



Journal Article

Computational Screening of new High Voltage Insulation Gases with Low Global Warming Potential

Author(s):

Rabie, Mohamed; Franck, Christian

Publication Date:

2015-02-12

Permanent Link:

<https://doi.org/10.3929/ethz-b-000097899> →

Originally published in:

IEEE Transactions on Dielectrics and Electrical Insulation 22(1), [http://doi.org/10.1109/](http://doi.org/10.1109/TDEI.2014.004474)

[TDEI.2014.004474](http://doi.org/10.1109/TDEI.2014.004474) →

Rights / License:

[In Copyright - Non-Commercial Use Permitted](#) →

This page was generated automatically upon download from the [ETH Zurich Research Collection](#). For more information please consult the [Terms of use](#).

Computational Screening of new High Voltage Insulation Gases with Low Global Warming Potential

Mohamed Rabie and Christian M. Franck

Power Systems and High Voltage Laboratories, ETH Zurich, 8092 Zurich, Switzerland

ABSTRACT

We systematically screen chemical compounds for their suitability as high voltage insulation gases on the basis of electrical, environmental and safety characteristics. Recently, 1234 compounds were identified out of a library of over 56000 chemicals by means of virtual screening. The authors applied filters for the global warming potential (GWP), toxicity, stability, flammability and critical temperature to find promising candidate refrigerant fluids. We estimate the electric strength (ES) and the boiling point of these environmentally friendly compounds to select promising SF₆ replacement candidates. The most promising candidates within our method are predominantly Fluoro-alkenes, -alkylsulfides, -alcohols and-alkylamines. In addition, risk and safety data was compiled for compounds that are supplied by chemical vendors at this date, resulting in 7 preliminary candidates.

Index Terms — Dielectric breakdown, gas insulation, SF₆.

1 INTRODUCTION

SULFUR hexafluoride (SF₆) has a high electric strength value (ES) and therefore is widely used in electrical equipment. In addition to its very good insulation properties SF₆ is non-toxic, inert and has a low boiling point (T_B). Due to its long atmospheric lifetime and large radiative forcing it is a greenhouse gas with high global warming potential (GWP). A reduction of the atmospheric concentration of this long-lived gas can only be achieved by stopping emissions. Therefore, considerable effort has been undertaken for finding substitute insulation gases or gas mixtures with significantly lower GWP [1-4].

Characteristics sought in SF₆ replacement gases are mainly chemical stability, low toxicity, low flammability, low GWP, high ES and boiling point ranges that are suitable for high voltage applications. Considering the enormous number of all conceivable molecules it is time consuming to determine their properties by performing individual experiments. Thus, a systematic search using computer programs is desirable to find promising candidates. Such filtering techniques, known as virtual screening [5], are an integral part of e.g. drug discovery research and material design. They are used to identify structures with the desired properties from a very large library of compounds. It is efficient to apply first filters for properties that can be determined directly, without high computational costs, such as the mass or the elemental composition of a molecule. Subsequently, filters that are estimated by computationally expensive methods such as molecular geometry optimizations can be applied.

A set of 1234 candidate refrigerant fluids was identified by means of virtual screening from the PubChem database of the National Institute of Health [6, 7]. The environmental and safety criteria applied by the authors to this large number of molecules were: low GWP, low LFL (lower flammability limit), and filters for toxicity and chemical stability.

In this work, we subsequently investigate the remaining 1234 molecules by a computational method that estimates the ES and T_B of electronegative gases, to identify potential SF₆ substitutes [8, 9]. The present paper is structured as follows: Section 2 reviews the methods and constraints of the environmental and safety filters from [6]. Then we briefly describe our method that estimates the ES and T_B of electronegative gases by means of density functional theory (DFT) calculations. Further, the filtering procedure to select the most promising compounds is given. In Section 3 we present the results of our analysis. We compare the estimated values of T_B for the most promising candidates with values given in literature. In addition, risk factors and safety features for the gas handling are collected for commercially available compounds. In section 4 our filtering results as well as the underlying filtering procedure are discussed. Finally, in section 5 we conclude with the benefit of our study based on the applied screening criteria.

2 METHODS

2.1 ENVIRONMENTAL CHARACTERISTICS

We attempt to calculate the ES of only environmentally friendly and safe molecules. To avoid unnecessary computation of molecules that may reveal good insulation

properties but are harmful to health or environment, the starting point of our gas screening is, instead of the entire library of the PubChem database, only the set of molecules that are the filtering results from [6]: The authors limit the molecular size to maximum 15 atoms and allow only compositions of the elements: C, H, F, Cl, Br, N and S. Further, filters for toxicity and stability were based on functional groups. The critical temperature T_c of chemicals used as refrigerant fluids should be in the range of $300 \text{ K} < T_c < 550 \text{ K}$, due to technical aspects described in [6]. The lower flammability was limited to $\text{LFL} > 0.1 \text{ kgm}^{-3}$. The chosen LFL is the boundary value of "Class 2" flammability in the ASHRAE refrigerant classification standard [10], which corresponds to a "moderate" [6] flammable compound.

For the estimation of the GWP the authors calculated two properties of a compound, the atmospheric lifetime (τ) and the radiative efficiency (RE) [6]. The GWP is defined as the radiative forcing (RF) due to an instantaneous release of 1 kg of a trace substance integrated over a chosen time horizon, relative to that of 1 kg of CO_2 . For the RF, the IPCC uses the following definition: "The RF of the surface-troposphere system due to the perturbation in or the introduction of an agent (say, a change in greenhouse gas concentrations) is the change in net (down minus up) irradiance (solar plus long-wave, in Wm^{-2}) at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values" [11]. The RE is the change of the RF per unit increase in atmospheric concentration. The authors selected the PM6 [12] semiempirical method for computing vibrational frequencies and IR intensities, providing in comparison to other semiempirical methods more consistent results for RE. Even though the computationally more expensive DFT methods are in better agreement with experimental RE data, the accuracy of the PM6 method is still reasonable for screening purposes. To obtain RE, the authors calibrated the semiempirical calculations by a uniform vibrational frequency factor, based on a comparison between the predicted data and a given experimental data set. The GWP was evaluated over a time horizon of 100 years assuming an exponential decay for the time evolution of the gas in the atmosphere with a rate of $1/\tau$. Here, the decay mechanism accounts for compound removal via reactions with OH only. The rate coefficient for this reaction was calculated by means of group-contribution method [13]. Subsequently, the lifetimes were estimated as the inverse reaction rate coefficient times an empirical parameter which was determined by comparison with reported lifetime data. Chemical reactions with atmospheric compounds other than OH as well as loss mechanisms such as ultraviolet photolysis, rainout or wet deposition were not considered by the authors. The calculations for the lifetimes and RE were performed with the Gaussian 09 package [14].

The constraint for the GWP was set to $\text{GWP} < 200$. This value is based on the current policy outlook [15]. For the remaining set of molecules the GWP is mainly controlled by atmospheric lifetimes, which are in the range from 0.02 years to 6 years.

2.2 ESTIMATION OF ES AND T_B

Those compounds that pass the environmental filtering criteria from Section 2.1 are given in [6]. We subsequently investigated these compounds in more detail estimating two crucial properties for their potential usage in high voltage equipment: the electric strength ES and the boiling point T_B . The calculation of the ES by means of simulation of electron dynamics on the basis of microscopic electron-molecule collisions is a challenging problem. The required input for the underlying fluid modelling is at least a complete set of cross sections for all relevant elastic and inelastic two-body processes [16]. In addition, Boltzmann solvers as well as Monte Carlo methods in general do not account for three-body processes, which may get relevant at higher pressures [17, 18]. Facing these difficulties of kinetic modelling, several empirical estimation methods for the ES have been developed, analyzing the correlation between the ES, as well as T_B , and certain molecular properties [19-23]. Stronger correlations than in these studies, we could find in a previous work by means of predictor variables [8], which are simple functions of the molecular properties: electric dipole moment, average static electronic polarizability, vertical/adiabatic ionization energy, vertical/adiabatic electron affinity, electron number and molecular mass. These properties were calculated ab-initio for isolated gas molecules whose structure has been optimized in the electronic ground state. Vibrational and temperature corrections have been neglected. The Kohn-Sham DFT calculations were performed with the Turbomole program package [24] employing the BP86 density functional [25, 26] together with density fitting techniques. We applied Ahlrichs' polarized valence triple-zeta basis def-TZVP [27] in the calculations of the vertical/adiabatic ionization energy and the vertical/adiabatic electron affinity. The larger def2-QZVPP basis set [28] was used for the calculation of the electronic polarizability and dipole moment. We evaluate energy differences between potential curves of neutral and cation and of neutral and anion, neglecting the discrete structure of the vibrational energy levels. The dipole moment and polarizability are then calculated for the geometry-optimized neutral molecule. In the following, we write E_r for the ES relative to SF_6 . Our method has a standard deviation of $\sigma = 0.35$ for E_r and $\sigma = 28\text{K}$ for T_B .

2.3 FILTERING BASED ON ES AND T_B

In a next step towards gases that are suitable for high voltage insulation we apply constraints for the ES and T_B . The remaining compounds are subsequently investigated by means of *Pareto efficiency* in the design space with E_r and T_B as parameters. Finally, to arrange the remaining substances according to their environmental impact, we subdivide our results into four groups of GWP. The reduction of the initial number of compounds by the individual steps is illustrated in Table 1.

The ideal insulation gas would suppress electron avalanches up to high electric fields, corresponding to high values of the

Table 1. Filtering steps for the 1234 molecules with GWP < 200.

Filter	constraint	# of remaining compounds
T_B	$T_B < 320$ K	408
E_r	$ER > 0.5$	384
Pareto front with σ -area	$\sigma = 0.35$ for E_r , $\sigma = 28$ K for T_B	141

ES. At the same time the breakdown voltage for typical dimensioning of high voltage equipment increases with increasing gas pressure, according to the linear regime of Paschen’s law [29]. Thus, a high vapor pressure at typical ambient temperatures, corresponding to a low T_B , is desirable to achieve high breakdown voltages without condensation of the gas. We do not want to exclude compounds which could be used in gas mixtures of two or more components. Therefore, we choose more generous constraints $ES > 0.5$ and $T_B < 320$ K as one would choose for a pure insulation gas.

Furthermore, we identify the Pareto efficient compounds of the remaining set with the most promising candidates. Here, a Pareto efficient molecule means the “best” option for the ES and simultaneously T_B : it is not possible to find a single molecule with higher E_r value and at the same time lower T_B . We determine the set of all Pareto efficient compounds, which is defined as the *Pareto frontier*. Again, to not exclude interesting candidates we incorporate all molecules in the σ -region around the Pareto frontier. This region we will call in the following *Pareto-area*.

In the context of high voltage insulation a molecule’s GWP is commonly compared to one of the two prominent greenhouse gases: SF_6 or CO_2 . On the one hand, all compounds would represent a drastic improvement to SF_6 in terms of environmental impact. On the other hand, in comparison to CO_2 , there is still a high variation between 0 and 200. Hence, to have an overview of the different environmental impacts of the remaining compounds we subdivide them into four different groups according to their GWP: $GWP < 1$, $1 < GWP < 10$, $10 < GWP < 100$ and $100 < GWP < 200$.

3 RESULTS

According to Section 2.2 we estimate E_r and T_B of a set of 1234 compounds that are the filtering results from [6], as described in Section 2.1. The results are presented in Figure 1a. The constraints for E_r and T_B result in 384 compounds. In Figure 1b we identify the Pareto frontier of the remaining data, created by a set of 15 molecules. Including all molecules in the σ -region we count 141 Pareto-compounds, which we identify as superior candidates.

These Pareto- compounds were split into four groups with respect to the GWP as described above. The results for the estimated T_B and E_r are illustrated in Figure 2. In addition, when available, values for T_B from literature were given. For better comparison between the different groups the Pareto frontier from Figure 1b is indicated in each panel. The number of compounds N in each GWP- windows is given in the inset of the corresponding panel.

$GWP < 1$: The set of compounds with $GWP < 1$ are

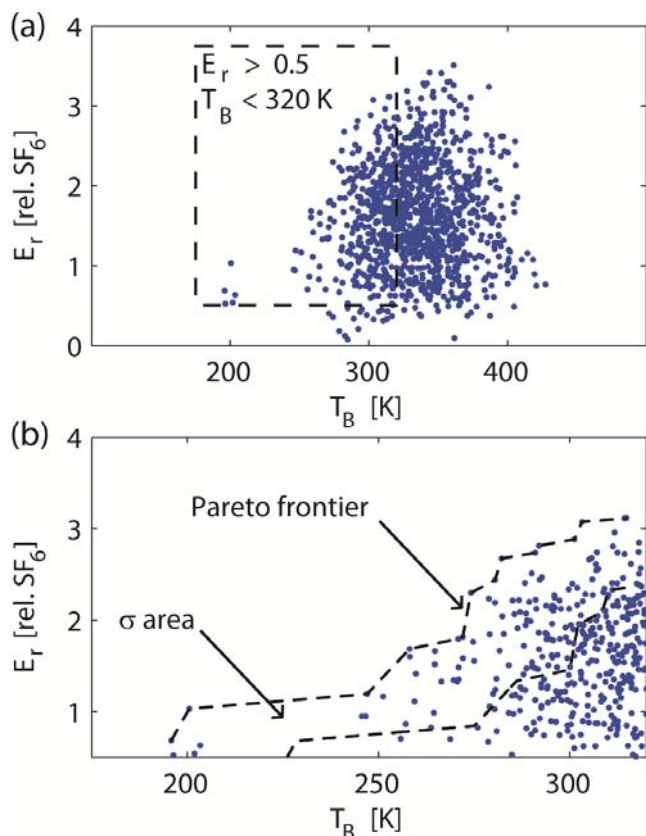


Figure 1. (a) estimated electric strength E_r relative to SF_6 vs estimated boiling point T_B for 1234 molecules (dots). (b) inset of upper panel: 384 remaining compounds (dots) after filtering with $T_B < 320$ K and $E_r > 0.5$. The Pareto frontier (upper dashed line) and its standard deviation (lower dashed line) confine the ideal candidate gases.

supposed to be the less detrimental to environment among the Pareto-compounds and are given in Table 2. The list contains only Fluoro-alkenes containing one or two hydrogen atoms. However, there is one exception: the Fluoroethanethiol C_2HF_5S . For the latter we estimated an ES clearly higher than SF_6 . At the same time it has a high reaction rate with OH resulting in an estimated lifetime below one day [6]. The ES of each of the four isomers of $C_4H_2F_6$ is around two times larger than for SF_6 . The atmospheric lifetimes of the same compounds are of around two days [6]. The compound 91450 has a vapor pressure of 1.2 bar at 20 °C [30], whereas 52991879 has a vapor pressure of 0.6 bar at 20 °C [30]. We find agreement between our calculated T_B values and values from literature within the 1σ - uncertainty. Furthermore, Table 2 contains seven Fluoro-alkenes of the form C_5HF_9 and two isomers of $C_5H_2F_8$. The list contains a single Perfluoro-alkene which is the cyclic alkene C_5F_8 .

$1 < GWP < 10$: Here, the Fluoro-alkenes represent again the dominant group. Further Table 3 contains the Fluoroalkyl-sulfides C_2F_6S , C_3F_8S and $C_4F_{10}S$, as well as the Fluoro-alcohols $C_4H_3F_7O$ and $C_4H_4F_6O$. The T_B values for the compounds found in literature agree all with the calculated values within the accuracy.

$10 < GWP < 100$: Table 4 shows the compounds of the Pareto frontier. Here, in addition to certain Fluoro-alkenes and Fluoro-alcohols, the group of Fluoroalkyl-amines such as

C3H2F7N or C3H3F6N, represent possible candidates. For the compounds 2776724, 13529, 9872 and 12223 the estimated values of T_B are clearly outside the 1σ -uncertainty.

$100 < GWP < 200$: The Pareto compounds with the highest GWP values are given in Table 5. Basically, the same chemical classes as before represent the most important candidates.

For all compounds from Tables 2-5 which are, to our level of

knowledge, commercially available at this date we collected information from safety data sheets provided by the vendors. Table 6 lists for these compounds the safety and risk phrases defined in Annex III and Annex IV of European Union Directive 67/548/EEC. For comparison the safety and risk phrases for SF₆ are given. According to our filtering procedure the final list of candidate gases should only contain non-toxic and non-flammable compounds. However, Table 6 contains certain gases that are in terms of risk phrases (R23) “toxic by

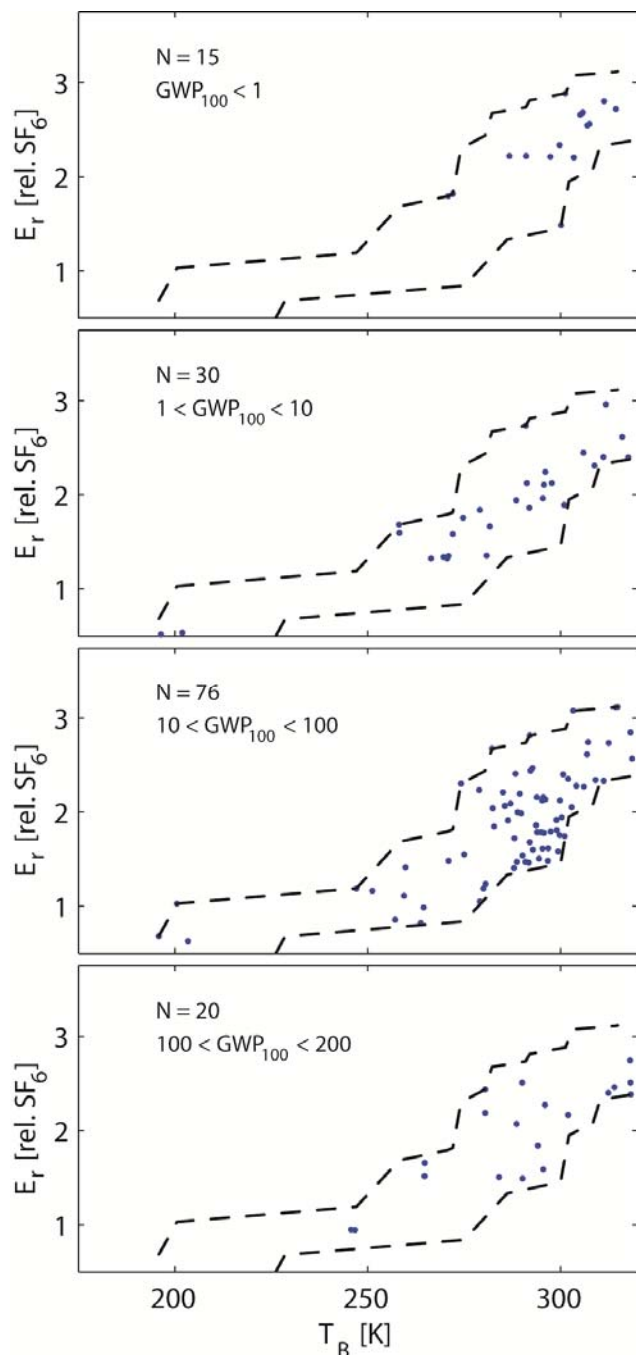


Figure 2. Estimated electric strength E_r relative to SF₆ vs estimated boiling point T_B for the 141 Pareto efficient molecules (dots). From top to bottom panel: compounds with $GWP < 1$, $1 < GWP < 10$, $10 < GWP < 100$ and $100 < GWP < 200$. The number of compounds N in each GWP interval is given in the inset of each panel. The dashed lines correspond to the Pareto frontier and its standard deviation of Figure 1(b), as described in the text.

Table 2. Compounds in the Pareto-area with $GWP < 1$.

CID	formula	T_b	T_b (lit.)	E_r
4713114	C2HF5S	300		1.5
5708528	C4H2F6	271	282 [30]	1.8
2774975	C4H2F6	272		1.8
91450	C4H2F6	297	288 [30]	2.2
52991879	C4H2F6	303	306 [30]	2.2
11212	C5F8	300	300 [30]	2.3
18520951	C5H2F8	291		2.2
53395640	C5H2F8	287		2.2
53395686	C5HF9	305	303-306 [30]	2.7
12530412	C5HF9	306		2.7
12951075	C5HF9	307		2.5
53395684	C5HF9	307		2.6
11053485	C5HF9	301	306-307 [30]	2.9
23234730	C5HF9	311		2.8
12951076	C5HF9	314		2.7

Table 3. Compounds in the Pareto-area with $1 < GWP < 10$.

CID	formula	T_b	T_b (lit.)	E_r
8301	C2F4	202	197 [31]	0.5
136206	C2F6S	281		1.4
5365501	C2H2F2	196	231 [30]	0.5
14841	C2H2F2	196		0.5
19779344	C3F8S	295		2.0
19920814	C4F10S	306		2.4
21732342	C4F10S	316		2.6
11389728	C4F6O	292		1.9
61109	C4F8	296	280 [7]	2.2
2775851	C4F8	258	274 [30]	1.7
3034116	C4F8	282		1.7
9678	C4F8	258		1.6
12705729	C4F8S	311		2.4
21838907	C4H2F6	271		1.4
53395682	C4H2F6	270		1.3
21096849	C4H2F6	272		1.6
13238222	C4H3F7O	309		2.3
21096871	C4H4F4	266		1.3
4712696	C4H4F6O	301		1.9
20496975	C4HF7	271		1.3
5708514	C4HF7	288	281 [30]	1.9
6110611	C4HF7	296		2.1
498797	C4HF7	289		1.9
12633092	C4HF7	298		2.1
12576087	C5F10	312		3.0
12576086	C5F10	291		2.7
155748	C5F10	275		1.8
2736749	C5F10	279		1.8
12534876	C5F10	291		2.1
11471944	C5HF9	318		2.4

inhalation”, namely 11212 and 16924. The compound 61109 is “very toxic by inhalation” (R26). The gases 52991879 and 2776724 are “flammable” (R10). The compounds 15914919 and 5365501 are “extremely flammable” (R12), whereas 10154032 “in use, may form flammable/explosive vapor-air

Table 4. Compounds in the Pareto-area with $10 < \text{GWP} < 100$.

CID	formula	T_B	T_B (lit.)	E_r
19350069	C2H2F4O	257		0.9
14529362	C2H2F4O	264		1.0
185647	C2H3F3O	264		0.8
12223	C2H4F2	196	304 [30]	0.7
21222306	C2HBrF4O	300		2.1
20342513	C2HClF4O	283		1.8
2759276	C2HF5O	260		1.4
26343944	C3H2F6O	294		1.9
13529	C3H2F6O	289	331 [30]	2.0
26343943	C3H2F6O	294		1.9
13350568	C3H2F6O	294		1.9
148644	C3H2F6O	294		2.2
11665471	C3H2F6O	286		2.1
19390374	C3H2F7N	295		2.2
144608	C3H2F7N	290		2.0
15032138	C3H3BrF4	300		1.9
2782294	C3H3ClF4	296		1.8
14066890	C3H3ClF4	292		1.7
22465807	C3H3F5O	294		1.5
9872	C3H3F5O	297	354 [30]	1.5
23510551	C3H3F5O	295		1.6
19006646	C3H3F5O	282		2.0
21645339	C3H3F5O	289		1.5
21732907	C3H3F6N	299		1.6
144609	C3H3F6N	259		1.1
12927175	C3H4ClF3	280		1.2
18786703	C3H4ClF3	279		1.1
2776724	C3H4F4	247	302-303 [30]	1.2
17763161	C3H4F4O	293		1.6
20225807	C3HClF6O	309		2.3
2759273	C3HF7O	285		2.2
144610	C3HF8N	279		2.2
12653369	C4F4N2	301		1.7
11275686	C4H2F8	282		2.7
15162467	C4H2F8O	301		2.4
21243755	C4H2F8O	312		2.7
4407544	C4H2F8O	307		2.7
18457462	C4H2F8O	315		3.1
2736596	C4H3ClF6	307	321-322 [30]	2.6
12025746	C4H3F7	292		2.4
15044627	C4H3F7	274		2.3
23236258	C4H3F7	289		2.2
21731035	C4H3F7	287		2.1
22178537	C4H3F7O	304		2.3
5206	C4H3F7O	306	331 [30]	2.3
19788901	C4H3F7O	299		1.9
12554037	C4H3F7O	302		2.4
53436611	C4H3F7O	303		2.1
22102014	C4H3F7O	311		2.3
19037094	C4H3F7O	318		2.8
21459300	C4H4ClF5	318		2.6
21459281	C4H4ClF5	297		1.8
2778258	C4H4F6	288	294 [30]	2.4
15576965	C4H4F6	288		1.7
67890	C4H4F6	293	298 [30]	2.5
10899043	C4H4F6	275		1.6
15044576	C4H4F6	295		2.1

CID	formula	T_B	T_B (lit.)	E_r
21922262	C4H4F6	296		2.1
21731031	C4H4F6	271		1.5
20715328	C4H4F6O	286		1.9
19788851	C4H4F6O	292		1.5
21136753	C4H5F5	300		1.8
21922298	C4H5F5	299		1.8
11094775	C4H5F5	295		1.8
15044628	C4H5F5	294		1.8
21731027	C4H5F5	297		1.6
21731805	C4H5F5	290		1.5
15914919	C4H6F4	291	315 [30]	1.5
15044629	C4H6F4	288		1.4
15162466	C4HClF8O	314		3.1
16924	C4HF9O	292	317-318 [30]	2.8
14620145	C4HF9O	303		3.1
17789749	CH2F2O	203		0.6
22314940	CHBrF2O	281		1.2
18532994	CHClF2O	251		1.2
73894	CHF3O	201		1.0

Table 5. Compounds in the Pareto-area with $100 < \text{GWP} < 200$.

CID	formula	T_B	T_B (lit.)	E_r
15939370	C3H3F5	265		1.5
164598	C3H3F5	265	296 [30]	1.5
2774090	C3H3F5O	290	299 [30]	1.5
22164456	C4H2F8	280		2.4
11042687	C4H2ClF7O	318		2.7
18335861	C4H3F7O	290		2.5
20606324	C3HCl2F5O	314		2.5
21922285	C4H3F7	289		2.1
56612536	C4H4F6O	318		2.4
19063460	C4H3F7O	296		2.3
15044575	C4H3F7	280		2.2
21922280	C4H4F6	265		1.7
10154032	C3H4F4	246		0.95
14709481	C4H4F6	294		1.8
20243757	C2H4F2O	247		0.94
21922265	C4H4F6	284		1.5
2774025	C4H2Cl2F6	318	356-357 [30]	2.5
87912	C3H3ClF4	295		1.6
3028248	C2HBr2F3	312	347-348 [32]	2.4
13597428	C4H4F6	302		2.2

mixture” (R18). The chlorofluorocarbon 2782294 is “dangerous for the ozone layer” (R59).

4 DISCUSSION

The ideal insulation gas would boil at $T_B = 0$ K. Then the gas pressure, and thus the breakdown voltage, in principle could be increased to infinitely high values, disregarding the mechanical stress on the equipment. Hence, for the usage in high voltage equipment the lower limit on T_B , and thus on T_c , should be as small as possible. Nevertheless, we expect not to prematurely exclude candidate gases by the boundary $T_c > 300$ K, as described in Section 2.1. For comparison, SF_6 has a critical temperature of $T_c = 318.7$ K [33], which is included by the used boundary. Compounds with T_B around room temperature may condensate at lower temperatures or elevated

pressures and are thus not suitable as insulation gases in pure form. Instead, they may be used as one component in a gas mixture. By this, the ES of a gas such as nitrogen might be significantly increased already by adding only small percentages of a strongly electron-attaching substance [34].

We note that the GWP is a quantity that is uncoupled from the initial gas release of electrical equipment. It reflects the environmental impact in terms of global warming after the emission of 1 kg of an insulating gas into the atmosphere, as described in Section 2.1. However, the amount of emitted insulating gas from electrical equipment strongly depends on the molecular mass and the viscosity of the gas species. For example, poor gas handling during maintenance work can lead to the entire release of an insulating gas volume into the atmosphere. In this case the amount of emitted gas is proportional to its molecular mass. Another source of gas

Table 6. Safety and Risk phrases for the Pareto efficient compounds that are commercially available [30].

CID	Risk phrases	Safety phrases
SF6	36/37/38-44	9-24/25-26-36/37/39-38-45-47
5708528	36/37/38	23-24/25-36/37/39-38-45
91450	36/37/38-44	9-23-24/25-26-36/37/39-38-45-47
52991879	10-36/37/38	16-23-24/25-26-36/37/39-45
11212	23/24/25-36/37/38-44	13-20-23-24/25-26-36/37/39-38-45-47
53395686		36/37/39-41
11053485	36/37/38	23-24/25- 36/37/39- 45
61109	26-36/37/38-44	9-23-24/25-26-36/37/39-38-45-47
2775851	36/37/38	26-36
5708514	36/37/38-44	9-23-24/25-26-36/37/39-38-45-47
2776724	10,36/37/38,67	9,16,23,24/25,26,36/37/39,45,51
2782294	36/37/38-59	3/7-23-24/25-26-36/37/39-45-57-61
67890	44	9-23-24/25-26-36/37/39-38-45-47
15914919	12	9,16
16924	21/22-23-36/37/38	23-24/25-26-36/37/39-45
2736596		3/7-23-24/25-26-36/37/39-45
13529	20/22-34	26-36/37/39-45
5206	18-36/37/38	15-16-23-24/25-33-36/37/39-45
164598	44	9-23-24/25-26-36/37/39-38-45-47
10154032	18	9-15-16-33
5365501	12-18-44	9-16-23-24/25-26-33-36/37/39-38-45-47
12223	10-23/24/25-36/37/38	23-24/25-26-36/37/39-45

emission is durable leakage from gas-insulated equipment. For this scenario the leak rate increases with decreasing viscosity of the gas species. The viscosity in turn depends on the molecular mass and microscopic properties of the gas. Nevertheless, we measured the environmental effect of an insulating gas solely by means of its GWP. The GWP is a well-established quantity widely used in literature. It allows rapid comparison of environmental aspects between different compounds and sources. In addition, we wanted to follow a universal screening procedure, which filters out certain compounds independent from technical issues such as different leakage scenarios.

For all compounds, we clearly observe certain trends for the ES and T_B . The values of these quantities strongly vary with the elemental composition and the molecular structure. Certainly, for increasing number of F-atoms in a molecule the ES increases due to the higher rate of electron attachment, as can be seen from Table 2 to Table 5. Furthermore, increasing number of C-atoms in a molecule increases the rate of elastic collisions, and thus the ES. The increased value of T_B for larger molecules is the result of increasing van der Waals interaction. It appears particularly interesting that substances of the same molecular formula but different chemical structures may reveal very different values for ES.

The initial set of 1234 compounds does not contain any perfluoro- or hydrofluoro- carbonyl compounds. This chemical class was investigated in detail in previous work [9]. Most ketones and aldehydes with more than 4 carbon atoms were already filtered out by the constraint that the molecular size is limited to 15 atoms, as described in Section 2.1. We can only speculate here that their GWP might be higher than set by the given constraint.

We want to note that our estimation method for E_r and T_B , as well as the estimation methods [6] for the GWP, flammability and toxicity are subject to significant uncertainties, and outliers may exist. In general, we find good agreement between our calculated T_B values and values from literature, as shown in Table 2-5. Furthermore, not all identified substitutes meet the desired toxicity- and flammability- criteria, as shown in Table 6. For example one identified compound is the fluorocarbon alkene perfluoroisobutene (CID = 61109), which is very toxic as mentioned in Section 3. The commercially available compounds in Table 6 which, according to safety data sheets, might fulfill basic requirements for a substitute gas are: 5708528, 91450, 11053485, 2775851, 5708514, 164598 and 13529. The latter is “harmful by inhalation and if swallowed” [30]. For the compound 53395686 no safety data sheet was available.

The compounds of Table 2-5 which are not supplied by chemical vendors, might be seen as a proposal list for SF₆ substitutes. In addition to the physical and chemical properties of an alternative insulation gas its commercialization is driven by the price of its synthesis. Certainly, a promising candidate might not be an alternative to SF₆, if its production is complicated and cost-intensive or in terms of regulatory basis highly restrictive. Providing methods for synthesis, isolation

and production of chemical compounds to increase its commercial potential for the industry is subject to the large field of organic synthesis, and it is not within the scope of this work.

5 CONCLUSION

Out of a large library of 56000 compounds from the PubChem database a few most promising gaseous dielectrics were identified. We therefore adopted the subset of around 1200 compounds, which the authors derived by virtual screening based on environmental, safety and thermodynamic criteria. For these compounds of low global warming potential, low toxicity and low flammability the electric strength and boiling point were estimated. A quantitative investigation of the electric strength should follow for the top-candidates, e.g. by swarm parameter measurements and the derivation of the critical electric field strength.

REFERENCES

- [1] J.C. Devins, "Replacement Gases for SF₆", IEEE Trans. Dielectr. Electr. Insul., Vol. 15, pp. 81-86, 1980.
- [2] L.G. Christophorou and R.J. Van Brunt "SF₆/N₂ mixtures: basic and HV insulation properties", IEEE Trans. Dielectr. Electr. Insul., Vol. 2, pp. 952-1003, 1995.
- [3] L.G. Christophorou, J.K. Olthoff, and D.S. Green, "Gases for Electrical Insulation and Arc Interruption: Possible Present and Future Alternatives to Pure SF₆", National Inst. Sci. Techn. (NIST), Washington Dc, USA, Technical Note 1425, 1997.
- [4] L. Niemeyer, "A Systematic Search for Insulation Gases and Their Environmental Evaluation", Gaseous Dielectrics VIII, pp. 459-464, 1998.
- [5] B. K. Shoichet, "Virtual screening of chemical libraries", Nature, Vol. 432, pp. 862-865, 2004.
- [6] A. Kazakov, M. O. McLinden, and M. Frenkel, "Computational design of new refrigerant fluids based on environmental, safety and thermodynamic characteristics", Ind. Eng. Chem. Res., Vol. 51, pp. 12537-12548, 2012.
- [7] E. Bolton, Y. Wang, P. A. Thiessen, and S. H. Bryant, "PubChem: Integrated platform of small molecules and biological activities", Annual Reports in Computational Chemistry, American Chemical Society: Washington, DC, Vol. 4, Chapter 12, 2008.
- [8] M. Rabie, D. A. Dahl, S. M. A. Donald, M. Reiher, and C. M. Franck, "Predictors for gases of high electric strength", IEEE Trans. Dielectr. Electr. Insul., Vol. 20, No 3, pp. 856-863, 2013.
- [9] M. Rabie and C. M. Franck, "Predicting the electric strength of proposed SF₆ replacement gases by means of density functional theory", Int'l. Sympos. High Voltage Eng. (ISH), Seoul, Korea, pp. 1381-1386, 2013.
- [10] ANSI/ASHRAE Standard 34-2010: Designation and Safety Classification of Refrigerants; American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.: Atlanta, GA, 2010.
- [11] J. T. Houghton, L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg, and K. Maskell (eds.) "Climate Change 1995: The Science of Climate Change", Cambridge University Press: New York, 1996.
- [12] J. J. P. Stewart, "Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements", J. Mol. Model., Vol. 13, pp. 1173-1213, 2007.
- [13] E. S. C. Kwok and R. Atkinson, "Estimation of hydroxyl radical reaction rate constants for gas phase organic compounds using a structure reactivity relationship: An update", Atmos. Environ., Vol. 29, pp. 1685-1695, 1995.
- [14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2010.
- [15] A. L. Mascarelli, "A bright future for the Montreal Protocol", Environ. Sci. Technol., Vol. 44, pp. 1518-1520, 2010.
- [16] R.E. Robson, P. Nicoletopoulos, B. Li, and R.D. White, "Kinetic theoretical and fluid modelling of plasmas and swarms: the big picture", Plasma Sources Science and Technology, Vol. 17, pp. 024020, 2008.
- [17] N. L. Aleksandrov, "Three-body electron attachment to a molecule", Usp. Fiz. Nauk., Vol 154, pp. 177-206, 1988.
- [18] S. Pancheshnyi, "Effective ionization rate in nitrogen-oxygen mixtures", J. Phys. D: Appl. Phys., Vol. 46, pp. 155201, 2013.
- [19] W. A. Wilson, J.H. Simons, and T.J. Brice, "The Dielectric Strength of Gaseous Fluorocarbons", J. Appl. Phys., Vol. 21, pp. 203-205, 1950.
- [20] R. W. Crowe and J. C. Devins, "Sparking Potential and Molecular Structure of Unsaturated Hydrocarbon Gases", J. Chem. Phys., Vol. 33, pp. 413-18, 1960.
- [21] A. E. D. Heylen and T.J. Lewis "The electrical strength of hydrocarbon gases", British. J. Appl. Phys., Vol. 7, pp. 411-415, 1956.
- [22] K. P. Brand, "Dielectric strength, boiling point and toxicity of gases - different aspects of the same basic molecular properties", IEEE Trans. Dielectr. Electr. Insul., Vol. 17, pp. 451-456, 1982.
- [23] N. Meurice, E. Sandre, A. Aslanides, and D.P. Vercauteren, "Simple theoretical estimation of the dielectric strength of gases", IEEE Trans. Dielectr. Electr. Insul., Vol. 11, pp. 946-948, 2004.
- [24] R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, "Electronic structure calculations on workstation computers: The program system turbomole", Chemical Phys. Lett., Vol. 162, pp. 165-169, 1989.
- [25] A.D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior", Phys. Rev. A, Vol. 38, pp. 3098-3100, 1988.
- [26] J.P. Perdew, "Density-functional approximation for the correlation energy of the inhomogeneous electron gas", Phys. Rev. B, Vol. 33, pp. 8822-8824, 1986.
- [27] A. Schaefer, C. Huber, and R. Ahlrichs, "Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr", J. Chem. Phys., Vol. 100, pp. 5829-5835, 1994.
- [28] F. Weigend, F. Furche, and R. Ahlrichs, "Gaussian basis sets of quadruple zeta valence quality for atoms H-Kr", J. Chem. Phys., Vol. 119, pp. 12753-12762, 2003.
- [29] F. Paschen, "Ueber die zum Funkenübergang in Luft, Wasserstoff und Kohlensäure bei verschiedenen Drucken erforderliche Potentialdifferenz", Annalen der Physik, Vol. 273, pp. 69-96, 1889.
- [30] SynQuest Laboratories, <http://www.synquestlabs.com/>, 2013.
- [31] Royal Society of Chemistry, <http://www.chemspider.com/>, 2014.
- [32] Matrixscientific, <http://www.matrixscientific.com/>, 2013.
- [33] Air Liquide Gas Encyclopedia. Retrieved 02 June 2013.
- [34] C. M. Franck, D. A. Dahl, M. Rabie, P. Haefliger, and M. Koch, "An Efficient Procedure to Identify and Quantify New Molecules for Insulating Gas Mixtures", Contrib. Plasma Phys., Vol. 54, pp. 3 - 13, 2014.



(M'04-SM'11)
from the University

Mohamed Rabie was born in Innsbruck, Austria in 1985. He received a diploma in physics from the University of Innsbruck in 2011. There he was working on one-dimensional quantum gases. Currently he is doing his Ph.D. degree at the Institute for Power Systems and High Voltage Technology, ETH Zurich, Switzerland.



Christian M. Franck received a diploma in physics of Kiel, Germany in 1999

and the Ph.D. degree in physics from the University of Greifswald, Germany in 2003. He was with the Swiss corporate research center of ABB during 2003-2009 as a Scientist and Group Leader for gas circuit breakers and high

voltage systems. Currently, he is an Assistant Professor for High Voltage Technology at the Swiss Federal Institute of Technology (ETH), Zurich, Switzerland.