Gas mixture candidates for SF$_6$ replacement in medium voltage switchgear: Analysis and modeling of the filling episodes

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Abstract. A more environmentally friendly replacement for SF$_6$ must be found for medium voltage switchgear, as a change in European regulations will come into force soon. The mixing process of alternative binary and ternary gas mixtures is studied, which are made up of the hydrofluoroolefin HFO-1336mzz(E) (C$_4$F$_6$H$_2$) and the heptafluoroisopropil trifluoromethyl ketone (C$_5$F$_{10}$O), using dry air or N$_2$ as carrier gases. The mixture's monitoring, meaning the evolution of the concentration concerning time and position, is carried out by UV-VIS spectroscopy technology in a gas chamber that has been designed to be analogous to a medium voltage cell. The mixing process is described using a mathematical model that considers molecular diffusion, Fick's Law, and natural convection, the effect of gravity. This work aims to configure a tool for predicting the dynamics of gas mixtures of different components, estimating the diffusivities of the mixture's components, and analyzing the behaviors derived from the use of different concentrations.

Keywords: Global warming potential; Dielectric strength; Gas mixing modeling; Gas diffusivity; Multicomponent mixing.

1. Introduction

Sulfur hexafluoride (SF$_6$) is the most employed gas for electrical switchgear insulation because of its low toxicity, high stability, inertness, and high dielectric strength. However, it is considered one of the most potent greenhouse gases, as it has a Global Warming Potential higher than 23500 in a 100-year horizon and a lifetime in the atmosphere of 3200 years (Tsai, 2007). SF$_6$ must be replaced with other gas or gas mixtures that are more environmentally friendly before an imminent change in European regulations (The European Parliament and the Council of the European Union, 2014).

Hydrofluoroolefins, fluoroketones, fluoronitriles, or halomethanes have been widely studied as alternatives for SF$_6$ in medium voltage switchgear; for example, HFO-1234ze(E) (C$_3$F$_4$H$_2$), C$_6$F$_{12}$O, C$_4$F$_7$N, and CF$_3$I, because of their lower *GWP* and similar or higher dielectric strength than SF$_6$ (Xiao *et al.*, 2018; Zhang *et al.*, 2020). However, their boiling point is higher than the one for SF$_6$, so the gases must be mixed with a carrier gas to avoid liquefaction.

This study is focused on the binary mixtures containing the hydrofluoroolefin C$_4$F$_6$H$_2$ (HFO-4), and the ternary mixtures containing HFO-4 and the fluoroketone C$_5$F$_{10}$O (C5K). The molecular weight (*MW*), global warming potential in a 100-year time horizon (*GWP*), normal boiling point (*NBP*), toxicity threshold limit values (*TLV-TWA*), and estimated relative dielectric strength (*E$_r$*) of each component are shown in **Table 1** (Preve, Piccoz and Maladen, 2015; Mateu-Royo et al., 2019). After dilution with a carrier gas such as dry air or N$_2$, mixtures would have a similar dielectric strength as SF$_6$. The fact that both C5K and HFO-4 have lower toxicity values would be compensated, as less concentration would be used.

Table 1. Main physical properties of C5K and HFO-4 (Preve, Piccoz and Maladen, 2015; Mateu-Royo et al., 2019).

Property	SF$_6$	C5K	HFO-4
MW (g mol^{-1})	146	266	164
GWP	23500	1	18
NBP (ºC)	- 64.0	26.5	7.5
TLV-TWA (ppm$_v$)	1000	225	500
E$_r$	1.0	2.0	1.8

The diffusional behavior of these new insulating gas mixtures is analyzed by monitoring the mixing process using UV-VIS spectroscopy technology in a gas chamber, which has been designed specifically to be similar to a medium voltage switchgear cell.

2. Methods

2.1. Experimental procedure

The gas chamber is a 60 L tank, 800 x 500 x 150 mm, designed to hold the gas mixtures while they mix. The UV-VIS spectroscopy system consists of a DH-2000 light source that emits light, *I$_0$*, into three lenses at three different

heights of the gas tank and a Maya2000 Pro spectrophotometer from Ocean Insight that measures the received light, I. The measurement lines are located at Absorbance, A, is calculated using the Beer-Lambert Law (1). The concentration, c, is calculated using a calibration line obtained measuring the absorbance of mixtures with known concentrations. The molar extinction coefficient, ε_M, of each component can also be calculated when the absorbance, concentration, and path length, l.

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon_M \cdot c \cdot l \tag{1}$$

The composition of the mixtures that were carried on is shown in **Table 2**. Experiments of binary mixtures BM1 and BM2 were first conducted, using N_2 as carrier gas; and then, TM1 and TM2 were examined, with dry air as the carrier.

Table 2. Composition of the binary and ternary mixtures.

	C5K	HFO-4	AIR	N2
BM1		20		80
BM2		40		80
TM1	5	40	55	
TM2	10	40	50	

The components of the gas mixtures are inserted in the chamber according to their molecular weight, from heaviest to lightest, through a wall bushing located at the top, resulting in an initial state of stratification. The experiments were run at atmospheric temperature and pressure.

2.2. Mathematical model

The evolution of the concentration will depend on molecular diffusion, Fick's Law, and natural convection, the overall transport produced by the difference in the density of the fluids (Seader, Henley and Roper, 2011).

Combining both effects, a modified version of Fick's Law of diffusion is obtained (2), where C_i is the concentration, D is the diffusional constant, z is the height of the gas chamber and v_i is the velocity (3) caused by the difference in the density of the fluids, being K the convection constant, ρ_m the density of the fluid mixture and ρ_i de density of the compounds.

$$\frac{dC_i}{dt} = D \cdot \left(\frac{\partial^2 C_i}{\partial z^2}\right) + \frac{\partial(v_i \cdot C_i)}{\partial z} \tag{2}$$

$$v_i = K \cdot (\rho_m - \rho_i) \tag{3}$$

For multicomponent mixtures, however, the equations that are used are based on the Stefan-Maxwell equation (4), which is derived from the Boltzmann equation (Taylor and Krishna, 1993), modified for a ternary mixture with the natural convection component (5). The element [D] represents a size N–1 square matrix, composed of the practical diffusion coefficients (D_{11}, D_{12}, D_{21}, and D_{22}), and a convective constant is used (K_1 and K_2) for each v_i.

$$\left(\frac{dC_i}{dt}\right) = [D] \cdot \left(\frac{\partial^2 C_i}{\partial z^2}\right) \tag{4}$$

$$\begin{pmatrix} \frac{dC_1}{dt} \\ \frac{dC_2}{dt} \end{pmatrix} = \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \cdot \begin{pmatrix} \frac{\partial^2 C_1}{\partial z^2} \\ \frac{\partial^2 C_2}{\partial z^2} \end{pmatrix} + \begin{pmatrix} \frac{\partial(v_1 \cdot C_1)}{\partial z} \\ \frac{\partial(v_2 \cdot C_2)}{\partial z} \end{pmatrix} \tag{5}$$

Moreover, the effective diffusivity coefficients, D_{eff}, are calculated (6), which give us the value of the diffusivity for each component in the mixture.

$$D_{i,eff} = \sum_{k=1}^{n-1} D_{ik} \frac{\nabla y_k}{\nabla y_i} \tag{6}$$

The differential equations (2) and (5) are solved using SCILAB to obtain the concentration values of the mathematical model. An error objective function, OF, (7) is minimized to calculate the optimal values of the constants, D and K.

$$OF = \frac{\sum_1^{N_T}(C_{exp} - C_{model})^2}{N_T} \tag{7}$$

The relative standard error, RSE, (8) of each mixture has also been calculated.

$$RSE\ (\%) = \sqrt{\frac{\sum_1^{N_T}\left(\frac{C_{exp} - C_{model}}{C_{model}}\right)^2}{N_T - 1}} \cdot 100 \tag{8}$$

3. Results and discussion

3.1. Calibration

The calibration lines are obtained measuring the absorbance of several gas mixtures of which concentration is known. The results are linearly adjusted and are represented in **Figure 1**.
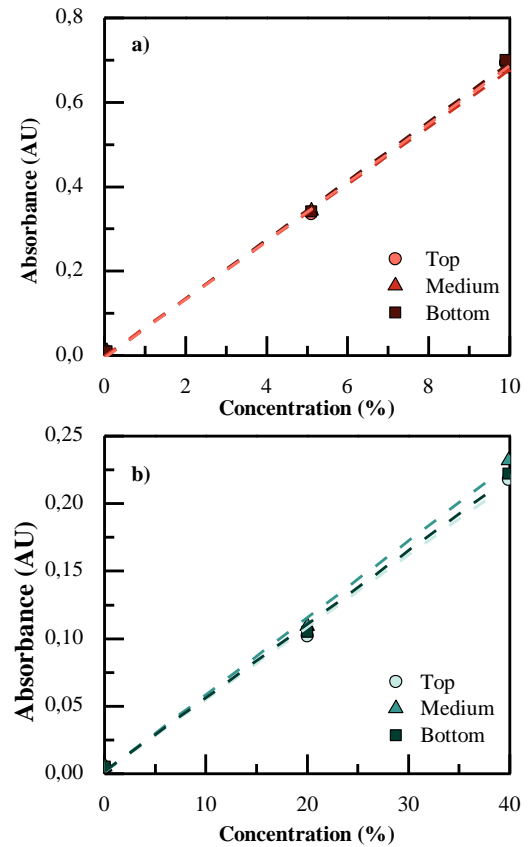

Figure 1. Calibration lines of a) C5K and b) HFO-4.

Also, the molar extinction coefficient, ε_M, of each component is calculated, which is shown in **Table 3**, considering that the path length is 15 cm. The results show that C5K absorbs nearly ten times more than HFO-4.

Table 3. Molar extinction coefficients of C5K and HFO-4.

	C5K	HFO-4
ε_M (M^{-1} cm^{-1})	4.59	0.38

3.2. Diffusional behavior

Thanks to the calibration lines, the concentration of the components is obtained from the absorbance measured in the UV-VIS system. The concentration profiles, in mol m^{-3}, of the binary mixtures BM1 and BM2 are represented in **Figure 2** against time and position (height) in the cell. It can be appreciated that both mixtures stabilize approximately after 8.5 h.
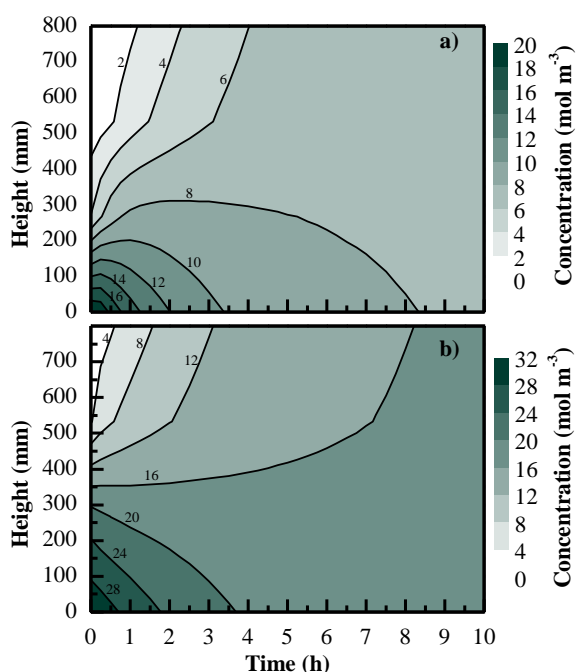

Figure 2. Concentration profiles, in mol m^{-3}, for the binary mixtures: a) BM1, and b) BM2.

The diffusional parameters that have been calculated in SCILAB are shown in **Table 4**: the final concentration at which the mixture stabilizes, C_f, the diffusion and convection coefficients, D and K, and the weighted standard deviation, σ, of the experimental and modelled concentration data.

Table 4. Diffusional parameters for the binary mixtures.

Property	BM1	BM2
C_f (mol m^{-3})	7.8	16.6
C_f (%)	19.0	40.5
D (m^2 h^{-1})	0.028	0.025
K (m^4 g^{-1} h^{-1})	5·10^{-11}	7·10^{-11}
RSE (%)	12.7	12.5

Diffusion constants in binary mixtures should not be concentration dependent, which can be proved by the fact that both mixtures stabilize at a similar time and present a similar diffusion coefficient, even though their concentration is different. Besides, the convection constant is very low, possibly implying that the effect of the convection is negligible. The relative standard error is similar for both mixtures and is smaller than 15 %.

The concentration profiles, in mol m^{-3}, of the ternary mixtures TM1 and TM2 are represented in **Figure 3** and **Figure 4**. For The TM1 mixture, it must be considered that C5K has a very low concentration and varies very little, so the limiting compound will be HFO-4, which stabilizes after nearly 9 h. In the TM2 mixture, however, the concentration of C5K is higher and it gains significance; HFO-4 stabilizes at roughly 6 h and C5K becomes the limiting component, stabilizing after almost 8 h.
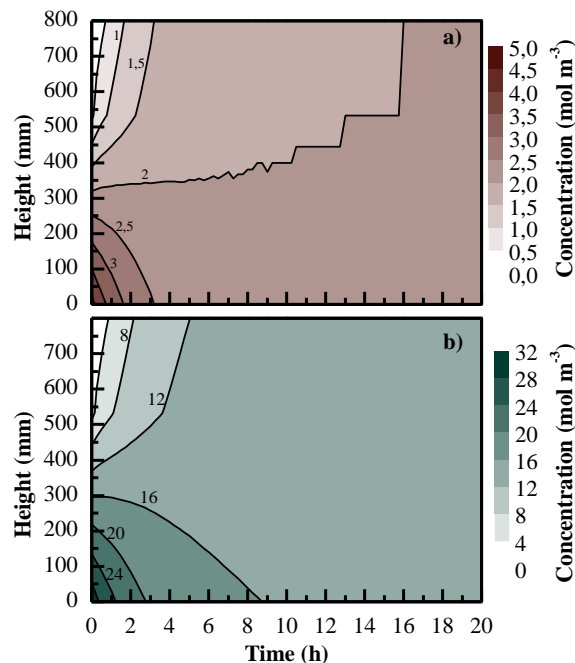

Figure 3. Concentration profiles, in mol m^{-3}, for the ternary mixture TM1: a) C5K and b) HFO-4.
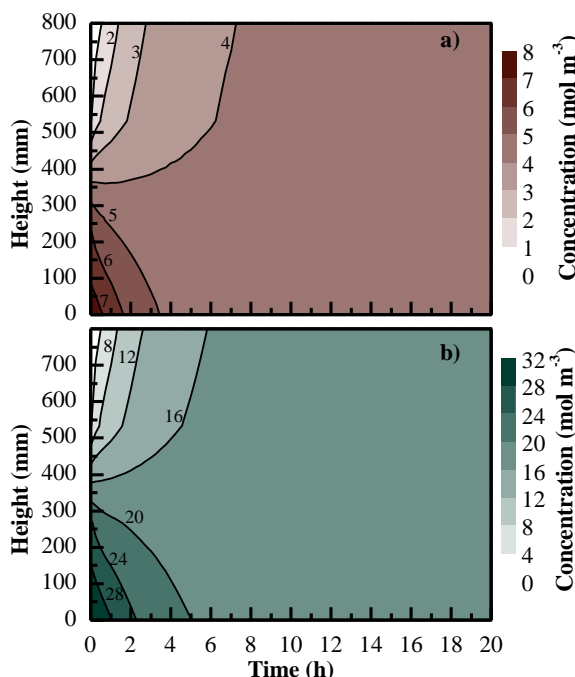

Figure 4. Concentration profiles, in mol m^{-3}, for the ternary mixture TM2: a) C5K and b) HFO-4.

The diffusional parameters that have been calculated in SCILAB are shown in **Table 5**: the final concentration at which the components of mixture stabilize, $C_{i,f}$, the effective diffusion and convection coefficients, $D_{i,eff}$ and K_i, and the weighted standard deviation, σ, of the experimental and modelled concentration data.

Table 5. Diffusional parameters for the ternary mixtures.

Property	TM1		TM2	
	C5K	HFO-4	C5K	HFO-4
C_f (mol m^{-3})	2.0	14.7	4.2	17.8
C_f (%)	4.9	35.9	10.2	43.4
$D_{i,eff}$ (m^2 h^{-1})	0.028	0.256	0.027	0.267
K_i (m^4 g^{-1} h^{-1})	- 3$\cdot$10^{-10}	5$\cdot$10^{-11}	3$\cdot$10^{-10}	- 5$\cdot$10^{-11}
RSE (%)	7.8	7.4	8.8	7.7

In ternary mixtures can also be seen that the effective diffusion coefficients of the components are similar, being higher the diffusivity of HFO-4, which is consistent with C5K being the limiting compound in TM2. Also, the effective diffusivity of HFO-4 is almost ten times higher than the binary diffusivity obtained in the binary mixtures, probably affected by the interaction between both heavy compounds. The convective constant can also be said to be negligible in the ternary mixtures. In the ternary mixture the relative standard error is also similar for both mixtures, being smaller that 10 %, and also between both components, C5K and HFO-4, the difference is also small.

4. Conclusions

An experimental equipment to monitor the gas concentration of mixtures in the filling process of electrical switchgear has been designed, using UV-VIS technology. Thus, it has been possible to determine the time that the binary mixtures containing HFO-4 and the ternary mixtures containing also HFO-4 take less than 9 h to mix inside a gas chamber that is similar to a medium voltage switchgear cell.

Besides, the molar extinction coefficient of both components has been calculated, being that HFO-4 ($\varepsilon_M = 0.38$ M^{-1} cm^{-1}) is 10 times lower than C5K ($\varepsilon_M = 4.59$ M^{-1} cm^{-1}), requiring and adjustment in the optical path length of the measurement elements of the UV.

In addition, a mathematical model that considers both molecular diffusion and natural convection has been proposed to describe the mixing process of the binary and ternary mixtures. The RES of the mixtures is in every case lower that 15 %. Also, binary mixtures show higher RES than the ternary mixtures.

Moreover, the diffusional parameters have also been numerically calculated in SCILAB. Convection coefficients of all mixtures are significantly low, which may mean that the effect of natural convection is negligible in comparison with molecular diffusion.

Finally, both binary mixture concentrations show similar diffusional behavior, verifying that diffusion in binary mixtures does not depend on concentration. In the ternary mixtures HFO-4 has been proved to diffuse faster than C5K, making this the limiting component on the mixtures; however, all binary and ternary mixtures reach uniformity in the concentrarion after a similar period of time, around 8-9 hours.

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