltage Engineering Research Centre, School of Engineering, Cardiff University, The Parade, Cardiff CF24 3AA, UK; Haddad@cardiff.ac.uk

[*] Correspondence: Abderrahmane.Beroual@ec-lyon.fr; Tel.: +33-47-2186-110

Abstract: The growing environmental challenge of electrical energy systems has prompted a substantial increase in renewable energy generation. Such generation systems allow for significant reduction of CO$_2$ emissions compared with a traditional fossil fuel plant. Furthermore, several improvements in power systems network configuration and operation combined with new technologies have enabled reduction of losses and energy demand, thus contributing to reduction of CO$_2$ emissions. Another environmental threat identified in electrical networks is the leaking of insulating sulfur hexafluoride (SF$_6$) gas used in electrical gas insulated substations (GIS) and equipment. Because of its Global Warming Potential (GWP) of nearly 24,000 and its long life in the atmosphere (over 3000 years), SF$_6$ gas was recognized as a greenhouse gas at the 1997 COP3; since then its use and emissions in the atmosphere have been regulated by international treaties. It is expected that as soon as an alternative insulating gas is found, SF$_6$ use in high-voltage (HV) equipment will be banned. This paper presents an overview of the key research advances made in recent years in the quest to find eco-friendly gases to replace SF$_6$. The review reports the main properties of candidate gases that are being investigated; in particular, natural gases (dry air, N$_2$ or CO$_2$) and polyfluorinated gases especially Trifluoroiodomethane (CF$_3$I), Perfluorinated Ketones, Octafluorotetra-hydrofuran, Hydrofluoroolefin (HFOs), and Fluoronitriles are presented and their strengths and weaknesses are discussed with an emphasis on their dielectric properties (especially their dielectric strength), GWP, and boiling point with respect to the minimum operating temperature for HV power network applications.

1. Introduction

Sulfur hexafluoride, SF$_6$, has been the most common compressed gas used in high-voltage (HV) power transmission line and substation applications since the 1960s. About 80% of the SF$_6$ gas produced worldwide is used in HV circuit breakers (GCB) and in gas insulated switchgear (GIS) because of its excellent properties such as its dielectric strength, which is 2.5 times that of air, good heat transfer capacity, and interruption of electric arcs. Unfortunately, the excessive size, radiative effect, and atmospheric lifetime (several centuries due to the resistance to chemical and photochemical

degradation) of the SF_6 molecule makes this gas an aggravating agent for the greenhouse effect. The Global Warming Potential (GWP) of SF_6 is one of the highest. Table 1 gives a comparison of GWP and lifetimes of SF_6 with carbon dioxide (CO_2) [1].

Table 1. Atmospheric lifetime and GWP at different time horizon for SF_6 and CO_2 [1].

Chemical Formula	Lifetime (Years)	Global Warming Potential for Given Time Horizon		
		20 Years	100 Years	500 Years
CO_2	30–95	1	1	1
SF_6	3200	16,300	22,800	32,600

Whilst SF_6 is chemically stable (non-toxic, inert gas, non-flammable), it can be asphyxiating when its concentration in the air exceeds 12 mg/m^3 [2]. When subjected to an electric arc and when the temperature of the gas exceeds 600 °C, it decomposes and recomposes extremely rapidly when the temperature drops again, allowing the gas to recover its dielectric strength. This recovery property makes it particularly suitable for HV AC circuit breakers. However, at 140 °C, after operating for more than 25 years, it decomposes by approximately 5%. Some breakdown byproducts are known to be of greater toxicity, particularly those that occur during discharges in the presence of oxygen and hydrogen atoms (water). Table 2 reports some decomposition products of SF_6 as well as their toxicity depending on their tolerated quantity [2]. Among these byproducts, $S_2O_2F_{10}$ and HF are very toxic in addition to being very corrosive.

Table 2. Toxicity of some byproducts resulting from the decomposition of SF_6 [2].

Gas	Toxicity	
	Tolerated Quantity (mg/m^3)	Degree of Toxicity
SF_4	0.1	Moderately toxic
SOF_4	2.5	Little toxic
SOF_2	2.5	Little toxic
SO_2F_2	5	Moderately toxic
SO_2	2	Moderately toxic
S_2F_{10}	0.025	Very toxic
SiF_4	2.5	Little toxic
HF	3	Moderately toxic

To reduce the amounts of SF_6 in HV apparatus, one solution consists of diluting it in N_2 or CO_2. Many investigations have been conducted on this topic. A well-documented synthesis on SF_6–N_2 mixtures has been published by L. G. Christophoru and R. J. Van Brunt [3]. These authors reported that such mixtures may help to reduce SF_6 rate of release into atmosphere from power-system applications and serve as an intermediate step in the environmental control of this gas. However this solution requires high pressure and does not eliminate the potential contribution of SF_6 to global warming.

Thus the various negative characteristics of SF_6, indicated above, have led the international community to designate it as a greenhouse gas (the 1997 Kyoto Protocol-COP3) and to regulate its use, encouraging at the same time research into new more environmentally friendly alternatives gases and the reduction of SF_6 emissions in the atmosphere [1]. Note that, despite a high GWP, it should be emphasized that SF_6 gas contribution to the global greenhouse effect is less than 0.3% because of its low concentration relative to CO_2 and this number is steadily decreasing.

Naturally, the initial investigations were focused on natural gases (N_2, CO_2 [4], and dry air [5]) and the halogenated products that have reduced GWP such as trifluoroiodomethane (CF_3I) [6], perfluorinated ketones [7], hydrofluoroolefins (HFOs) [8] and fluoronitriles [9]. The goal of such investigations was to identify new eco-friendly candidates with equivalent dielectric strength to SF_6.

Unfortunately, polyfluorinated gases have a high boiling point, which is a drawback for their use in low-temperature electrical apparatus applications. To overcome this shortfall, these halogenated gases are mixed with ordinary carrier gases such as dry air, N_2, or CO_2. Note that the substitute gas or gas mixture must be non-corrosive and must not interact with materials (insulating materials and metals) of the gas-insulated systems in which it is used.

The aim of this paper is to carry out a review of the main characteristics of the candidate gases and gas mixtures with a low environmental impact that have a potential to replace SF_6. This will allow better understanding of their performance under the conditions of electrical (especially the dielectric strength) and thermal stresses with the complex geometries encountered in GIS equipment.

2. Properties Required for Gas/Gas Mixture Substitutes

The properties required for the use of a gaseous dielectric in HV equipment vary according to the nature of the application and the operating conditions. The intrinsic properties are those inherent to the molecular structure and atomic physics of the gaseous molecule. These properties are independent of the application and environment where the gas is placed. The dielectric strength of the gas/mixture depends mainly on its capability to reduce the density of electrons that are generated when it is subjected to an electric field. For this purpose, the gas must be electronegative to reduce the number of electrons by attachment. This attachment capability is efficient up to an energy level of the electrons and is dependent on the temperature of the gas. Also, the gas must be able to slow down electrons to capture them efficiently at lower energies and thus avoid the generation of other electrons by impact ionization.

Before considering the use of a given insulation gas in industrial applications, it is necessary to understand the secondary process that covers the emission of electrons by impact of ions and photons on the surface of the cathode, with the photonic processes being a factor controlling the development of a discharge in a non-uniform electric field, ion–molecule reactions, dissociation under the action of collision decomposition, reactions with surfaces, and traces of impurities. Furthermore, the gaseous dielectric must also have a high saturation vapor pressure for low temperatures, high thermal conductivity to provide a cooling function, high specific heat, thermal stability at a temperature above 400 K over long periods of time, chemical stability and insensitivity to conductive or insulating materials, non-flammability, non-explosivity, and toxicity acceptable for industrial exposure including epidemiological effects (eco-toxicity, mutagenic or carcinogenic effects on health). If used as a mixture, the candidate gas must have thermodynamic properties suitable for uniformity of composition and separation of the mixtures.

As far as the extrinsic properties are concerned, the gas must not undergo extensive decomposition or polymerization, and no formation of carbon or other types of deposition. Independently, the gas must be ecologically compatible with the environment, not contribute to global warming or stratospheric depletion of ozone, and must not persist in the environment for long periods of time.

3. Perfluorocarbons (PFCs)

It is accepted that fluorinated compounds have the best insulation performance. This is helped by the presence of fluorine, a very electronegative element. In research efforts, particular attention was paid to some families of fluorinated molecules including perfluorocarbons (PFCs), which are gaseous halogen compounds of the fluorocarbon family (FC). These fluorinated electronegative gases are composed exclusively of carbon and fluorine atoms. The main PFCs proposed as gaseous dielectric are CF_4, C_2F_6 C_3F_8, and C_4F_8. These have high dielectric strength (breakdown voltage); Figure 1 gives the variation of the breakdown voltage versus the pressure—electrode gap product (P.d), i.e., Paschen curves of these gases [10]. Table 3 gives the main properties of these gases. Note that among these gases, C_4F_8 appears to be the most interesting from the point of view of the dielectric strength, which is 1.25 to 1.31 times higher than that of SF_6 [11]. However, its high liquefaction temperature makes

its use very difficult. Nevertheless, it remains a promising gas component for mixtures intended for gaseous insulation [12,13].
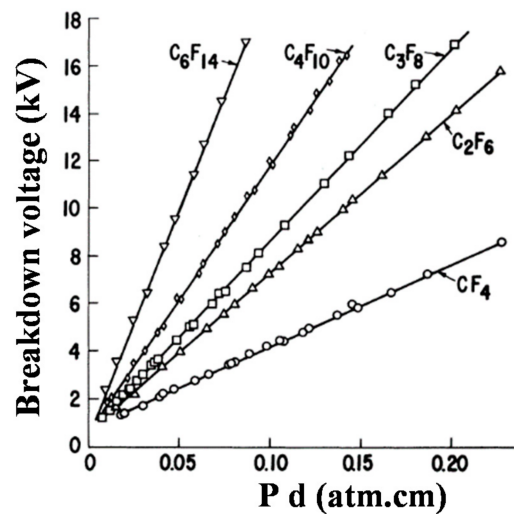

Figure 1. Paschen curves for some fluoroalkanes [14].

Most of these compounds generate corrosive and toxic decomposition products. To add to these undesirable properties, the GWP of PFCs and HFCs are in the high ranges from 5700 to 11,900 and from 9700 to 12,000, respectively [15], which makes most of these molecules not suitable as candidates as an insulation gas alternatives.

Table 3. The main properties of CF_4, C_2F_6 C_3F_8, and C_4F_8 [13,16]; the dielectric strengths of these gases is expressed in relative value with respect to that of SF_6, which is taken to be equal to 1.

Gas	Relative Dielectric Strength with Respect to SF_6	Toxicity	GWP for 100 Years	Lifetime (Years)	Boiling Temperature at 1 Bar ($°C$)
SF_6	1.0	Non-toxic	23,900	3200	−64
c-C_4F_8	1.11–1.80	Non-toxic	8700	3200	−6
C_3F_8	0.88	Non-toxic	7000	2600	−36,6
C_2F_6	0.67–0.90	Non-toxic	9200	10,000	−78
CF_4	0.39–0.62	Low-toxicity	6500	50,000	−128

To circumvent the problem associated with the high liquefaction temperature and to reduce the GWP, these fluorinated components can be mixed with buffer gases as CO_2 and N_2. Table 4 gives the boiling temperature and other characteristic parameters of the selected gases. Thus, many investigations have been conducted on the dielectric strength of the above gases when mixed with N_2 and CO_2 in different electrodes geometry under AC, DC, and lightning impulse voltages [11–13,17]. So, it was reported that to obtain 20% C_3F_8–80% N_2, equivalent to 20% SF_6–80% N_2 in terms of dielectric strength, a pressure of 1.25 times greater is required; the GWP of this mixture is 0.37 times that of 20% SF_6–80% N_2 [17]. Note that the breakdown voltage of C_3F_8 alone is comparable to that of SF_6. Under the same pressure, a proportion of 50% C_3F_8–50% N_2 is required for a GWP of 0.73 times that of the 20% SF_6–80% N_2 mixture. When it is desired to obtain 20% C_3F_8–80% N_2 comparable to 100% SF_6, always in terms of dielectric strength, the pressure must be increased by 1.59 times for a GWP of 0.009 times. It is a mixture that makes it possible to obtain a weak GWP. It is also a good candidate to replace SF_6 within reasonable pressure ranges.

Table 4. Some properties of other selected gases [14].

Gas	Relative Dielectric Strength with Respect to That of SF_6	Toxicity	GWP	Boiling Temperature [°C]
SF_6	1.00	Non-toxic	23,900	−64
Air	0.37–0.40	Non-toxic		0
Ar	0.04–0.10	Non-toxic		−186
C_2ClF_5	0.92–1.16	Relatively non-toxic	9300	−39
C_2F_5CN	1.80–1.85	Highly toxic		−32
C_3F_7N	2.20–2.33	Toxic		−2
CCl_4	1.33–2.32	Toxic	1400	78
c-ClF_3	0.47–0.58	Low toxicity	11,700	−81
CF_3CN	1.34–1.40	Highly toxic		−62
CF_3NO_2	1.34	Toxic		−31
CF_3NSF_2	2.05	Toxic		−6
CO	0.40	Toxic	1–3	−19
CO_2	0.32–0.37	Non-toxic	1	−79
H_2	0.20	Non-toxic		−253
He	0.02–0.06	Non-toxic		−269
N_2	0.34–0.43	Non-toxic	0	−196
N_2O	0.50	Non-toxic	320	−89
Ne	0.01–0.02	Non-toxic		−246
SeF_6	1.10	Toxic		−64
SO_2	0.52–1.00	Toxic		−10
SOF_2	1.00–1.42	Very irritating		−44

Also, to obtain a 20% C_3F_8–80% CO_2 mixture comparable to 20% SF_6–80% N_2 in terms of dielectric strength, a pressure of 1.35 times greater is required for a GWP of 0.40 times that of SF_6–N_2 [17]. At the same pressure, a proportion of 60% C_3F_8–40% CO_2 mixture is required with a GWP of 0.87 times. Finally, to obtain a 20% C_3F_8–80% CO_2 mixture comparable to pure SF_6, a pressure of 1.69 times greater is necessary, which lowers the GWP by 0.10 times. The C_2F_6 alone has a breakdown voltage of 76% that of SF_6. To obtain 20% C_2F_6–80% N_2 comparable to 20% SF_6–80% N_2 in terms of dielectric strength, the pressure must be 1.35 times greater for a GWP of 0.52 times that of SF_6-N_2. To obtain the same gas mixture equivalent to pure SF_6, the pressure must be 1.69 times greater, for a GWP of 0.13 times that of SF_6–N_2 [17]. All this shows that C_2F_6–N_2 is better than SF_6 from the GWP point of view, but seems slightly less realistic than C_3F_8–N_2 in terms of gas pressure. To obtain a 20% C_2F_6–80% CO_2 mixture comparable to 20% SF_6–80% N_2 in terms of dielectric strength, the pressure must be increased by 1.49 times for a GWP of 0.58 times that of SF_6–N_2. And to obtain the same proportions of the previous mixture comparable to 100% SF_6, the pressure must be 1.89 times greater, which lowers the GWP by 0.15 times.

The breakdown voltage of C_2F_6 is lower than that of C_3F_8 and SF_6. Among these gases, the 20% C_3F_8–80% N_2 mixture has attracted a lot of attention because it not only reduces GWP below 1/10 compared to SF_6–N_2 but also gives good dielectric properties without the addition of SF_6. For this mixture, the required gas pressure is 0.79 MPa (realistic value) and the obtained GWP is 9.3%.

It has also been reported that the 2-C_4F_8–N_2 mixtures constitute promising substitutes for SF_6 [18]. Such mixtures have extremely low GWP in comparison to SF_6. However, for outdoor application down to low temperatures, 2-C_4F_8 mixtures might not be possible due to the liquefaction.

Although this paper is mainly focused on gases/mixtures without SF_6, the SF_6–CO_2 mixture has to be underlined. Indeed, this mixture has been successfully applied in outdoor circuit breakers designed in Manitoba (Canada) [19]. An equally proportioned SF_6–CF_4 mixture (50–50%) makes it possible to obtain excellent arc extinguishing properties and reduce the liquefaction temperature. Berg [20] showed that AC and impulse breakdown voltages in a quasi-uniform field (sphere-sphere electrodes) increases when SF_6 content is increased. These results have been confirmed by the experimental studies carried out by Kuffel and Toufani [21] at 60 Hz alternating voltage (AC), DC (for both polarities), and

impulses in a highly non-uniform field, with SF_6–CF_4 mixtures and percentages of SF_6 varying from 0 to 100% at a pressure of 0.3 MPa. The breakdown voltage of the SF_6–CF_4 mixture (SF_6 content ranging from 0 to 100%) in a highly inhomogeneous field increases under DC (+) and AC voltages when a few percent of SF_6 is added. This effect is more pronounced for large inter-electrode distances when the divergence of the field increases and stabilization of the corona effect can occur, leading to high breakdown values. Under impulse voltage without stabilization of the corona effect, the breakdown voltage increases almost linearly with the percentage of SF_6. Note that theoretical analyses have been conducted on the synergism in the dielectric strength for SF_6–CF_4 mixtures [22] and assessment of electron swarm parameters and limiting electric Fields in SF_6 + CF_4 + Ar gas mixtures [23].

However, it is important to note that the use of the SF_6–CF_4 mixture in practice requires special attention because the combination of these two compounds could increase the rate of decomposition. Moreover, in countries where the moisture content is very high, it is possible that the formation of the HF compound could lead to high corrosion. Although the decomposition rate of CF_4 is unlikely to be greater than that of SF_6, it could lead to carbon deposition. As for the formation of the HF compound, due to a very high humidity level, the presence of water in SF_6 or in equipment insulated with SF_6–CF_4 mixtures should be avoided at all costs.

Although molecules without the fluorine atom do not have the same dielectric characteristics, several gases such as N_2, CO_2, air, H_2, and CH_4 allow good stabilization and extinguishing of the electric arc. H_2 and CH_4 are unusable because of the danger of explosion in case of electrical discharge. Carbon dioxide (CO_2) has a 35% insulation capability compared to that of SF_6. CO_2 has some advantages compared to N_2 or air due to its better current interruption capabilities. Its reduced dielectric strength can be compensated for either by increasing the operating pressure or by enlarging the dimensions of the high-voltage equipment.

4. Natural Gases: N_2, CO_2, and O_2

These are freely available in the atmosphere and are abundant poly-atomic gases; Table 5 gives a typical composition of atmospheric air. They are commonly used at high pressure as insulating materials and as a medium for extinguishing the electric arc in HV switches. It should be noted that CO_2 and N_2 are the most environmentally suitable candidates given their low ozone depletion potential (ODP). Table 6 gives the dielectric strength of these gases [24].

Table 5. Chemical composition of dry air.

Components	Molar Fraction (% in Volume)
Nitrogen (N_2)	78.09
Oxygen (O_2)	20.95
Argon (Ar)	0.93
other gases	0.03

Table 6. Comparison of breakdown voltages of natural gases with SF_6.

Gas	N_2	CO_2	SF_6
Breakdown voltage [kV/cm.bar]	32.9	30.1	89.0
GWP for 100 Years	0	1	23,900

In practice, the dry air insulation and mixtures of N_2-O_2 (80% N_2–20% O_2, 60% N_2–40% O_2 and 40% N_2–60% O_2) under lightning impulse voltages exhibit better performance (dielectric strength) than those of N_2 or CO_2 on their own [25]; and the dielectric strength under positive lightning impulse voltages for dry air, CO_2, N_2, and their mixtures are higher than the negative ones. Also, the dielectric strength of N_2 and N_2–CO_2 mixtures increases quasi-linearly with pressure up to 1.6 MPa under

lightning impulse voltage (LI) [4]. This quasi-linearity has been also observed for N_2 and CO_2 in AC, DC, and lightning impulse voltages by Beroual and Coulibaly [26].

On the other hand, the dielectric strength of CO_2 is higher than that of N_2 under impulse voltage [27]. Unlike for CO_2, the dielectric breakdown in N_2 occurs on the tail of the lightning impulse. This phenomenon can be explained by the electropositive nature of N_2. Indeed, CO_2 is a low electronegative gas, attaching when the electrons have an energy in the range of 7–9 eV or 20–50 eV. The mechanisms of generation of the first avalanche are different for carrier gases, which are weakly attaching or non-attaching (CO_2 and N_2). Under negative impulse voltage and for non-uniform fields, electrons generated at the cathode surface immediately enter the intense electric field (cathode). However, most of the free electrons generated in the low electric field zone have lower energy and velocity so that their attachment to CO_2 molecules is easier. Therefore, additional energy is required to cause the growth of the electronic avalanche in such cases. In addition, it was found that CO_2 breakdown values are stable and reproducible, and represent less dispersion than those of N_2 [4]. In contrast to SF_6, the total attachment of electrons in dry air is extremely low, especially at low energy (0–1 eV). This is due to the effective cross-section of O_2 being small and N_2, which is the main component of the air (see Table 5), being an un-attaching gas for electrons. On the other hand, an 85% CO_2/15% O_2 mixture shows a marked improvement of more than 15% compared with CO_2 in a divergent field under positive polarity [27].

Extensive experimental testing has demonstrated that CO_2 exhibits better repeatability of dielectric performance compared with N_2 [4,25]. This is an influencing parameter that should be taken into account during the design process.

It appears from the above that pure CO_2 gas and/or its mixtures are suitable candidates for insulation in HV equipment. The dielectric strength can be improved by increasing the gas pressure to obtain a gas/gas mixture having the same static breakdown voltage as that of pure SF_6; CO_2 pressure needs to be three times than that of SF_6 to achieve the same level of insulation performance. It should be emphasized that, with the increase of the working pressure in GIS, a new dimensioning of the mechanical structure would be required to withstand the higher pressure. Thus, the economic impact of such a solution needs to be taken into account.

5. Trifluoroiodomethane (CF_3I) and Mixtures CF_3I/CO_2

Trifluoroiodomethane (CF_3I) has excellent dielectric properties equivalent to SF_6. Its GWP is of the same order as CO_2, and its ozone depletion potential is less than 0.08 [28]. In addition, it has a very short life time in the atmosphere (less than one day), and hence is considerably more environmentally friendly. It is a colorless, non-flammable electronegative gas. Its molecular geometry is given in Figure 2. It has a molecular weight of 195.91 g/mol. However, CF_3I has a boiling point of about $-22.5\ ^\circ C$, which is not suitable for use in cold regions. Table 7 lists the main properties of this chemical element.
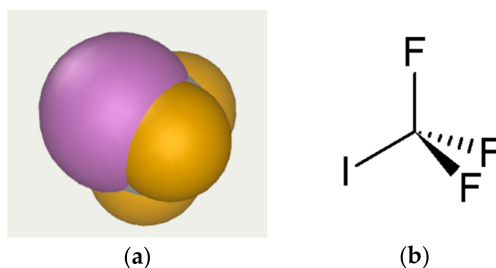

(a)   (b)

**Figure 2.** Topology (**a**) and formulation (**b**) of trifluoroiodomethane.

Table 7. Physical and chemical properties of CF_3I [29,30].

Physical and Chemical Properties	CF_3I
Molecular weight (g/mol)	195.91
Vapor density (air = 1)	6.9
Boiling point (°C)	−22.5
liquefaction pressure at −20 °C (MPa)	0.11
Thermal conductivity at 1.013 bar and 0 °C (mW/mK)	6.594
Viscosity (Cp)	0.2361
Specific heat at constant pressure of 1 bar [kJ/(mol.K)]	0.031
Convection heat constant	20.0
Critical value E/N	437 Td

Table 8. Toxicological data for CF_3I [32].

Gas	Toxicology	CF_3I
	Non-toxic Dose (NOAEL)	2000 ppm
Toxicity	Observable minimum dose of toxic effect (LOAEL)	4000 ppm
	Lethal concentration 50 (LC_{50})	27.4%/15 min

CF_3I is a moderately toxic gas [31]; it is classified as a mutagen type 3 [32]. Table 8 gives the toxicity indicators and their values for CF_3I. However, these properties are being investigated again to examine the evidence presented before. Indeed, the C–I bond of the molecule is easily dissociable even at a low intensity of radiation in the UV or visible region. Consequently, CF_3I produces di-iodine I_2 (acute toxicity) by decomposition, following the appearance of a partial discharge or an electric discharge [33]. If not adequately taken care of, the production of di-iodine can cause pollution of the HV apparatus and considerably affect the interruption (extinguishing) capacity and the dielectric strength of the gas.

$$2CF3I \rightarrow 2CF3 + 2I \rightarrow C2F6 + I2$$
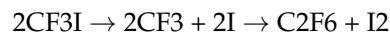
CF_3I has better insulation properties than SF_6, both in uniform and non-uniform electric fields. The critical field of CF_3I is about 1.2 times higher than that of SF_6.

Because of its high liquefaction temperature, this gas cannot be used on its own in HV equipment. Indeed, its boiling point is 25 °C at 0.5 MPa which is the SF6 filling pressure in GIS. That is why it is used with a gas buffer such as CO_2. Such a mixture (CF_3I/CO_2) has very good insulation performance. Its breakdown voltage increases linearly with the molar fraction of CF_3I. A 60% mixture of CF_3I with CO_2 has similar insulating characteristics to pure SF_6 (Figure 3a,b) [34]. The dielectric strength of the CF_3I/CO_2 mixture (30%/70%) is 0.75 to 0.80 times of that of pure SF_6. With this gas mixture, good insulating properties have been demonstrated. Further investigation of its interruption capability needs to be undertaken. Figure 4 shows the effective ionization coefficients of CF_3I and its mixtures compared with SF_6 and air. It clearly shows the suitability of the dielectric insulating properties of CF_3I mixtures.
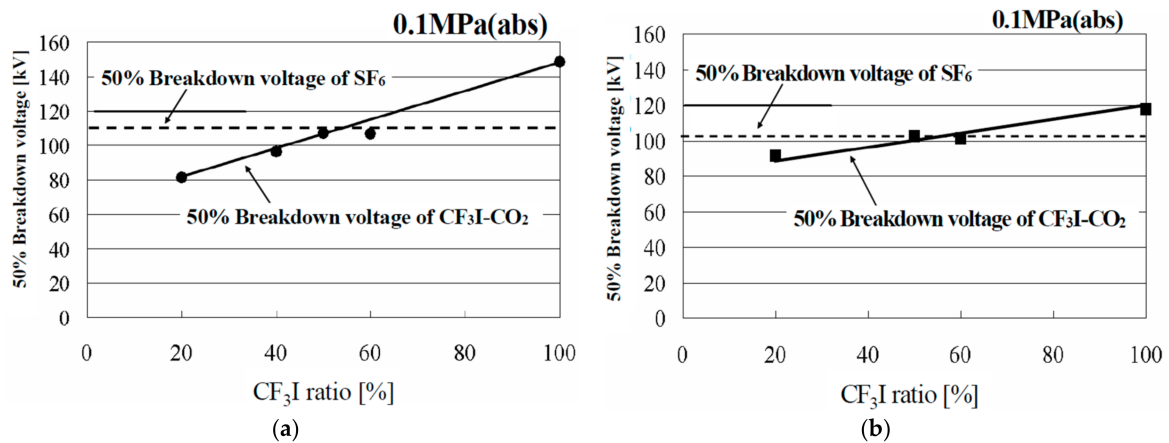
Figure 3. Breakdown voltage characteristics of CF_3I-CO_2 mixtures in a sphere-sphere electrodes geometry in positive (**a**) and negative (**b**) polarity: the diameter of sphere is 50.8 mm and the electrode gap is 10 mm [34]; the *y*-axis indicates the absolute values of 50% breakdown voltage.
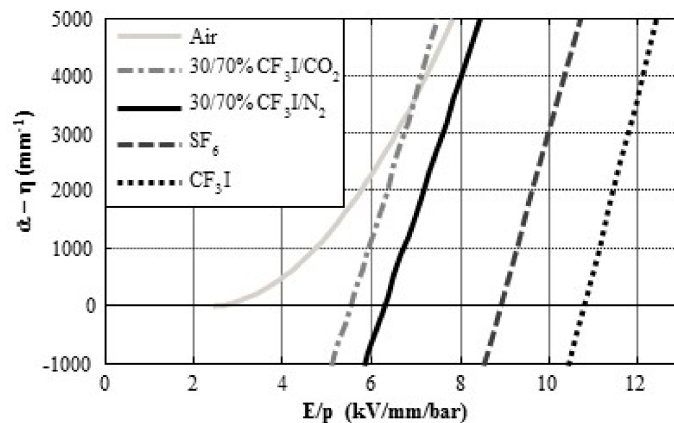

Figure 4. Effective ionization coefficients in various gases (Air, SF_6 and CF_3I,) and gas mixtures (30/70% CF_3I/N_2 and 30/70% CF_3I/CO_2) [35].

6. Fluoroketones (FKs) and Fluoroketone Mixtures

The fluoroketones (FKs) or perfluorinated ketones have a crude formula of the form $C_nF_{2n}O$, in which n is an integer ranging from 3 to 8 (Figure 5). Table 9 summarizes the important characteristics of two perfluorinated ketone candidates.
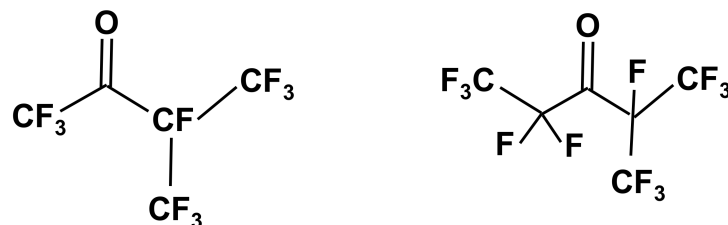

Figure 5. Molecular structure of two fluoroketones, $C_5F_{10}O$ (**left**) $C_6F_{12}O$ (**right**).

Table 9. Physicochemical and environmental properties of two fluoroketones [36,37].

Molecules	$C_5F_{10}O$	$C_6F_{12}O$
Molecular weight (g/mol)	266.04	316.04
Density (g/cm^3)	1.55	1.723
Boiling point (°C)	24	49.2
Saturated vapor pressure at 0 °C (mbar)	350	100
Saturated vapor pressure at 20 °C (mbar)	800	326
GWP	1	1
ODP	0	0
Atmospheric lifetime (years)	-	0.014
Flammability	non-flammable	non-flammable
Chemical stability	stable (SF_6 inert)	stable
Intrinsic dielectric strength (kV/mm.bar)	18 (8.7 for SF_6)	23.5

The vaporization of perfluoroketone is obtained above 24 °C. Because of this high boiling point, the gaseous state of this chemical element is maintained at a pressure lower than atmospheric pressure. Fluoroketones can only be used as an additive at a pressure below the saturated vapor pressure (Figures 6 and 7). Indeed, by adding fluorine (halogen element) in the chemical formulation, the dielectric strength of the complex molecule is improved. In contrast, the boiling point increases considerably. Therefore, this gaseous compound cannot be used alone for insulation applications where the operating temperature of the GIS may drop to −30 °C or below.

(**a**)   (**b**)
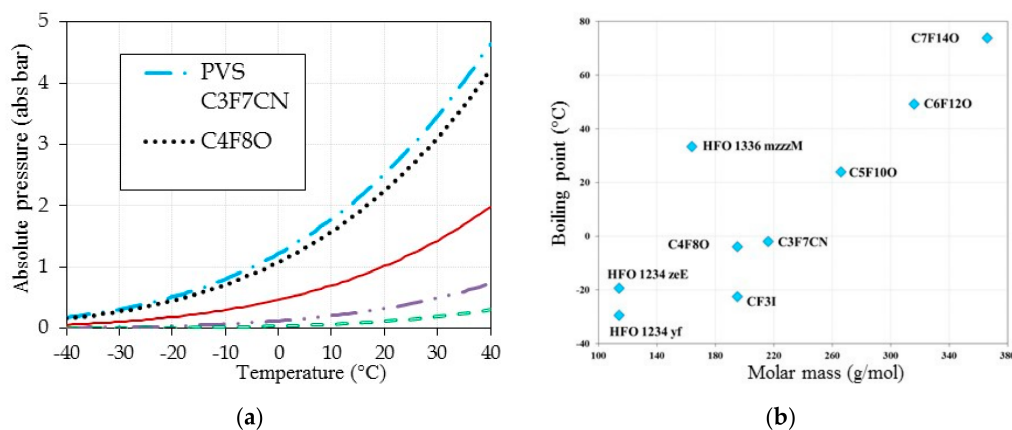
Figure 6. (**a**) Graph of the saturated vapor pressure as a function of the temperature of some complex fluorinated gases; (**b**) dependence of the boiling point on the molar mass of selected gas molecules [38].
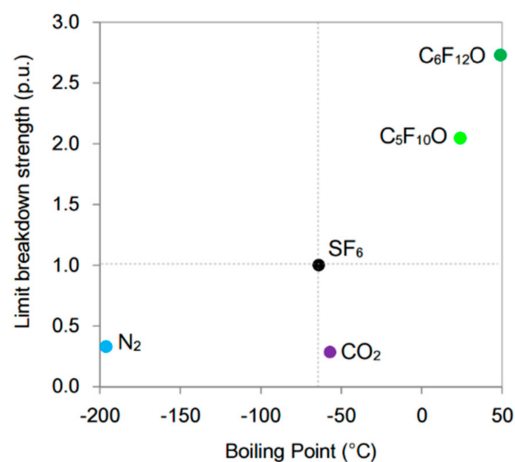
Figure 7. Relative dielectric strength as a function of boiling temperature at 1 bar [39].

A mixture with a low concentration of a fluoroketone and a buffer gas results in an improvement of the dielectric strength. The analysis of the effective ionization coefficients in C_4F_8O/CO_2 and C_4F_8O/N_2 mixtures shows a strong dependence of the effective ionization coefficient on the complex gas density [39]. For high values of gas density, the improvement of the attachment properties of complex molecules can be explained by the three-body electron attachment mechanism [40]. The critical reduced electric field varies linearly as a function of the C_4F_8O content for low concentrations. It is also important to take into account the slope of the straight line in the ionization zone in the vicinity of the critical value which corresponds to a zero effective ionization coefficient [40]. The slope plays a role in determining the limit value of the sensitivity of the gas mixture to the surface condition (state) of the electrodes (roughness, particles, etc.). The sensitivity value (pressure $\times$ defect height) is inversely proportional to the slope of ionization line (straight). Also, the increase of the attachment rate in the vicinity of the critical field is important for evaluating and comparing the potential of the gas mixture.

The fluoroketones do not exhibit, after ionization in plasma state, a capability to recompose analogous to that present in SF_6, and therefore the quantity of fluoroketone, which is initially present in the gaseous state in an extinguishing apparatus of an electric current, decreases as the number of extinctions achieved by this apparatus increases. Fluoroketones $C_5F_{10}O$ and $C_6F_{12}O$ are substantially non-toxic in the pure state (Table 10) and present high insulation capabilities, in particular a high dielectric strength (or breakdown field strength), and at the same time an extremely low global warming potential (GWP) can be obtained [36,41,42].

In a systematic dielectric test performed on all FKs in different mixtures, Hyrenbach et al. [43] showed that, thanks to a 20 °C lower boiling point, the C5 FK gas mixture's dielectric performance is superior compared to the C6 FK mixture. C4 FK mixtures have shown even better results; however, those mixtures have to be excluded due to their toxicity profile. The dielectric performance of the C5 FK gas mixture is not as good as 100% SF_6. Only 12% of the gas mixture is C5 FK.
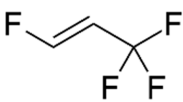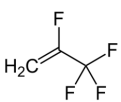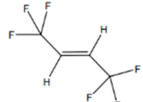
Table 10. Toxicological data of some perfluorinated ketones [44].

Perfluorinated Ketones	$C_5F_{10}O$	$C_6F_{12}O$	C_4F_8O	SF_6
TWA (ppm)	100	150	0.1	1000
Lethal concentration 50: LC_{50} (ppm)	20,000	>100,000	200	>100,000

7. Hydrofluoroolefins (HFOs)

The general formula of HFO gases is $C_n(H,F)_{2n}$. These are synthesized molecules of the hydrofluoroolefin family such as HFO-1234ze and HFO-1234yf, or HFO-1336mzz-Z. They have good dielectric strength properties, and their GWP is less than 9; the insulation properties of HFO-1234ze are closed to SF_6, with a dielectric strength in the range comprised of 0.8–0.95 that of SF_6. Table 11 summarizes the physicochemical properties of the hydrofluoroolefins candidates.

Table 11. Important properties of hydrofluoroolefins candidates [45,46].

Hydrofluoroolefin	HFO-1234ze	HFO-1234yf	HFO-1336mzz-Z
Boiling point	−19.4 °C (0.42 MPa @ 20 °C)	−29.4 °C	33.4 °C (453 torr @ 20 °C)
Molar mass (g/mol)	114.04	114.04	164
Dielectric strength (% SF_6)	85	-	220
Toxicity (LC_{50} 4 h/rat, ppm)	>200,000	>400,000	>102,900
GWP	6	4	8.9
flammability	flammable	flammable	flammable
Long term stability	stable	stable	stable
Molecular structure			

The performance of a hydrofluoroolefin is dictated by its large molecule, i.e., it has a large number of carbon and fluorine atoms, and the molecule is branched. However, the larger the hydrofluoroolefin is, the higher its liquefaction temperature will be, i.e., its saturated vapor pressure (SVP) at a given temperature is low; the gas liquefies already at around 0.42 MPa at room temperature. One of the downsides of HFO 1234 yf is its extremely flammable nature and, for HFO-1336mzz-Z, the high boiling point and the very limited SVP are crucial. For this reason, HFO-1234ze is chosen because it is nonflammable. HFO-1234ze can probably be used in its pure state for replacing SF_6 in medium-voltage applications (MV); the operating temperature is limited to -15 °C. On the other hand, mixtures of HFO-1234ze with other dilution gases such as nitrogen, carbon dioxide, or dry air are required for high- and medium-voltage applications at lower operating temperatures. However, HFO-1234ze is characterized by a high dielectric strength, $(E/N)_{critic}$, which is highly dependent on the pressure [47]. The attachment performance of the HFO-1234ze increases gradually with the increasing pressure of the pure gas [48]. The critical stationary value $(E/N) = 305$ Td (recall that 1 Td $= 10^{-21}$ V.m^2), which corresponds to 85% of that of SF_6, is obtained for pressures greater than 0.165 MPa.

Moreover, these molecules decompose in atmosphere to form trifluoroacetic acid (TFA), which is an extremely persistent substance that accumulates in nature without decomposing. On the other hand, a ternary mixture (HFO-1234ze, $C_5F_{10}O$, buffer gas) in gaseous form, which is suitable for low-temperature applications, improves the dielectric strength. However, because the molecules of fluoroketones and hydrofluoroolefins are very similar in composition, the generation of a liquid phase at a temperature above the liquefaction temperature of the gases in contact is noted and explained by Raoult's law. In addition, following a flashover in HFO1234ze, a carbon deposit appears on the solid insulation; this conductive layer can short-circuit the insulator support in GIS equipment.

8. Fluoronitriles and Fluoronitriles Mixtures

Heptafluoro-iso-butyronitrile or fluoronitrile gas belongs to the family of the fluorinated nitriles of the general formula $C_nF_{2n+1}CN$. The fluoronitrile dielectric fluid was synthetized, patented, and commercialized by 3M^{TM} Company (Saint Paul, MN, USA) under the name of NOVEC^{TM} 4710 according to the molecular model $(CF_3)_2CFCN$ shown in Figure 8 [49]. Unfortunately, fluoronitrile has a high liquefaction temperature. Given the minimum temperature at which the MV or HV equipment has to operate, for example -30 °C for temperate zones, the maximum absolute pressure without liquefaction of fluoronitriles (measured at 20 °C) is limited to 0.31 bar abs. Therefore, due to their high boiling point, fluoronitriles should be mixed with other buffer gases such as CO_2, dry air, or N_2. Fluoronitrile gas mixtures could form an ideal compromise between dielectric performance and minimum operating temperature of the apparatus while providing a considerable reduction of the environment impact.
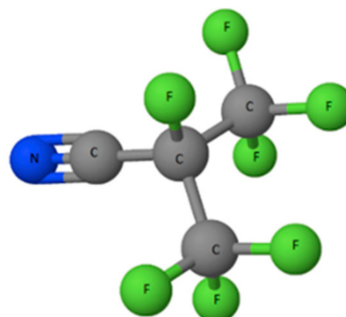

Figure 8. 3D representation of fluoronitriles $(CF_3)_2CFCN$ dielectric fluid.

The mixing of fluoronitriles with CO_2 is an effective technique that enables us to obtain optimized insulating properties combining the advantageous features of each component: the high dielectric

strength of NOVEC^{TM} and the low boiling point of CO_2. Therefore, to obtain a given gas mixture for a minimum operating temperature, the partial pressure of the fluoronitriles compound is adjusted to avoid liquefaction. Furthermore, the desired dielectric strength is obtained by adding a sufficient proportion of carbon dioxide. Figure 9 illustrates the variation of the saturating vapor pressure of the studied fluids versus the temperature.
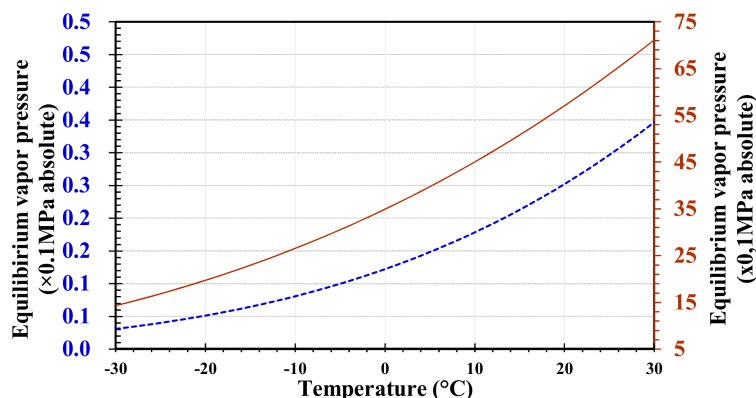

Figure 9. Saturating vapor pressure of fluoronitriles (left vertical axis) and CO_2 (right vertical axis) vs. temperature.

Fluoronitrile gas compound is a polar gas that has a specific mass of 8.11 kg/m^3; its purity is greater than 98.54%. It is odorless, highly electronegative, colorless, and chemically stable up to a temperature of about 700 °C (the appearance temperature of carbon monoxide) [50]. Tables 12 and 13 summarize the basic chemical and physical properties of fluoronitriles. Figure 10 gives the main degradation products and thermal stability of the dielectric fluid $(CF_3)_2CFCN$ analyzed by infrared spectroscopy (FTIR) [51]. Carbon monoxide is the main decomposition product; its dielectric strength is about 40% of that of SF$_6$ [51].

Table 12. Important properties of $(CF_3)_2CFCN$ [52].

Boiling Point	−4.7 °C
Molar mass (g/mol)	195.04
Molecular weight (kg)	3.238×10^{-25}
Molecular volume (Bohr^3)	932.985
Corrosion	Non-corrosive for common materials (Hard Metals and Plastics)
Flammability	Non-flammable
Long-term stability	Stable up to 700 °C
Toxicity (LC 50 (rat))	>10,000 and <15,000
No Observed Toxic Effect Level (NOAEC)	500 ppm for an exposure of 6 h/day (5 days/week for one month)
Occupational Exposure Limits (VLEP)	65 ppmv (5000 ppmv for CO_2)

Table 13. Physicochemical properties of some gases [45].

Physicochemical Properties	$(CF_3)_2CFCN$	SF$_6$	CO_2
Liquefaction pressure at −30 °C (MPa)	0.0311	0.52	1.43
Electrostatic Dipole μ (D)	1.51	0	0
Number of electrons	77	48	16
Static electronic polarizability α (10^{-30}m^3)	9.03	4.48	2.59
Vertical ionization energy ε_i^v (eV)	12.31	14.27	13.74
Adiabatic ionization energy ε_i^a (eV)	11.62	14.21	13.73
Vertical electron affinity ε_a^v (eV)	0.43	−1.33	3.5
Adiabatic electronic affinity ε_a^a (eV)	−1.05	−1.06	0.6

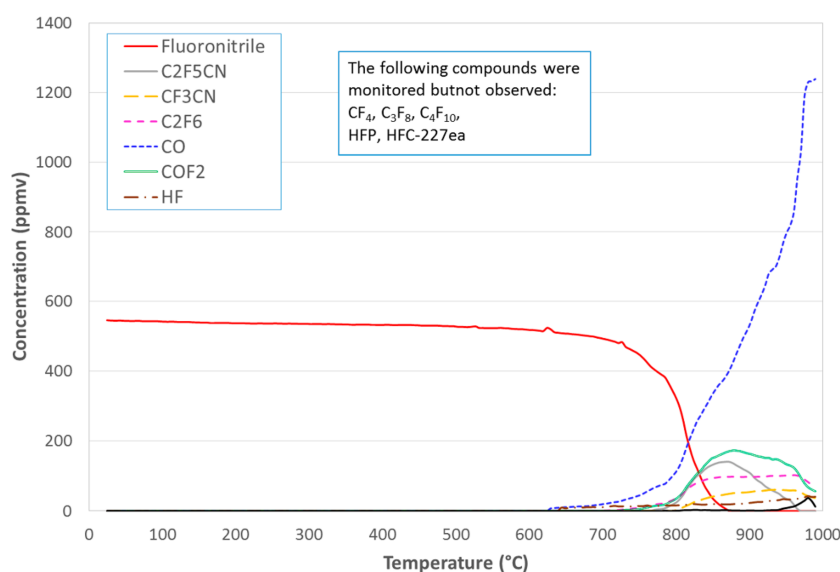**Figure 10.** Degradation byproducts and thermal stability of the dielectric fluid $(CF_3)_2CFCN$ analyzed by infrared spectroscopy (FTIR) [50].

The global warming potential (GWP) of fluoronitrile gas, computed according to Regulation (EC) No. 842/2006 of the European Parliament and of the Council of 17 May 2006, is less than 2400 [1] and its ozone depletion potential (ODP) is zero. For example, the 4% fluoronitriles/96% CO_2 mixture has a GWP that is 98.4% lower than that SF_6.

The mixtures of fluoronitriles with CO_2 are classified in the lowest risk category according to Regulation (EC) No. 1272/2008 of the European Parliament and of the Council of 16 December 2008 on the classification, labeling, and packaging of substances and mixtures [53]. Indeed, the calculated lethal CO_2 concentration is above 300,000 ppmv, and it is 12,000 ppmv for fluoronitriles [53]. The recent tests and analysis performed on the NOVEC 4710 conclude that this gas is not CMR (Carcinogens Mutagenic Reprotoxic) and the TLV TWA (Threshold Limit Values Time Weighted Average) is equal to 65 ppm [54]. Table 14 summarizes the toxicity of degradation products of Fluoronitriles and Table 15 summarizes the main characteristics of fluoronitrile gas compared with SF_6 and CO_2.

Table 14. Toxicity of degradation products of fluoronitriles [54].

Gas	Toxicity	LC_{50} (ppm) [38]	GWP
C_2F_5CN	Very toxic	-	
CF_3CN	Very toxic	500 (1 h mouse)	
C_4F_6	Very toxic	82 (4 h mouse)	
CO	Extremely toxic at 10 mg	1807 (4 h mouse)	
COF_2	Extremely toxic for 8 h exhibition [35]	-	
HF	Very toxic	483 (4 h mouse)	
C_2N_2	Very toxic	350 (1 h mouse)	
C_4F_8	Extremely toxic	0.5 (4 h mouse)	8700

Recent studies have shown that fluoronitriles mixed with a buffer gas such as N_2 or CO_2 could be a potential alternative to SF_6 [54]. Such mixtures represent an ideal compromise between the operating temperature, the global warming potential, and a dielectric strength that is comparable to that of SF_6. The fluoronitrile/CO_2 mixture was presented for the first time at CIGRE 2014 by Alstom Grid (Villeurbanne, France), now GE Grid Solutions (Villeurbanne, France), and at CIRED 2015 as a candidate gas to replace SF_6 for HV switchgear insulation [55–57].

Table 15. Fundamental physical and chemical characteristics of some gases [9].

Gases	Fluoronitriles NOVEC^{TM} 4710	SF$_6$	CO$_2$
Boiling point at 760 torr [°C]	−4.7	−63	−79
Relative dielectric strength (% of SF$_6$)	>200	100	32~37
Toxicity (LC 50 (rat))	>10,000 and <15,000	>500,000	>300,000
Corrosion	Non-corrosive towards materials of construction	Non-corrosive	Non-corrosive
Flammability	No	No	No
Long term stability	stable	inert	Inert
Liquefaction pressure at −30 Celsius (MPa absolute)	0.0311	0.52	1.43
GWP (IPCC 5th)	2400 [11]	23,500	1

The fluoronitrile has a dielectric strength 2.7 times greater than that of SF$_6$ in uniform field [58] for both AC and DC voltages. The ratio $V_{Fluoronitriles}/V_{SF6}$ decreases for divergent fields, in particular for the positive impulse voltage. Figure 11 depicts examples of the breakdown voltage characteristics for sphere-to-sphere and rod-to-plane electrodes configurations.
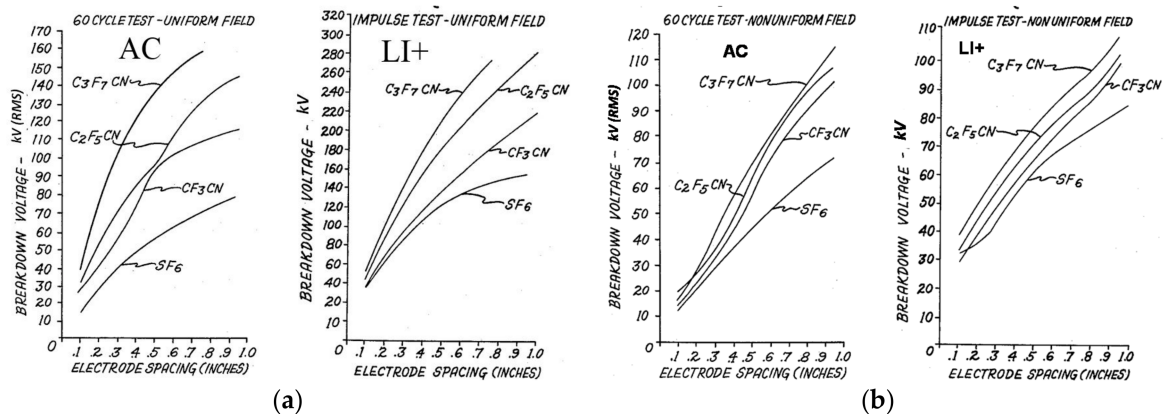

Figure 11. Dielectric performances of fluorinated nitriles [59]: (**a**) Configuration: sphere-sphere (diameter = 1 inch); (**b**) configuration: rod (d = 0.1 inch)-sphere (D = 1 inch).

Experiments conducted on gas mixtures consisting of CO$_2$ and fluoronitrile Novec^{TM} 4710 in concentrations ranging 3.7 to 20% with different electrode geometries (namely plane-to-plane, sphere-to-sphere, sphere-to-plane, and rod-to-plane; and different field utilization factors), under AC and lightning impulse (LI) voltages show that in a quasi-homogeneous electric field, the equivalent dielectric strength with 0.1 MPa SF$_6$, at identical total pressure, is reached by a mixture containing 20% fluoronitriles [58]. The 3.7% fluoronitriles/96.3% CO$_2$ mixture constitutes a good compromise and an appropriate gas mixture for high-voltage apparatus insulation in view of the pressure and low ambient temperature applications (−30 °C). This compromise takes into account different criteria including the working pressure and temperature as well as the environmental impact (global warming potential). This mixture, in a uniform electric field, reaches 72% of the dielectric breakdown of pure SF$_6$ at 5.5 bar absolute. In homogeneous and quasi-homogeneous fields, equivalences to 0.55 and 0.65 MPa SF$_6$ are obtained with 3.7% Fluoronitriles/96.3% CO$_2$ mixtures at 0.88 and 1.04 MPa total pressure, respectively, and lead minimum operating temperatures of −30 and −25 °C, respectively.

Figure 12 depicts the variation of AC breakdown voltage of SF$_6$ and two fluoronitriles/CO$_2$ mixtures as a function of electrode gap distance at 0.1 MPa abs (absolute pressure) in a sphere-to-sphere electrode arrangement referred to the equivalent breakdown (BD) in uniform configuration using the field utilization factor. Figure 13 gives the negative LI breakdown voltages of 3.7% fluoronitriles/96.7% CO$_2$ mixture and pure SF$_6$ at different pressures as a function of the sphere-to-plane electrodes gap.
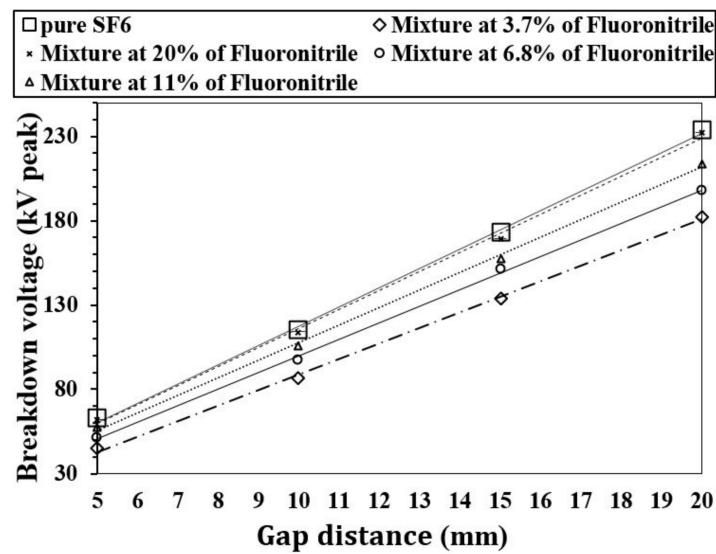
Figure 12. AC breakdown voltage of fluoronitrile/CO_2 mixtures, SF_6 at 0.1 MPa and 20 °C, in sphere-to-sphere configuration referred to plane-to-plane configuration [58].
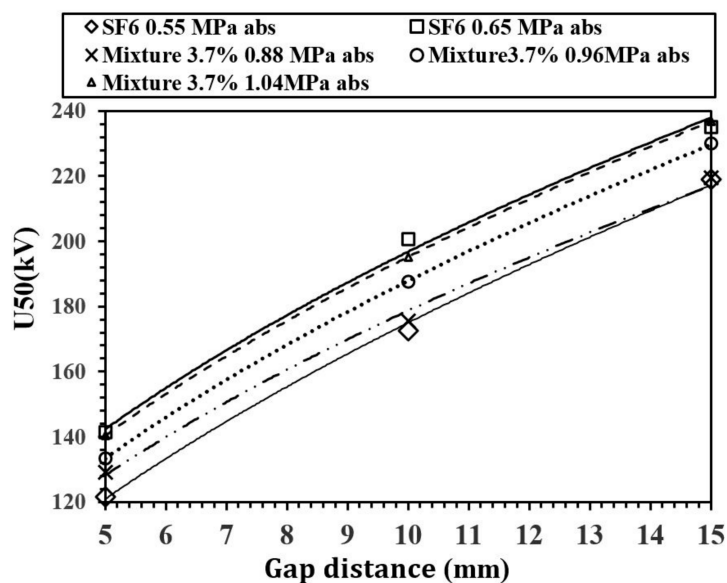

Figure 13. Negative LI breakdown voltages of 3.7% fluoronitriles/96.7% CO_2 mixture and pure SF_6 at different pressures versus the sphere-to-plane electrodes gap [58].

Thus, the addition of a small amount of fluoronitriles (a few percent by volume) to carbon dioxide (CO_2) results in an appreciable improvement of the breakdown voltage compared to CO_2 (3 times lower than SF_6) [60]. At atmospheric pressure, a mixture at a percentage of 20% reaches the same dielectric performance as pure SF_6. This mixture offers the possibility to be used below −30 °C without liquefaction and, as such, constitutes an interesting possibility for replacing SF_6 as a dielectric medium in MV switchgear.

9. Conclusions

In this paper, an overview of research into new eco-friendly candidates for replacing SF_6 has been presented. The main properties of natural gases and potential candidates have been discussed. These latter include trifluoroiodomethane (CF_3I), perfluorinated ketones, octafluorotetra-hydrofuran,

hydrofluoroolefin (HFOs), and fluoronitriles. One of the main drawbacks of these polyfluorinated gases is their high boiling point, which limits their use in low-temperature electrical apparatus applications. To overcome this shortfall, these halogenated gases are mixed with buffers (ordinary carrier gases) such as dry air, N_2, or CO_2. Such mixtures could form an ideal compromise between dielectric performance and the minimum operating temperature of the apparatus while providing a considerable reduction in the environment impact.

Through this synthesis, the following points are highlighted:

- The use of dry air, nitrogen, and carbon dioxide requires a significant increase in the pressure and size of equipment. In case of surface defects in equipment, a significant decrease withstand voltage was observed.
- The mixtures of trifluoroiodomethade and nitrogen or carbon dioxide (CF_3I/CO_2 and CF_3I/N_2) have promising insulation properties but concerns are raised about CF_3I due to its carcinogenic, mutagenic, and toxicity properties (type 3). Although CF_3I has a high boiling point (-22.5 °C at 0.1 MPa) in its pure form, the temperature can be improved when mixed with CO_2 and N_2. A mixture of 20% CF3I–80% CO2 gives an equivalent dielectric strength to SF_6.
- The mixtures of perfluorinated ketones ($C_5F_{10}O$ and $C_6F_{12}O$ /Technical air or CO_2) have a high boiling point (24 °C or 49 °C at 0.1 MPa) due to their higher molecular weight and higher minimum operating temperature compared with SF_6. Fluoroketones $C_5F_{10}O$ and $C_6F_{12}O$ present high insulation capabilities, in particular a high dielectric strength (or breakdown field strength), and at the same time enable an extremely low global warming potential (GWP).
- HFO-1234ze exhibits a higher operation temperature than SF_6 (limited to -15 °C). When subjected to breakdown, the gas can decompose, which results in carbon dust being deposited on the electrodes. However, despite the high boiling temperature, the insulation properties of HFO-1234ze are closed to SF6, with a dielectric strength in the range comprised of 0.8–0.95 times that of SF_6.
- The fluoronitriles could be also a potential alternative to SF_6. Unfortunately, they have a high boiling point. Like for CF_3I, this can be mitigated by mixing them with buffer gases such as CO_2, dry air, or N_2. As concerns the dielectric strength at atmospheric pressure, a mixture of 20% fluoronitriles–80% CO_2 reaches the same dielectric performance as pure SF_6.

References

1. Climate Change 2007: Working Group I: The Physical Science Basis. Cambridge University Press: Cambridge, UK; New York, NY, USA; Available online: https://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-10-2.html (accessed on 14 August 2017).
2. Segur, P. *"Gaz isolants", Techniques de l'Ingénieur, Traité Génie Électrique*; Techniques de l'Ingénieur: Paris, France, 1990; pp. D2530–D2531.
3. Christophorou, L.G.; van Brunt, R.J. SF_6/N_2 mixtures basic HV insulation properties. *IEEE Trans. Dielectr. Electr. Insul.* **1995**, *2*, 952–1003. [CrossRef]
4. Juhre, K.; Kynast, E. High pressure N_2, N_2/CO_2 and CO_2 gas insulation in comparison to SF_6 in GIS applications. In Proceedings of the 14th International Symposium High Voltage Engineering (ISH), Beijing, China, 25–29 August 2005; Paper C-01. p. 155.

5. Hopf, A.; Rossner, M.; Berger, F.; Prucker, U. Dielectric strength of alternative insulation gases at high pressure in the homogeneous electric field. In Proceedings of the IEEE Electrical Insulation Conference (EIC), Seattle, WA, USA, 7–10 June 2015.

6. Chen, L.; Widger, P.; Tateyama, C.; Kumada, A.; Griffiths, H.; Hidaka, K.; Haddad, A. Breakdown Characteristics of CF_3I/CO_2 gas mixtures under fast impulse in rod-plane and GIS geometries. In Proceedings of the 19th International Symposium on High Voltage Engineering, Pilsen, Czech Republic, 23–28 August 2015.

7. Simk, P.; Ranjan, N. Dielectric strength of C5 Perfluoroketone. In Proceedings of the 19th International Symposium on High Voltage Engineering, Pilsen, Czech Republic, 23–28 August 2015.

8. *HFO1234ze, New Low Global Warming Potential Aerosol Propellant, Brochure*; Honeywell International Inc.: Wabash, IN, USA, 2011.

9. Nechmi, H.E. Recherche de Gaz/Mélanges Gazeux Sans Hexafluorure de Soufre Pour des Applications Haute Tension. Ph.D. Thesis, Ecole Centrale de Lyon—Université of Lyon, Lyon, France, 2016.

10. Devins, J.C. Replacement Gases for SF_6. *IEEE Trans. Electr. Insul.* **1980**, *15*, 81–86. [CrossRef]

11. Zhang, L.; Xiao, D.; Zhang, D. Applying c-C_4F_8-CO_2 substituting SF_6 as an insulation medium at low E/N (<400 Td). In Proceedings of the XVI International Conference on Gas Discharge and Their Applications, Xi'an, China, 11–15 September 2006.

12. Christophorou, L.G. Insulating gases. *Nucl. Instrum. Meth. Phys. Res. A* **1988**, *268*, 424–433. [CrossRef]

13. Christophorou, L.G.; Olthoff, J.K.; Green, D.S. *Gases for Electrical Insulation and Arc Interruption: Possible Present and Future Alternatives to Pure Sf$_6$*; NIST Technical Note 1425; National Institute of Standards and Technology: Gaithersburg, MD, USA, 1997.

14. Kawamura, T.; Matsumoto, S.; Hanai, M.; Murayama, Y. SF_6/N_2 mixtures for HV equipment and practical problems. In *Gaseous Dielectrics VIII*; Christophorou, L.G., Olthoff, J.K., Eds.; Kluwer Academic/Plenum Publishers: New York, NY, USA, 1998; pp. 333–343.

15. *Information for Operation of Equipment Containing Fluorinated Greenhouse Gases*; European Commission: London, UK, 2009.

16. *Report of Working Group I of the Intergovernmental Panel on Climate Change: Summary for Policymakers*; IPCC Second Assessment; Lakeman, J.A. (Ed.) University Press: Cambridge, UK, 1995.

17. Okabe, S.; Yuasa, S.; Suzuki, H. Dielectrics properties of gas mixtures with carbon fluoride gases and N_2-CO_2. In *Gaseous Dielectrics IX*; Kluwer Academic/Plenum Publishers: New York, NY, USA, 2001.

18. Rabie, M. A Systematic Approach to Identify and Quantify Gases for Electrical Insulation. Ph.D. Thesis, ETH, Zurich, Switzerland, 2017.

19. Middleton, R.; Koschik, V.; Hogg, P.; Kulkarni, P.; Heiermeier, H. Development work for the application of 245 kV circuit breakers using a SF_6/CF_4 gas mixture on the Manitoba Hydro System. In Proceedings of the Canadian Electrical Association Spring Conference, Toronto, ON, Canada, 1 March 1996.

20. Berg, J.; Kuffel, E. Breakdown Voltage of characteristics of SF_6-CF_4 mixture in uniform and non-uniform field gaps. In Proceedings of the IEEE International Symposium on Electrical Insulation, Montreal, QC, Canada, 16–19 June 1996.

21. Kuffel, E.; Toufani, K. *Breakdown Strength of SF$_6$-CF$_4$ Mixtures in Highly Non Uniform Fields*; Gaseous Dielectrics VIII; Plenum Press: New York, NY, USA, 1998.

22. Larin, A.V.; Meurice, N.; Trubnikov, D.N.; Vercauteren, D.P. Theoretical analysis of the synergism in the dielectric strength for SF_6/CF_4 mixtures. *J. Appl. Phys.* **2004**, *96*, 109–117. [CrossRef]

23. Tezcan, S.S.; Duzkaya, H.; Dincer, M.S.; Hiziroglu, H.R. Assessment of Electron Swarm Parameters and Limiting Electric Fields in SF_6+CF_4+Ar Gas Mixtures. *IEEE Trans. Dielectr. Electr. Insul.* **2016**, *23*, 1996–2005. [CrossRef]

24. Meijer, S.; Smit, J.J.; Girodet, A. Comparison of the Breakdown Strength of N_2, CO_2 and SF_6 using the Extended Up-and-Down Method. In Proceedings of the 2006 IEEE 8th International Conference on Properties & Applications of Dielectric Materials, Bali, Indonesia, 26–30 June 2006; pp. 653–656.

25. Rokunohe, T.; Yagihashi, Y.; Endo, F.; Oomori, T. Fundamental Insulation Characteristics of Air, N_2, CO_2, N_2/O_2, and SF_6/N_2 Mixed Gases. *Electr. Eng. Jpn.* **2006**, *155*, 9–16. [CrossRef]

26.　Beroual, A.; Coulibaly, M.-L. Experimental investigation of breakdown voltage of CO_2, N_2 and SF_6 gases, and CO_2-SF_6 and N_2–SF_6 mixtures under different voltage waveforms. In Proceedings of the 2016 IEEE International Power Modular and High Voltage Conference (IPMHVC), San Francisco, CA, USA, 5–9 July 2016; p. 53.

27.　Hoshina, Y.; Sato, M.; Shiiki, M.; Hanai, M.; Kaneko, E. Lightning impulse breakdown characteristics of SF_6 alternative gases for gas-insulated switchgear. *IEE Proc. Sci. Meas. Technol.* **2006**, *153*, 1–6. [CrossRef]

28.　Solomon, S.; Burkholder, J.B.; Ravishankara, A.R.; Garcia, R.R. Ozone depletion and global warming potentials of CF_3I. *J. Geophys. Res.* **1994**, *99*, 20929–20935. [CrossRef]

29.　Urquijo, J.D.; Juárez, A.M.; Basurto, E.; Hernández-Ávila, J.L. Electron impact ionization and attachment, drift velocities and longitudinal diffusion in CF_3I and CF_3I-N_2 mixtures. *J. Phys. D Appl. Phys.* **2007**, *40*, 2205–2209. [CrossRef]

30.　National Research Council (US) Subcommittee on Iodotrifluoromethane. *Iodotrifluoromethane: Toxicity Review*; Physical and Chemical Properties and Efficacy; National Academies Press (US): Washington, DC, USA, 2004; Volume 2.

31.　McCain, W.C.; Macko, J. *Toxicity Review for Iodotrifluoromethane (CF_3I)*; Project No. 85-8823-99; U.S. Army Center for Health Promotion and Preventive Medicine: Avberdeen Proing Ground, MD, USA, 1999.

32.　Mitchell, A.D. Volume I: Results of Salmonella Typhimurium Histidine Reversion Assay (Ames Assay). In *Genetic Toxicity Evaluation of Iodotrifluoromethane (CF_3I)*; Genesys Study Number 94035; Genesys Research Inc.: Research Triangle Park, NC, USA, 1995.

33.　Zhang, X.; Xiao, S.; Han, Y.; Dai, Q. Analysis of the feasibility of CF_3I-CO_2 used in GIS by partial discharge inception voltages in positive half cycle and breakdown voltages. *IEEE Trans. Dielectr. Electr. Insul.* **2015**, *22*, 3234–3243. [CrossRef]

34.　Katagiri, H.; Kasuya, H.; Mizoguchi, H.; Yanabu, S. Investigation of the Performance of CF_3I Gas as a Possible Substitute for SF_6. *IEEE Trans. Dielectr. Electr. Insul.* **2008**, *15*, 1424–1429. [CrossRef]

35.　Chen, L.; Widger, P.; Kamarudin, M.S.; Griffiths, H.; Haddad, A. CF_3I Gas Mixtures: Breakdown Characteristics and Potential for Electrical Insulation. *IEEE Trans. Power Deliv.* **2017**, *32*, 1089–1097.

36.　Mantilla, J.D.; Gariboldi, N.; Grob, S.; Claessens, M. Investigation of the Insulation Performance of a New Gas Mixture with Extremely Low GWP. In Proceedings of the Electrical Insulation Conference, Philadelphia, PA, USA, 8–11 June 2014; pp. 469–473.

37.　3M™ Novec™ 1230 Fire Protection Fluid. Available online: http://multimedia.3m.com/mws/media/738882O/3mtm-novectm-1230-fire-protection-fluid (accessed on 14 August 2017).

38.　Dahl, D.A.; Rabie, M.; Häfliger, P.; Franck, C.M. Electron attaching properties of c-C_4F_8O derived from swarm parameter measurements in buffer gases. In Proceedings of the Gas Discharges, Orléans, France, 6–11 July 2014.

39.　Chachereau, A.; Janeckova, J.F.R.; Kocisek, J.; Rabie, M.; Franck, C.M. Electron attachment properties of c-C_4F_8O in different environments. *J. Phys. D Appl. Phys.* **2016**, *49*, 375201. [CrossRef]

40.　Aleksandrov, N.L. Three-body electron attachment to a molecule. *Sov. Phys. Usp.* **1988**, *31*, 101–118. [CrossRef]

41.　Claessens, M.-S.; Skarby, P. Dielectric Insulation Medium. U.S. Patent 8704095 B2, 22 April 2014.

42.　Mantilla, J.; Claessens, M.-S.; Gariboldi, N.; Grob, S.; Skarby, P.; Paul, T.A.; Mahdizadeh, N. Dielectric Insulation Medium. WO Patent 2012080246 A1, 21 June 2012.

43.　Hyrenbach, M.; Hintzen, T.; Müller, P.; Owens, J. Alternative gas insulation in medium-voltage switchgear. In Proceedings of the 23rd International Conference on Electricity Distribution, Lyon, France, 15–18 June 2015; p. 0587.

44.　Stahl, T.; Mattern, D.; Brunn, H. Toxicology of perfluorinated compounds. *Environ. Sci. Eur.* **2011**, *23*, 38. [CrossRef]

45.　Rabie, M.; Franck, C.M. Computational screening of new high voltage insulation gases with low global warming potential. *IEEE Trans. Dielectr. Electr. Insul.* **2015**, *22*, 296–302. [CrossRef]

46.　Denki-Kyodo-Kenkyu. *Standards for Handling SF_6 Gas Power Industry*; SF_6 Recycling Guide; Japanese Electric Technology Research Association: Tokyo, Japan, 1998; Volume 54. (In Japanese)

47.　Chachereau, A.; Rabie, M.; Franck, C.M. Electron swarm parameters of the hydrofluoroolefine HFO1234ze. *Plasma Sources Sci. Technol.* **2016**, *25*, 045005. [CrossRef]

48. Koch, M. Prediction of Breakdown Voltages in Novel Gases for High Voltage Insulation. Ph.D. Thesis, ETH-Zürich, Zurich, Switzerland, 2015.

49. Costello, M.G.; Flynn, R.M.; Bulinski, M. Fluorinated nitriles as dielectric gases. U.S. Patent 20150083979, 26 March 2015.

50. Pohlink, K.; Meyer, F.; Kieffel, Y.; Biquez, F.; Ponchon, P.; Owens, J.; Vansan, R. *Characteristics of Fluoronitrile/CO$_2$ Mixture—An Alternative to SF$_6$*; Cigré: Paris, France, 2016; Paper D1-204.

51. Rabie, M.; Dahl, D.A.; Donald, S.M.A.; Reiher, M.; Franck, C.M. Predictors for gases of high electric strength. *IEEE Trans. Dielectr. Electr. Insul.* **2013**, *20*, 856–863. [CrossRef]

52. *3M™ Novec™ 4710 Dielectric Fluid. 33-6330-6*; Version 2.03; 3M USA SDS; 3M Company: Maplewood, MN, USA, 2015.

53. Regulation (EC) No 1272/2008—Classification, Labelling and Packaging of Substances and Mixtures. Available online: https://osha.europa.eu/en/legislation/directives/regulation-ec-no-1272-2008-classification-labelling-and-packaging-of-substances-and-mixtures (accessed on 16 August 2008).

54. Preve, C.; Piccoz, D.; Maladen, R. *Validation Method and Comparison of SF$_6$ Alternative Gases*; Cigré: Paris, France, 2016; Paper D1-205.

55. Kieffel, Y.; Biquez, F.; Ponchon, P.; Irwin, T. SF$_6$ alternative development for high voltage Switchgears. In Proceedings of the IEEE Power & Energy Society General Meeting, Denver, CO, USA, 26–30 July 2015.

56. Kieffel, Y.; Girodet, A.; Ponchon, P.; Owens, J.; Costello, M.; Bulinski, M.; van San, R.; Werner, K. *SF$_6$ Alternative Development for High Voltage Switchgears*; Cigré: Paris, France, 2014; Paper D1-205.

57. Kieffel, Y.; Biquez, F.; Ponchon, P. Alternative Gas to SF$_6$ for use in High voltage switchgears: g^3. In Proceedings of the 23rd International Conference on Electricity Distribution, Lyon, France, 15–18 June 2015; p. 0230.

58. Nechmi, H.E.; Beroual, A.; Girodet, A.; Vinson, P. Fluoronitriles/CO$_2$ gas mixture as promising substitute to SF$_6$ for insulation in high voltage applications. *IEEE Trans. Dielectr. Electr. Insul.* **2016**, *23*, 2587–2593. [CrossRef]

59. Devins, J.C.; Plump, R.E. Electrical Apparatus and Gaseous Dielectric Material Therefor Comprising Perfluoroalkylnitrile. U.S. Patent 3048648 A, 7 August 1962.

60. Kieffel, Y.; Girodet, A.; Porte, J. Medium- or High Voltage Electrical Appliance Having a Low Environmental Impact and Hybrid Insulation. WO Patent 2014037566 A1, 13 March 2014.