Characterization of the combustion products of fluorinated compounds

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SCIENCES DES INCENDIES

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Characterization of the combustion products of fluorinated compounds

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- Experimental setup
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- Conclusions

Introduction

The Montreal protocol and the F-gas Regulation EU 2024/573 requests the substitution of compounds with high Global Warming and Ozone Depletion potentials with products that generate considerably lower impacts on the ozone layer.

Hydrochlorofluorocarbons (HCFCs)
Hydrofluorocarbons (HFCs).

→

Hydrofluoroolefins (HFOs)
Fluorinated ethers (HFEs)

F-compounds are usually considered to have a low flammability…

- The **flammability** of halogenated compounds is **usually decreased** by high halogenation levels.
- Certain fluorinated compounds can also be considered for **fire suppression applications**.

…but their thermal stability is limited

Nowadays, the **limited information about the toxic emissions** from emerging fluorinated compounds confirms the pertinence of further explorative studies.

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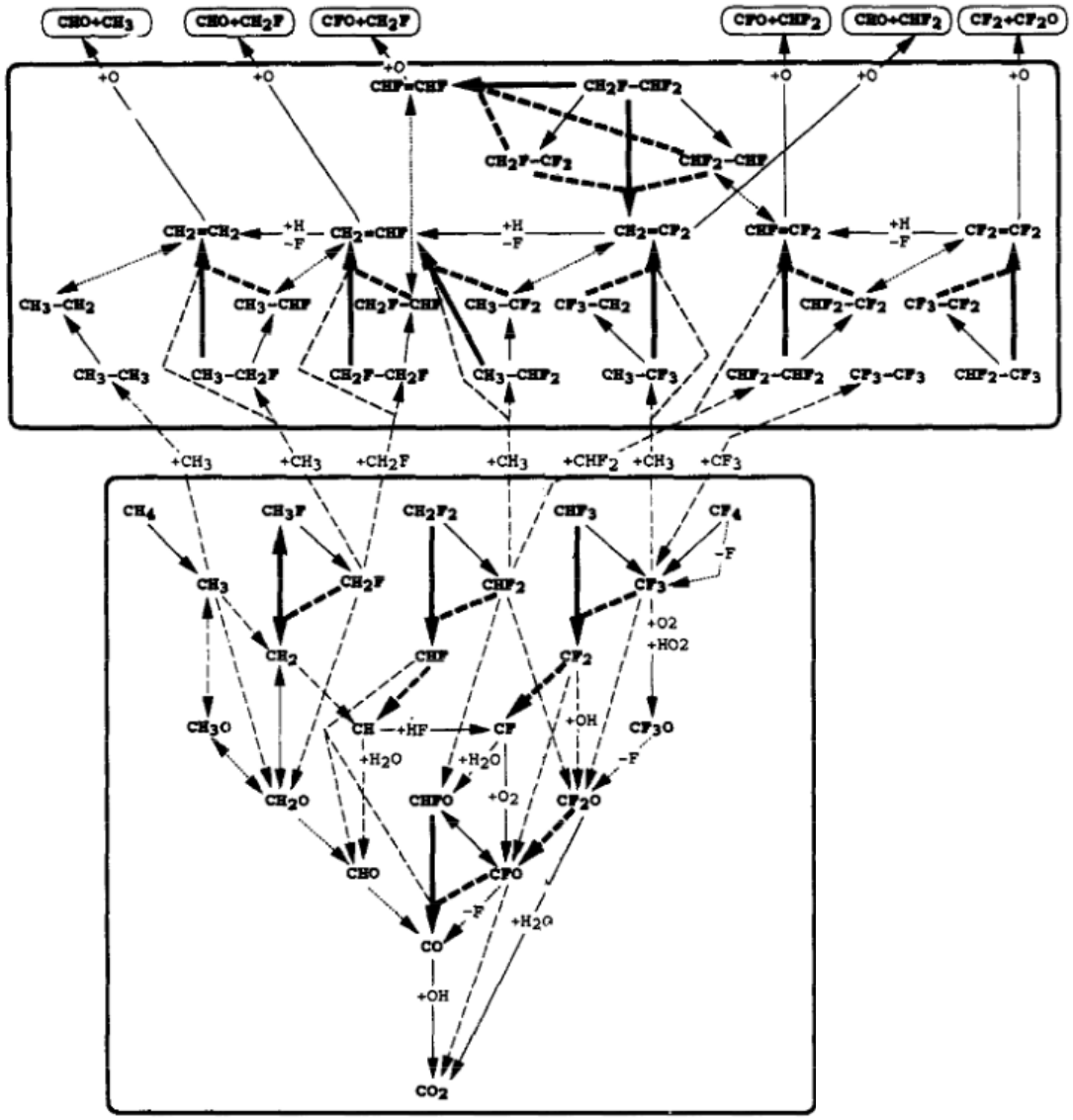
Decomposition of a fluorinated compound with 2 carbon atoms



Decomposition reactions

$$CF_3O \rightarrow CF_2O + F$$

$$CHF_2CF_3 \rightarrow CF_2 = CF_2 + HF$$

Bimolecular reactions

$$CH_2F + CH_3 \rightarrow CH_3CH_2F$$

Reactions with OH or O

$$CF_2 + OH \rightarrow CF_2O + H$$

Abstraction by H

$$CHF_2CF_3 \rightarrow CF_2CF_3 + H$$

Reaction with water

$$CF_2O + H_2O \rightarrow CO_2 + 2H + 2F$$

Burgess, D. R., Zachariah, M. R., Tsang, W., & Westmorelandt, P. R. (1995). Thermochemical and chemical kinetic data for fluorinated hydrocarbons. *Progress in Energy and Combustion Science*, *21*(6), 453–529.

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Hydrogen fluoride and carbonyl fluoride

Hydrogen fluoride

Corrosive Acute Toxic

HF

Threshold	Exposure time				
	10 min	30 min	60 min	240 min	480 min
AEGL-1	1	1	1	1	1
AEGL-2	95	34	24	12	12
AEGL-3	170	62	44	22	22

Carbonyl fluoride

Corrosive Acute Toxic

CF_2O

Threshold	Exposure time				
	10 min	30 min	60 min	240 min	480 min
AEGL-1	NR	NR	NR	NR	NR
AEGL-2	0.35	0.35	0.28	0.17	0.087
AEGL-3	1.00	1.00	0.83	0.52	0.26

Acute Exposure Guideline Levels

General population, including susceptible individuals

AEGL-1: Discomfort, irritation, or certain asymptomatic, non-sensory effects.

AEGL-2: Irreversible or other serious, long-lasting adverse health effects.

AEGL-3: Life-threatening health effects or death.

Fluorinated compounds

What are the emissions of long-chain fluorinated compounds?

MAIN OBJECTIVE OF THIS STUDY

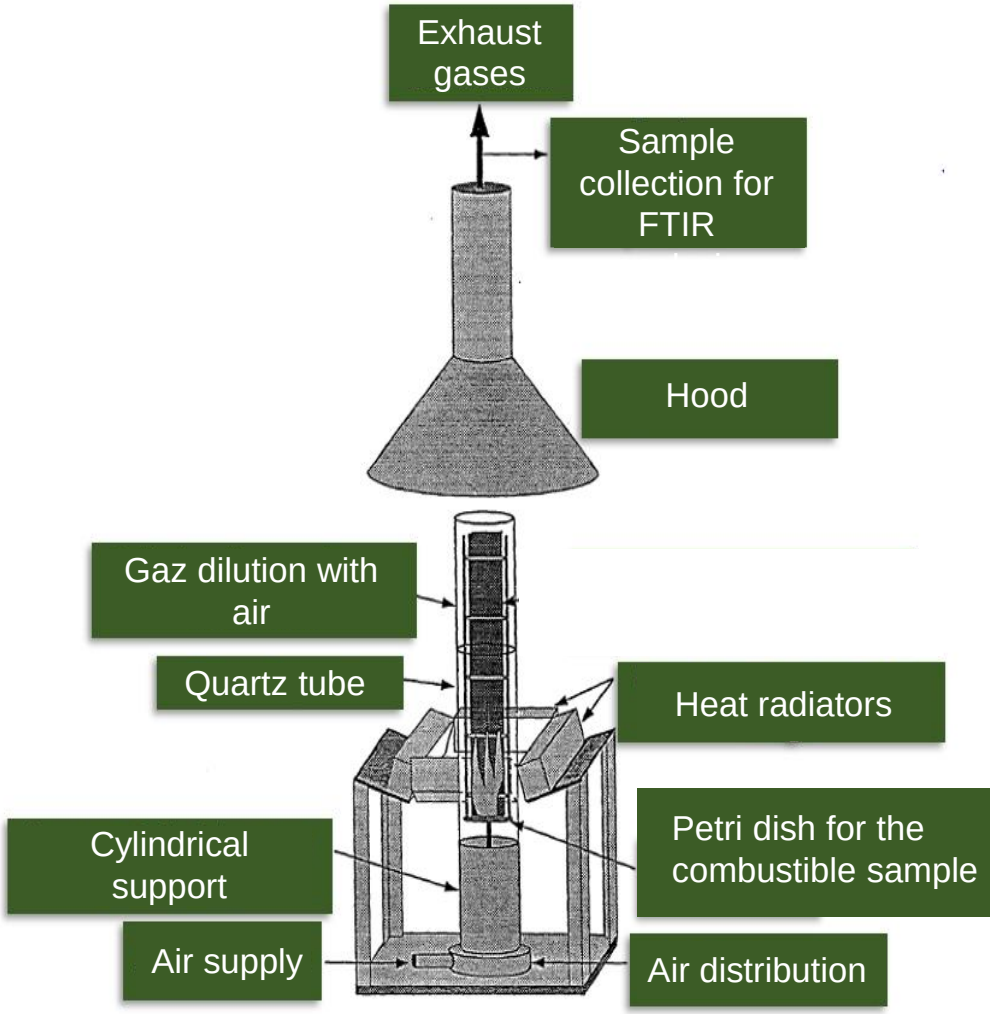
In this analysis, the vapours and fumes generated with different combustion flames are characterised to estimate the emission rate of the **fluorinated compound** as well as those of products such as **hydrogen fluoride (HF)** and **carbonyl fluoride (COF_2)**.

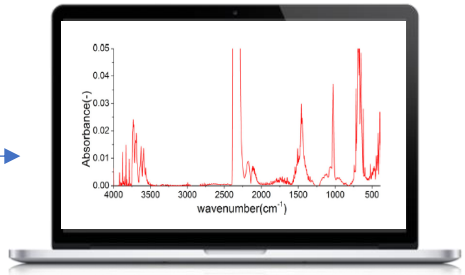
Chemical formula	CAS number	Main use	Normal boiling temperature (°C)	Molecular weight (g/mol)	H/F ratio
$C_6F_{12}O$	756-13-8	Cleaning agent for electric devices	49	316.0	0,00
$C_9H_5F_{15}O$	297730-93-9	Cleaning agent for medical devices	129	414.0	0,33
$C_4H_2F_6$	692-49-9	Foam-blowing agent & heat exchange fluid	33	164.0	0,33
$C_6H_5F_9O$	163702-06-5	Solvent, heat exchange fluid & hydraulic systems	76	264.0	0,55
$C_4H_5F_5$	406-58-6	Foam-blowing agent, solvent & heat exchange fluid	40.2	148.0	1,00

LIQUID FLUORINATED COMPOUNDS

Experimental setup

Fire propagation apparatus (FPA)

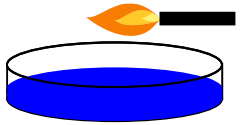




Fourier Transform Infrared (FTIR) spectrometry

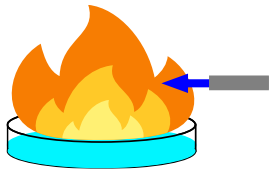
3 configurations were tested:

Liquid F-compound

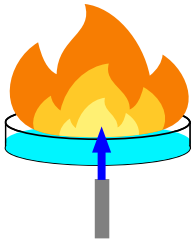


Pilot flame

Lean mixtures : F-compound and air 6%



Horizontal injection into a pool fire of acetone



Vertical injection into a pool fire of acetone

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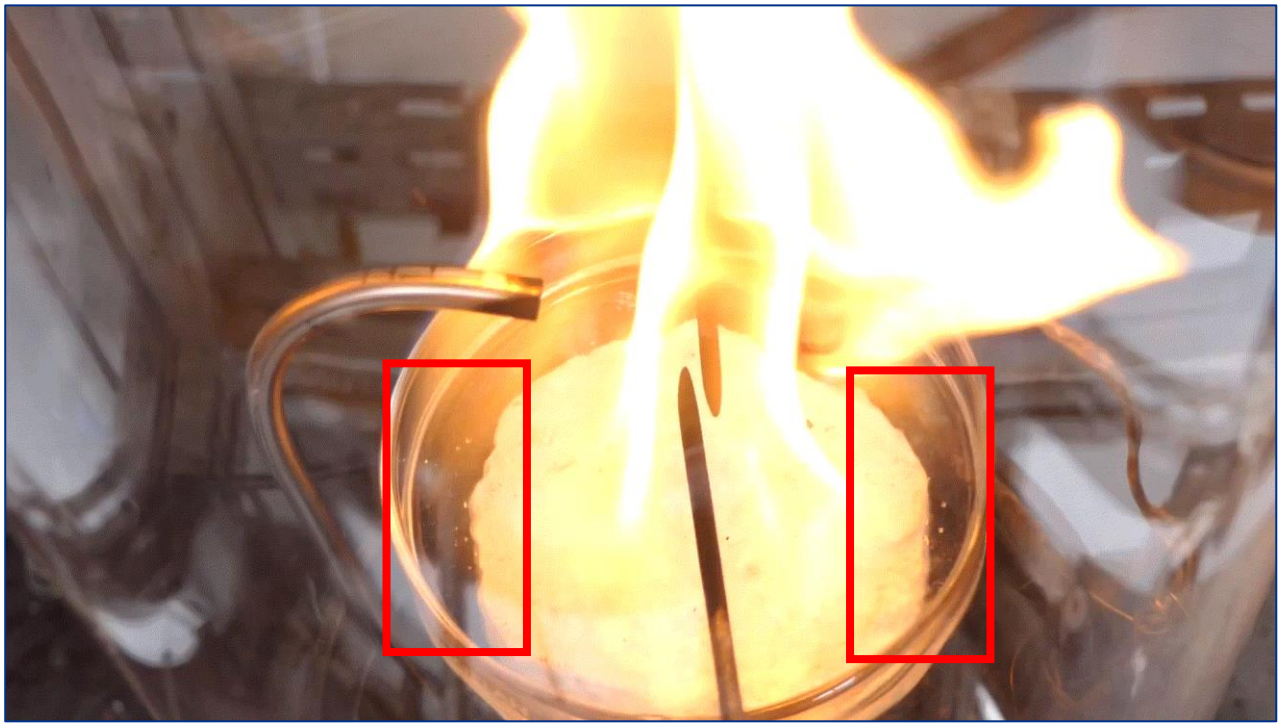
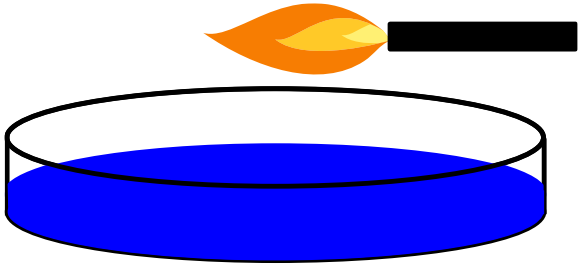
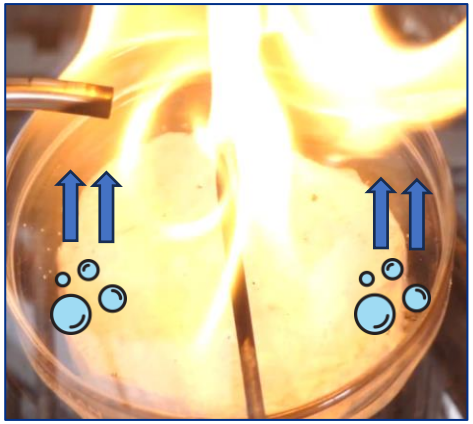
Test N°1: Pilot flame



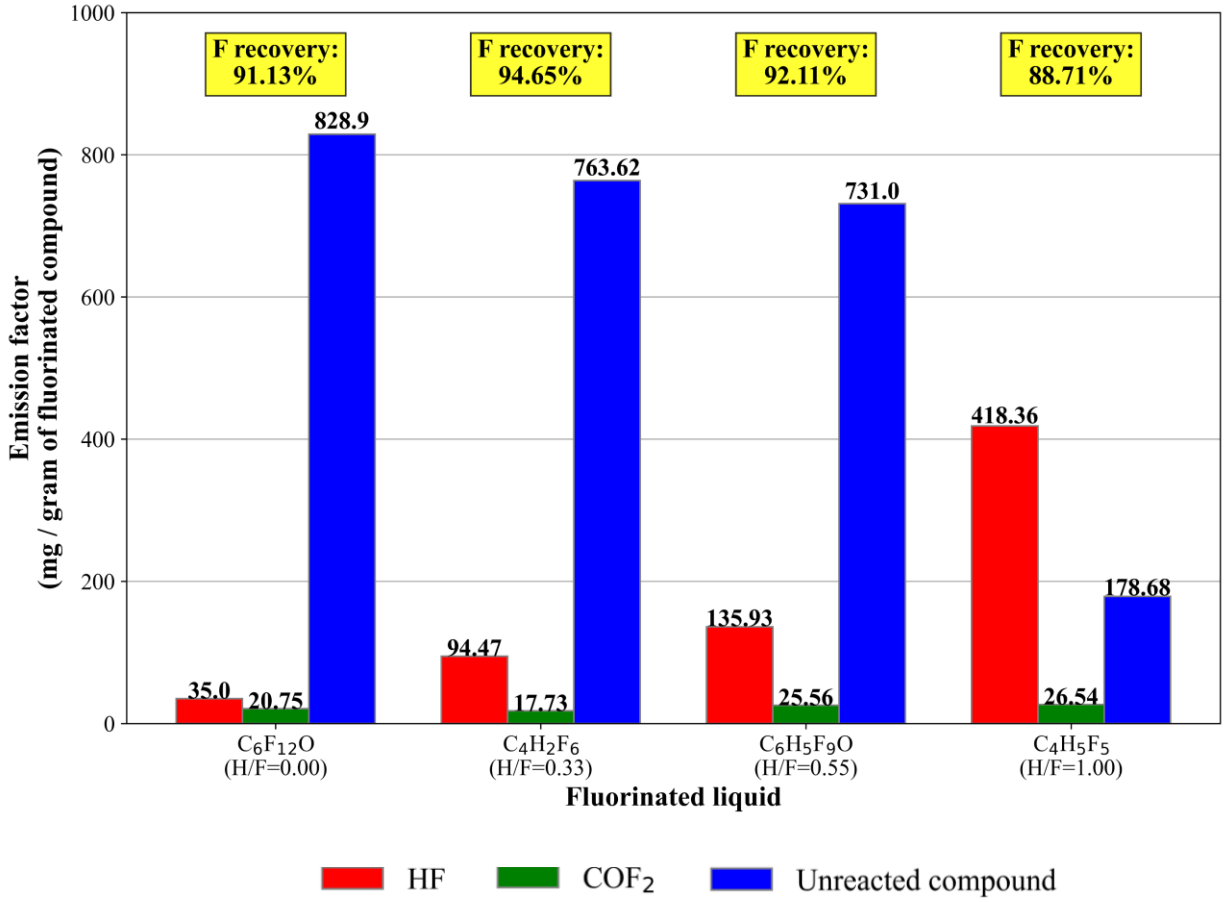




The liquid is only partially burned because the production of combustion radicals is not sufficient to overcome the evaporation rates of the liquid.

The flame shows a steady behavior characterized by small fluctuations and a low turbulence

Test N°1: Pilot flame

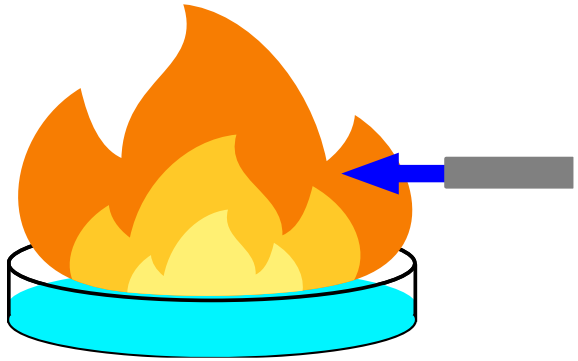


H/F ratio

- Enhancement of the combustion reactions due to higher concentrations of H radicals.
- More HF is rapidly produced by single-step mechanisms such as the unimolecular decompositions
- The preponderance of the fluid's evaporation leads to a reduction of the multi-step decompositions

H/F ratio → Conversion of fluorinated liquid Production of HF Production of COF_2

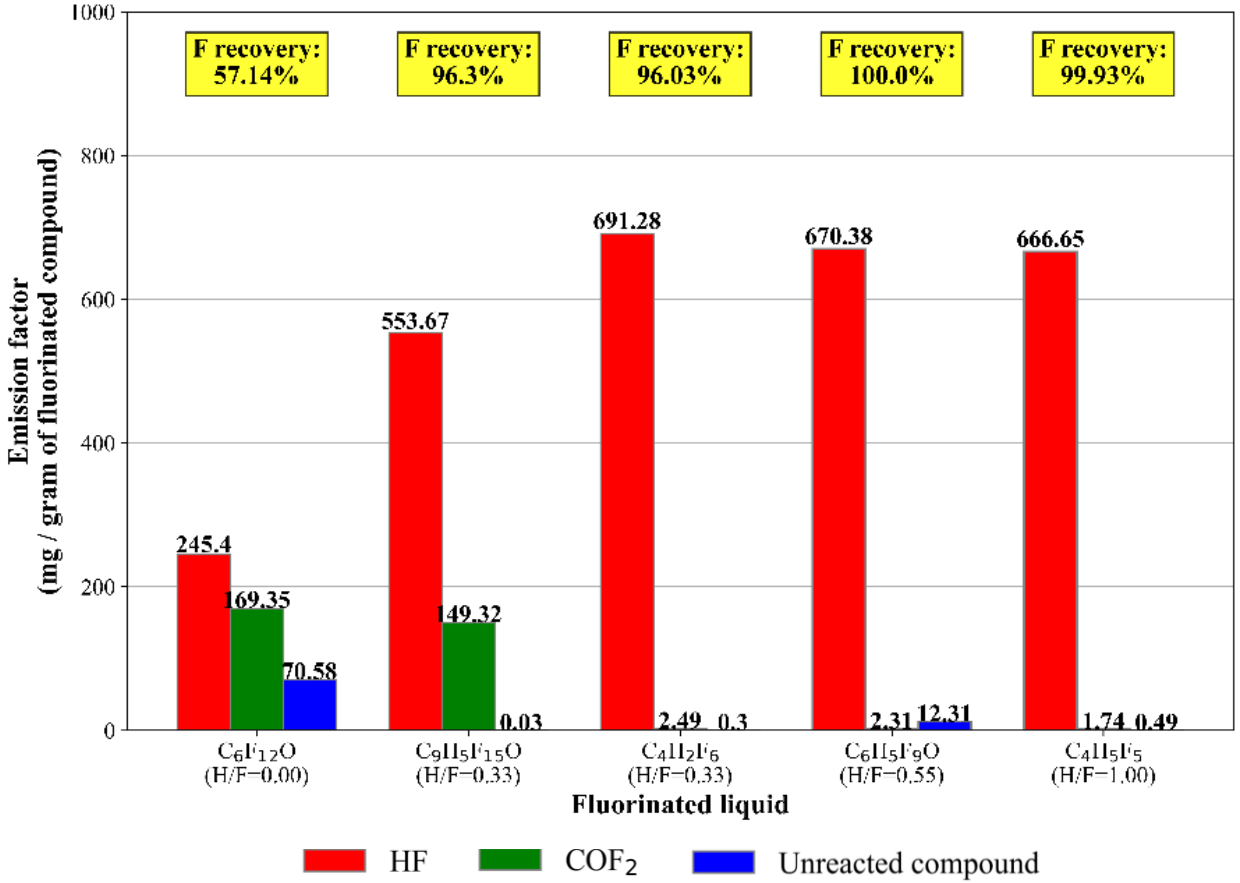
Test N°2: Horizontal injection



The fluorinated compound is injected into the flame of acetone

The injection of the mixture induces turbulence at the middle region the flame

Test N°2: Horizontal injection



Presence of the acetone pool fire

- The conversion of the F-compound is considerably high (almost complete).
- The pool fire becomes a heating source and increases the concentration of intermediate radicals.
- <u>Higher humidities:</u> Higher concentrations of OH and H radicals in the combustion zone

H/F ratio → Conversion of fluorinated liquid | Production of HF | Production of COF_2

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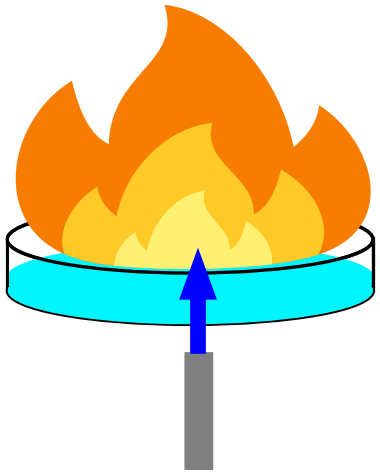
Test N°3: Vertical injection

Lean mixture of the F-compound with air

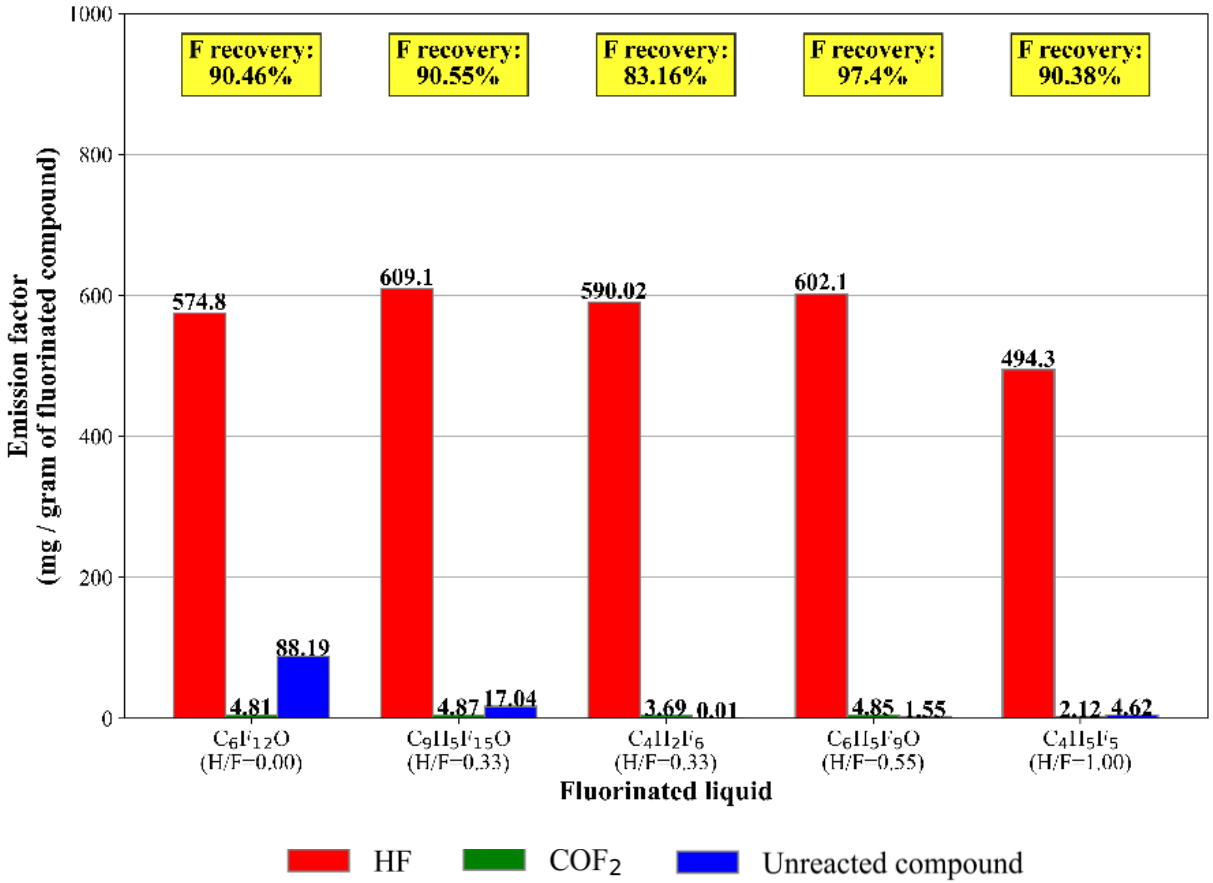
The fluorinated compound is injected at the bottom of the pool fire of acetone

Longer residence times within the flame

The flow perturbations are distributed at the low region of the flame.



Test N°3: Vertical injection



Variation in the direction of the injection

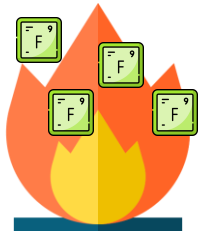
- The conversion of the F-compound is considerably high (almost complete).
- Longer residence within the flame and greater interaction probabilities with an intermediate radical.
- The air mixture is fed at a location closer to the center of the flame. This fact provides a better interaction with the pool of radicals.

H/F ratio → Conversion of fluorinated liquid | Production of HF | Production of COF_2

Conclusions

Conclusions

In spite of being considered as low-flammability compounds, fluorinated fluids are susceptible to thermal decomposition reactions.



When the combustion conditions are modified considerably, significant variations can be observed in the emission rates of the three toxic compounds. Some of these parameters are: