EP-DT
Detector Technologies

RPC 2024
Santiago de Compostela (Spain)

R134a and SF6 recuperation plants: status and plan

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Outline

- F-gas regulations
- Gas recirculation and recuperation systems
- R134a recuperation plant
- R&D for an SF6 recuperation plant
- Conclusions

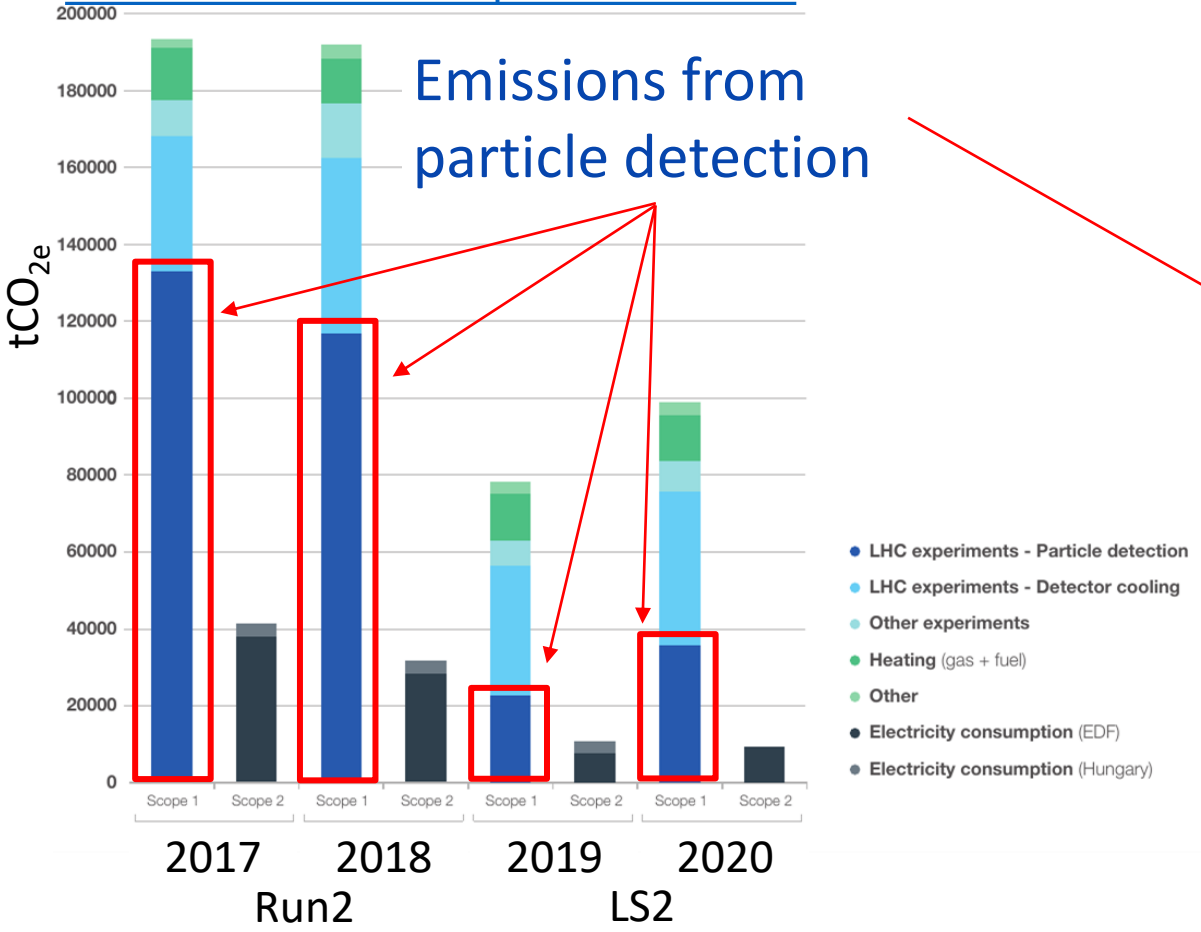
Greenhouse gas usage

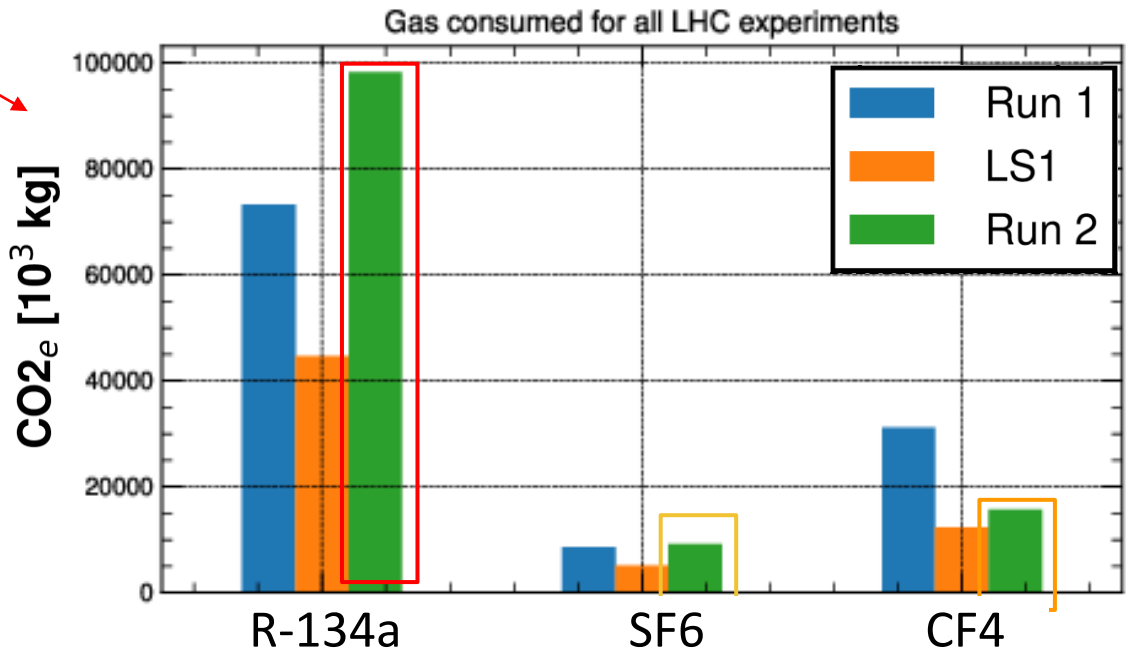
- CERN Environment Report 2019-2020
- 2021: CERN's Year of Environmental Awareness.
- CERN Environment workshop: 12 and 13 October 2022
- CERN Environment Report 2021-2022

Total CERN emissions during 1 year of Run 2 ~ **200 000 tCO2e**

~ 50% from particle detectors → mostly due to leaks and operation

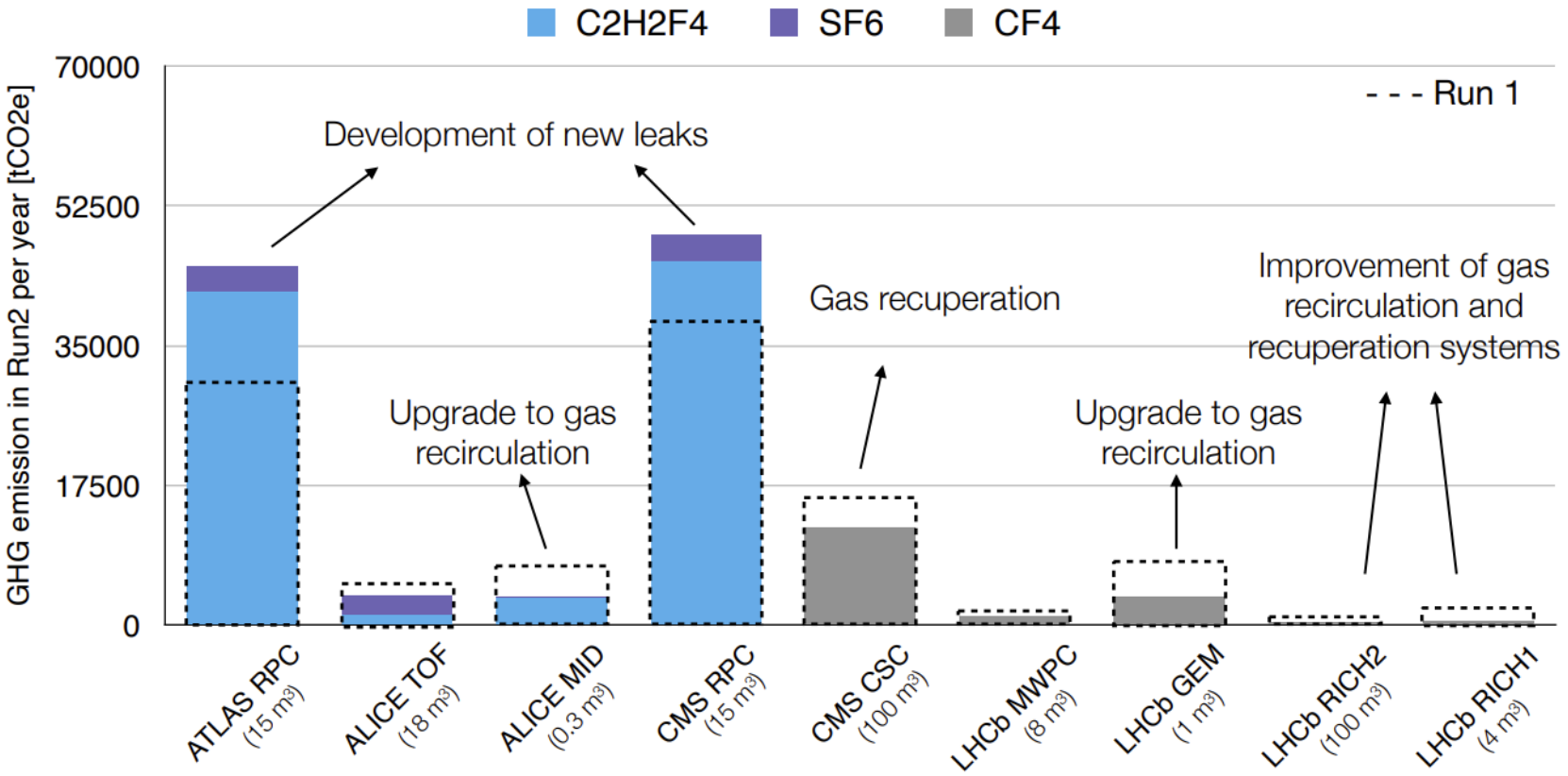
- **$C_2H_2F_4$/R-134a** biggest contributor → leaks from RPC detector
- **CF_4** → due to operation of CSC and RICH systems
- **SF_6** → Related to RPCs as R-134a

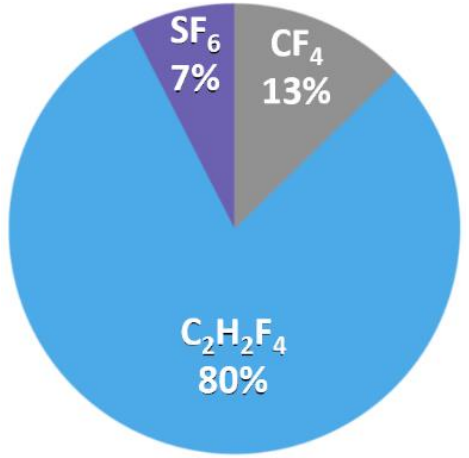




Gaseous detector systems at LHC

Of course, GHG usage in particle research is negligible wrt other activities.
However, **GHG optimization is mandatory**, and it can secure operation over the LHC run period and reduce costs.





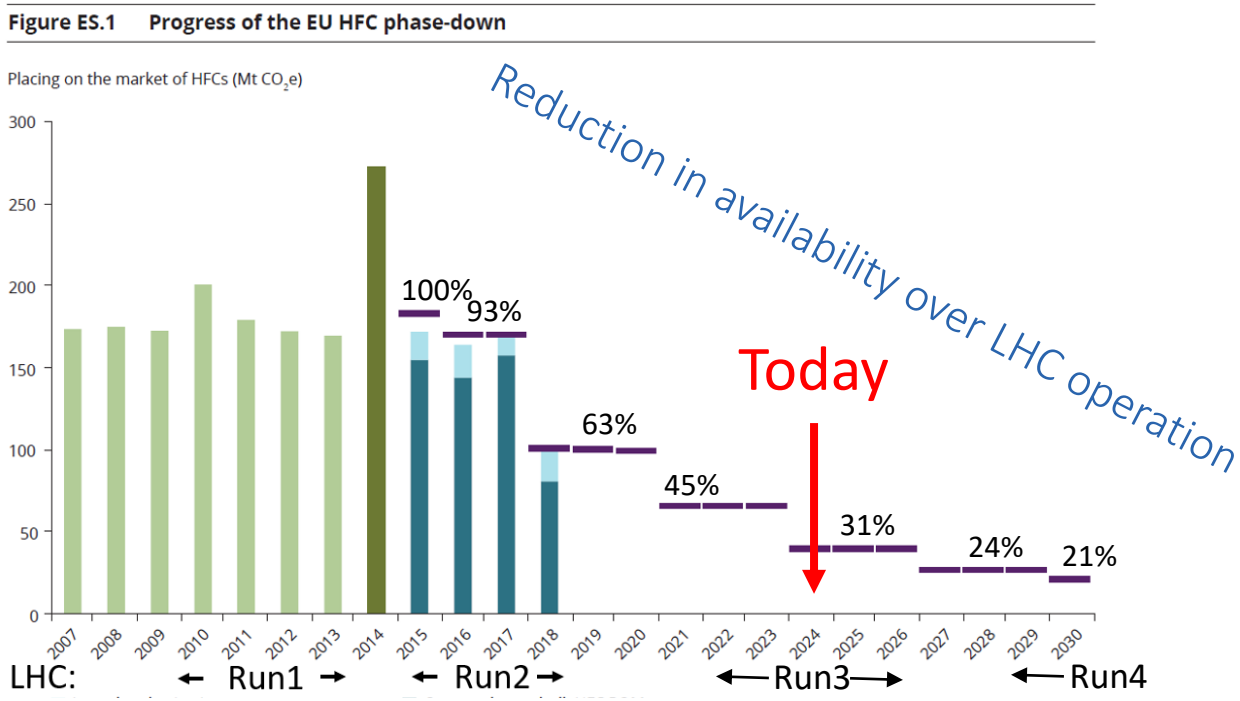
-40% GHG emissions from Run 1 to Run 2 excluding ATLAS and CMS RPC systems
-25% GHG emissions from Run 2 to Run 3 excluding ATLAS and CMS RPC systems

New objective: -28% by 2024 wrt 2018 (Run2)

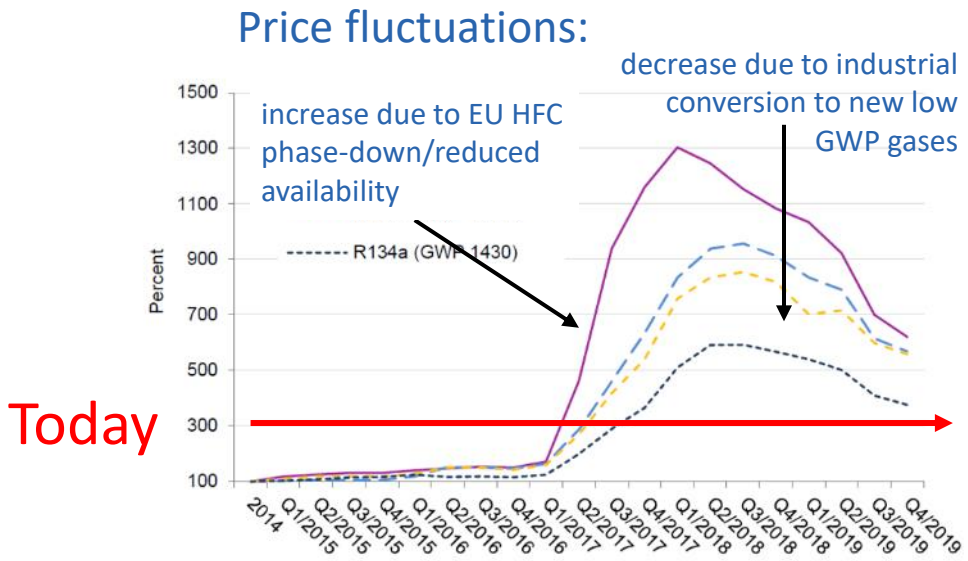
Greenhouse gas regulation

Due to the environmental risk, "**F-gas regulations**" started to appear. For example, the EU517/2014 is:

- **Limiting the total amount** of the most important F-gases that can be sold from 2015 onwards. By 2030, it limits the use to 1/5 of 2014 sales.
- **Banning the use of F-gases** in new equipment where less harmful alternatives are available.
- **Preventing emissions of F-gases** from existing equipment by requiring checks, proper servicing and recovery of gases.



HFC phase down: effects on HFC availability and prices

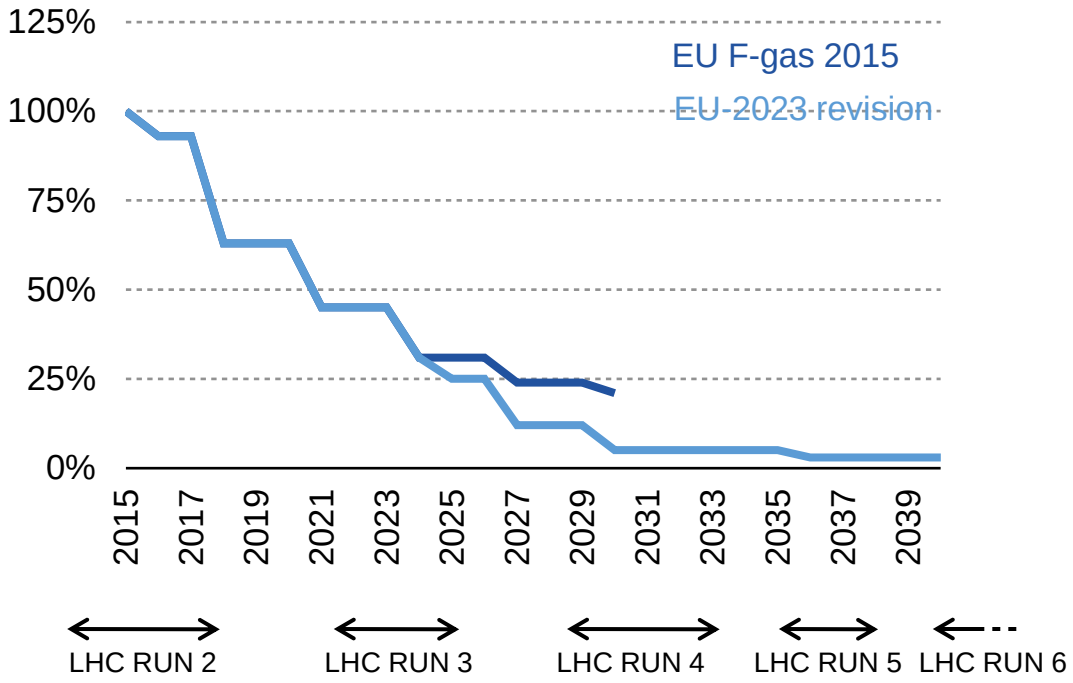


Sources: European Environment Agency, Fluorinated greenhouse gases 2019 report
Öko Recherche report, March 2020 J. Kleinschmidt et al.

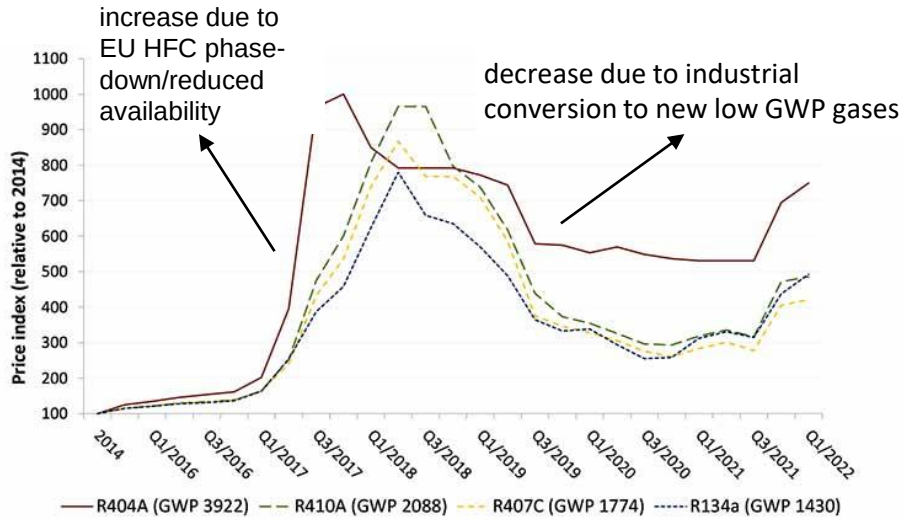
New F-gas regulation: from phase down to phase out

The new Regulation establishes the <u>total elimination of HFCs by 2050</u>

- It is a major step towards climate neutrality
- First goal: reduction of 55% GHG emissions by the end of this decade compared to 1990 levels
- New restrictions also in the use of SF_6 and especially for high GWP gases
- It will result in a reduction in production and reduced quotas for F-Gas refrigerants, leading to an inevitable increase in prices for higher GWP refrigerants
  - It will probably affect not-EU market
- Important also to consider possible new regulation for all PFAS



Average purchase prices of the most commonly used HFC refrigerants



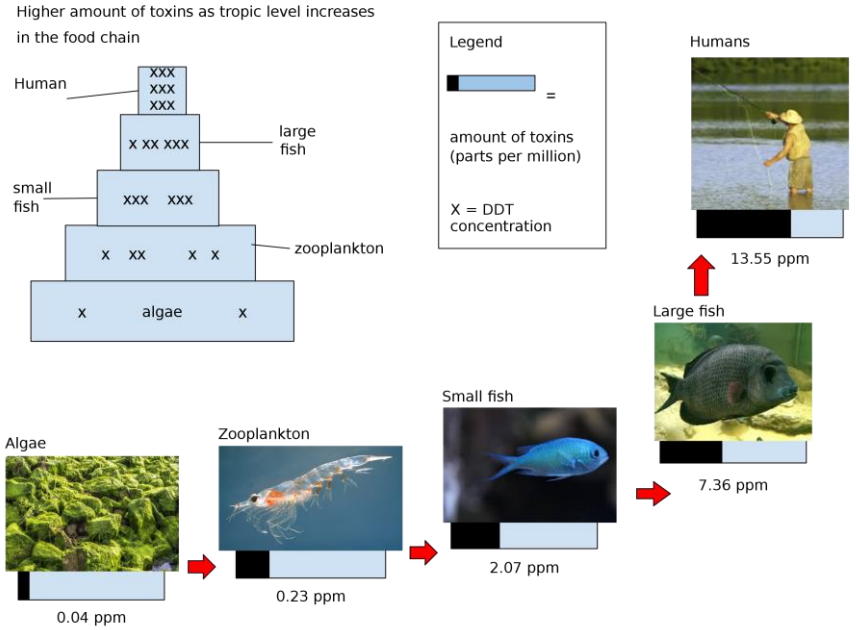
And now: PFAS - *"forever chemicals"*

PFASs: fluorinated substances containing at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–) is a PFAS

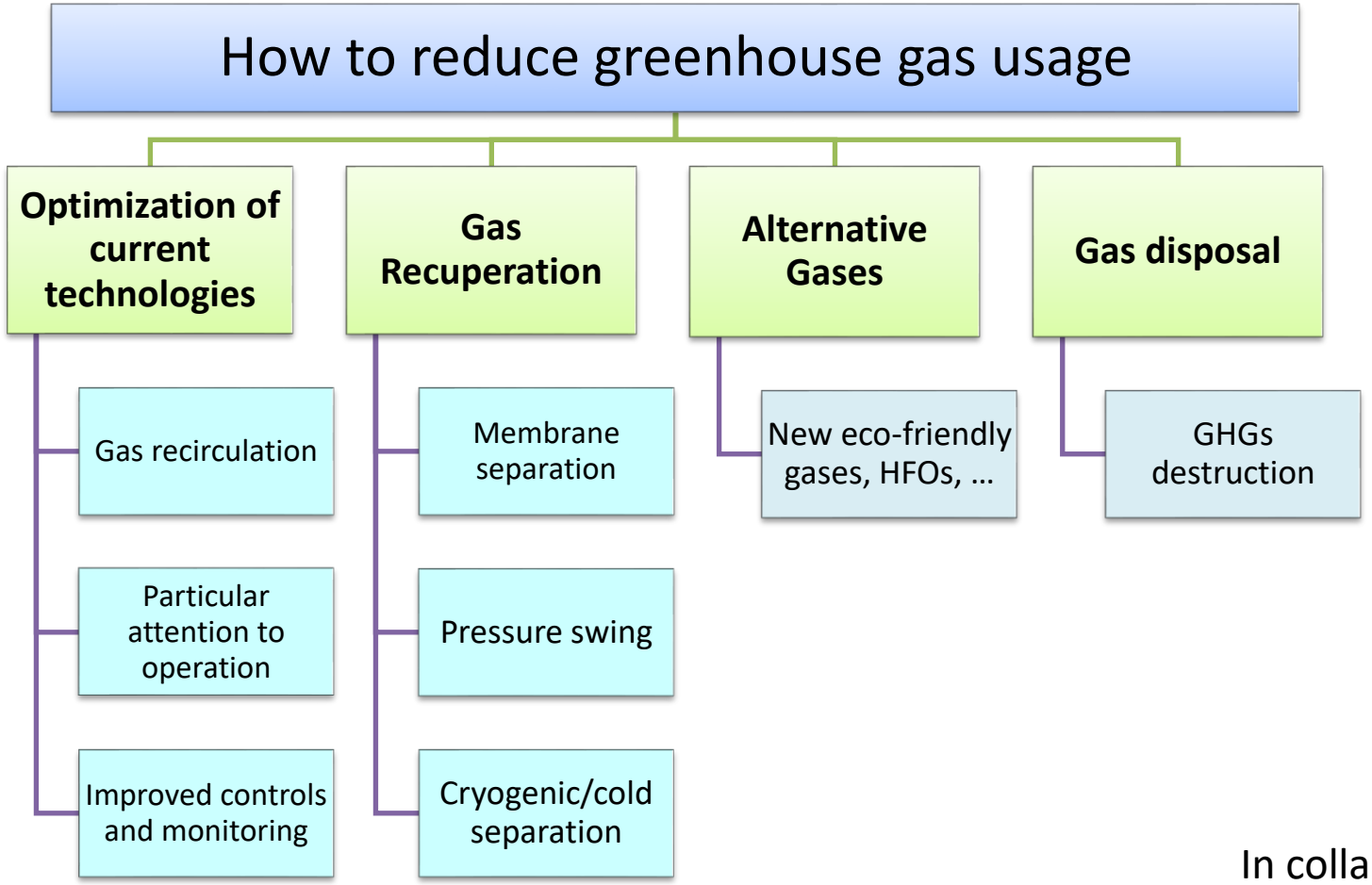
PFASs play a key economic role for companies such as DuPont, 3M, and W. L. Gore & Associates because they are used in emulsion polymerization to produce fluoropolymers. They have two main markets: a $1 billion annual market for use in stain repellents, and a $100 million annual market for use in polishes, paints, and coatings. In 2022, 3M announced that it will end PFAS production by 2025.

It aims to be the biggest chemical ban out of health considerations and biomagnification

Bioaccumulation and biomagnification



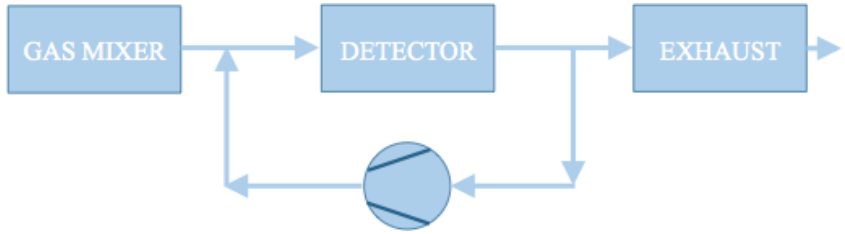
GHG Optimization: CERN Strategies



In collaboration with
HSE/CEPS
HostLab
EP R&D

Gas recirculation vs recuperation

Gas recirculation



Advantages:

- Reduction of gas consumption

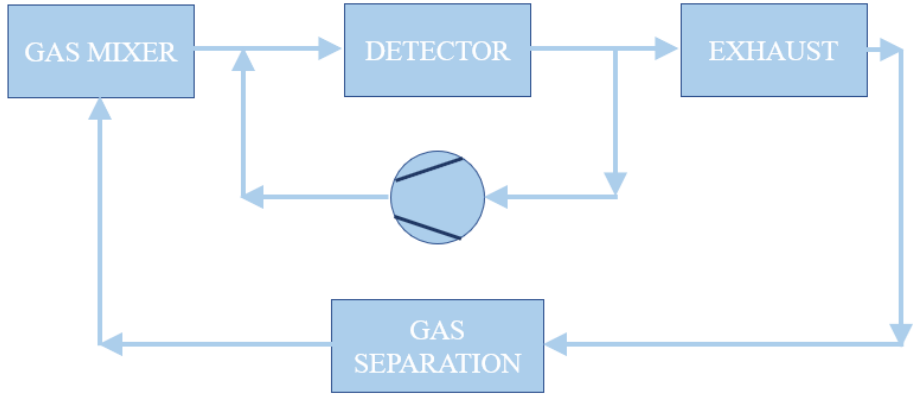
Disadvantages:

- Complex systems
- Constant monitoring (hardware and mixture composition)
- Use of gas purifying techniques

Not only for large experiments, but also for laboratory setups:

- 2013: Development of "A portable gas recirculation unit" JINST 12 T10002
- 2020: Development of Gas recirculation systems for RPC detectors: from LHC experiments to laboratory set-ups - RPC2022

Gas recirculation and recuperation



Advantages:

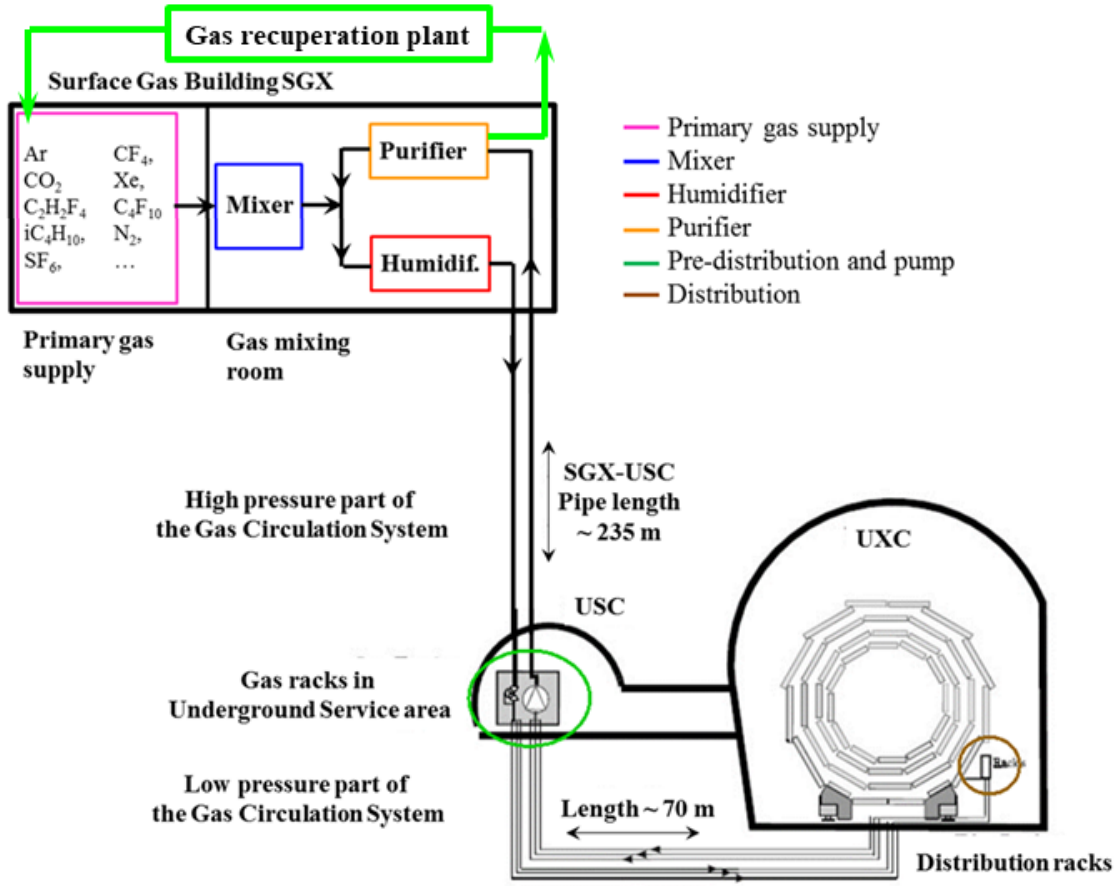
- Further reduction of gas consumption

Disadvantages:

- Higher level of complexity
- Dedicated R&D
- Gas mixture monitoring is fundamental

Gas recirculation and recuperation

Possibility to recuperate a single gas component from exhausted mixture



- ***New recuperation system***
  - **R134a for ALICE-RPC, ATLAS-RPC, CMS-RPC, ALICE-TOF**
  - ***Operational for* CMS-RPC since mid-2024**
- ***Ongoing R&D aims in testing the feasibility for new recuperation systems*:**
  - **SF6 for ALICE-RPC, ATLAS-RPC, CMS-RPC, ALICE-TOF**
- ***and substantial improvements of existing systems:***
  - **CF_4 for CMS-CSC, LHCb-RICH2**
  - **C_4F_{10} for LHCb-RICH1**
- Recuperation will be effective only if leaks at detector level will be reduced
- R134a recuperation can drastically decrease GHG consumption
- R&D costs for first R134a recuperation system can be potentially paid back with one year of operation

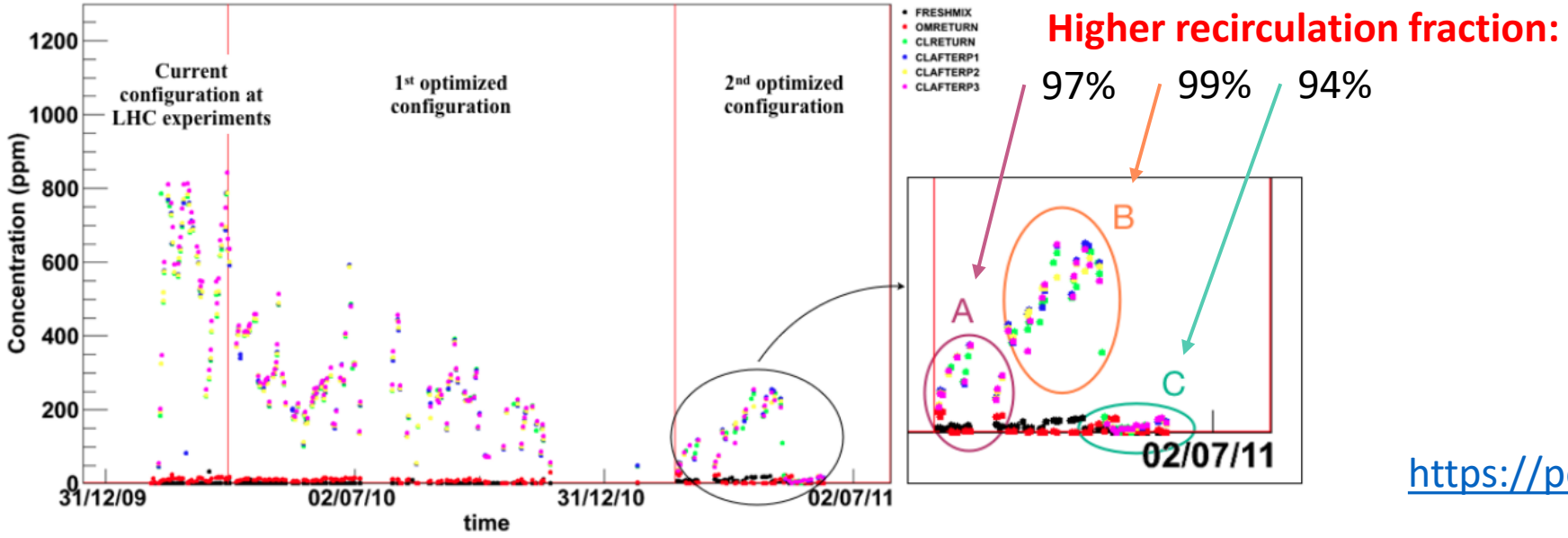
Beyond gas recirculation to gas recuperation: why?

Not always the recirculation fraction can be increased easily: two examples

1) Detector operation validated for ageing up to 90%
   - What about recirculating more? (example RPC: only short test performed in the past (2011) up to 97-99%)

2) N2 intake by diffusion trough detector material or points below atmospheric pressure

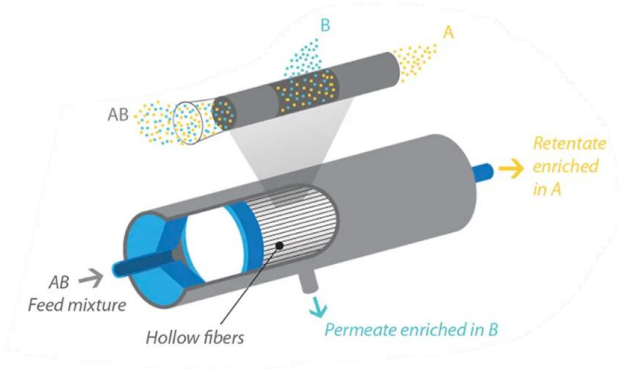
RPC: Gas recirculation and impurities in past test



https://pos.sissa.it/159/029/pdf

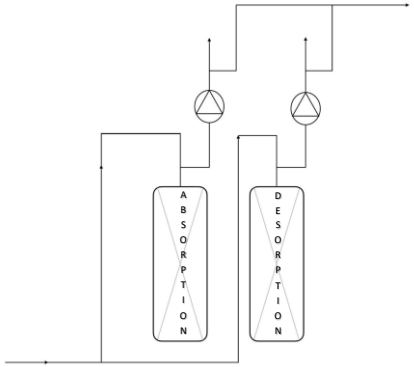
Gas separation techniques

MEMBRANE SEPARATION



- CMS CSC CF_4
- LHCb RICH2 CF_4

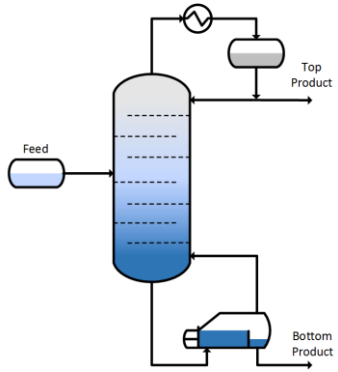
PRESSURE & THERMAL SWING ADSORPTION (PSA & TSA)



- CMS CSC CF_4
- LHCb RICH2 CF_4
- Old LHCb RICH1 C_4F_{10}

DISTILLATION

Method to separate two or more compounds based on differences in boiling points or volatility



- CMS RPC R134a
- CMS RPC SF_6
- Old LHCb RICH1 C_4F_{10}
- New LHCb RICH1 C_4F_{10}

R134a recuperation timeline

2018: Prototype0 tested in ATLAS-RPC (100 nl/h)

- encouraging results, air/N2 and iC4H10/SF6 removed

2019: Prototype0 moved to CMS

2020: test restarted at CMS with CMS-RPC

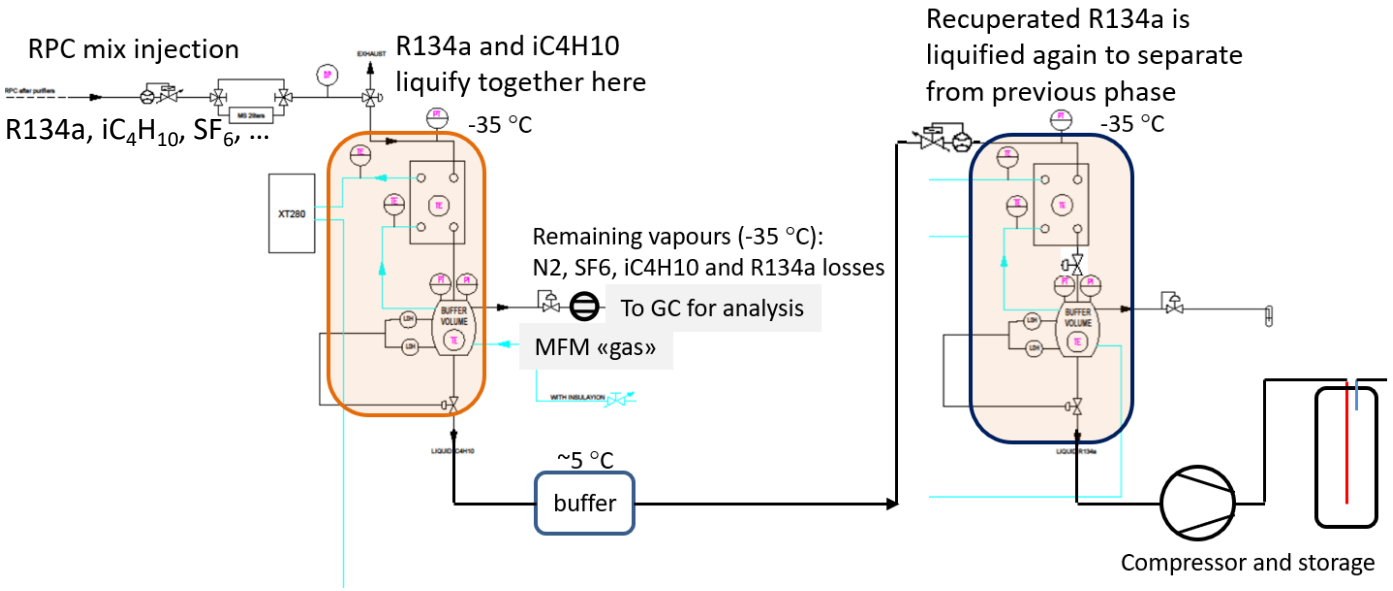
- R134a/iC4H10 form an **azeotrope** → simple separation thanks to difference in boiling points is not possible

2022: Good R134a quality, ~80% recuperation efficiency (limit due to azeotrope)

2023: installation of new Prototype1 for continuous operation

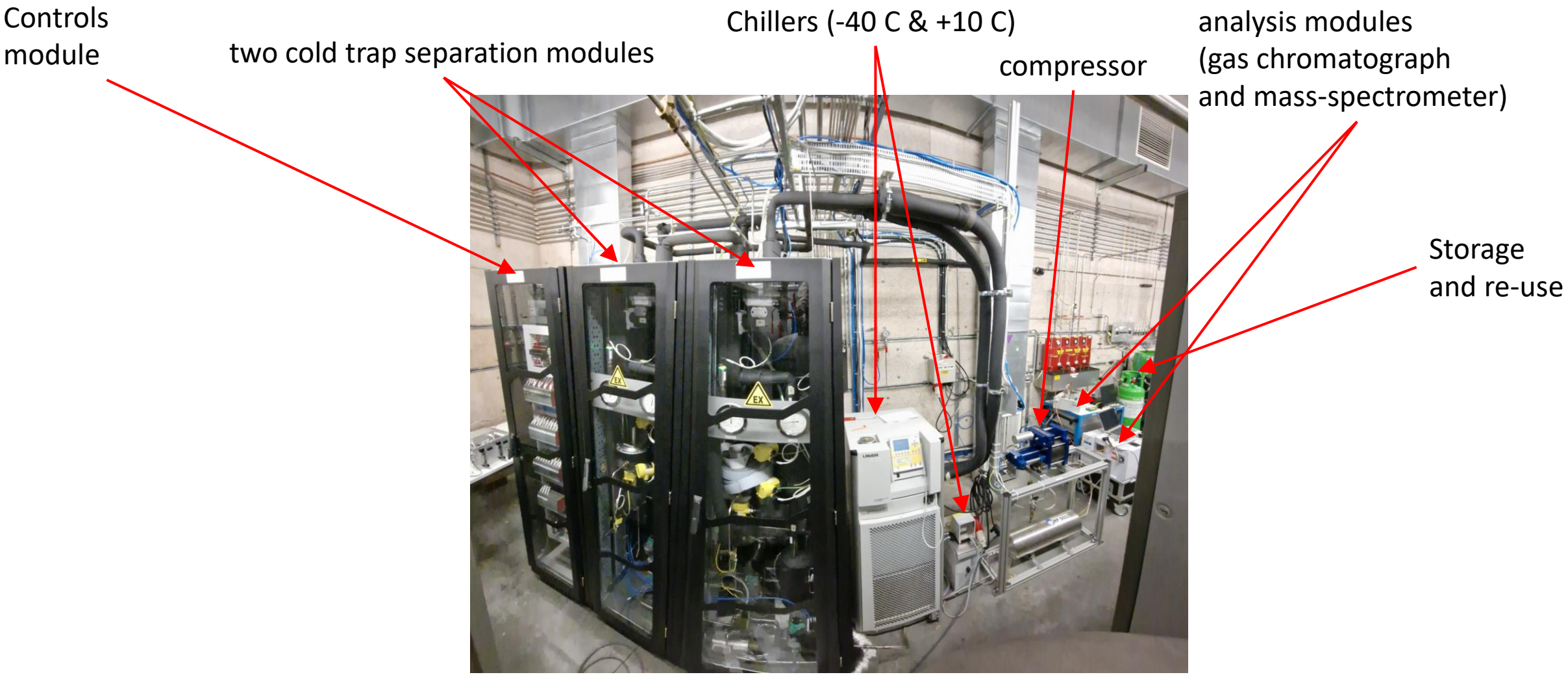
2024: Continuous operation at P5 for CMS-RPC

→ **about 5-6 years from first test to operation**



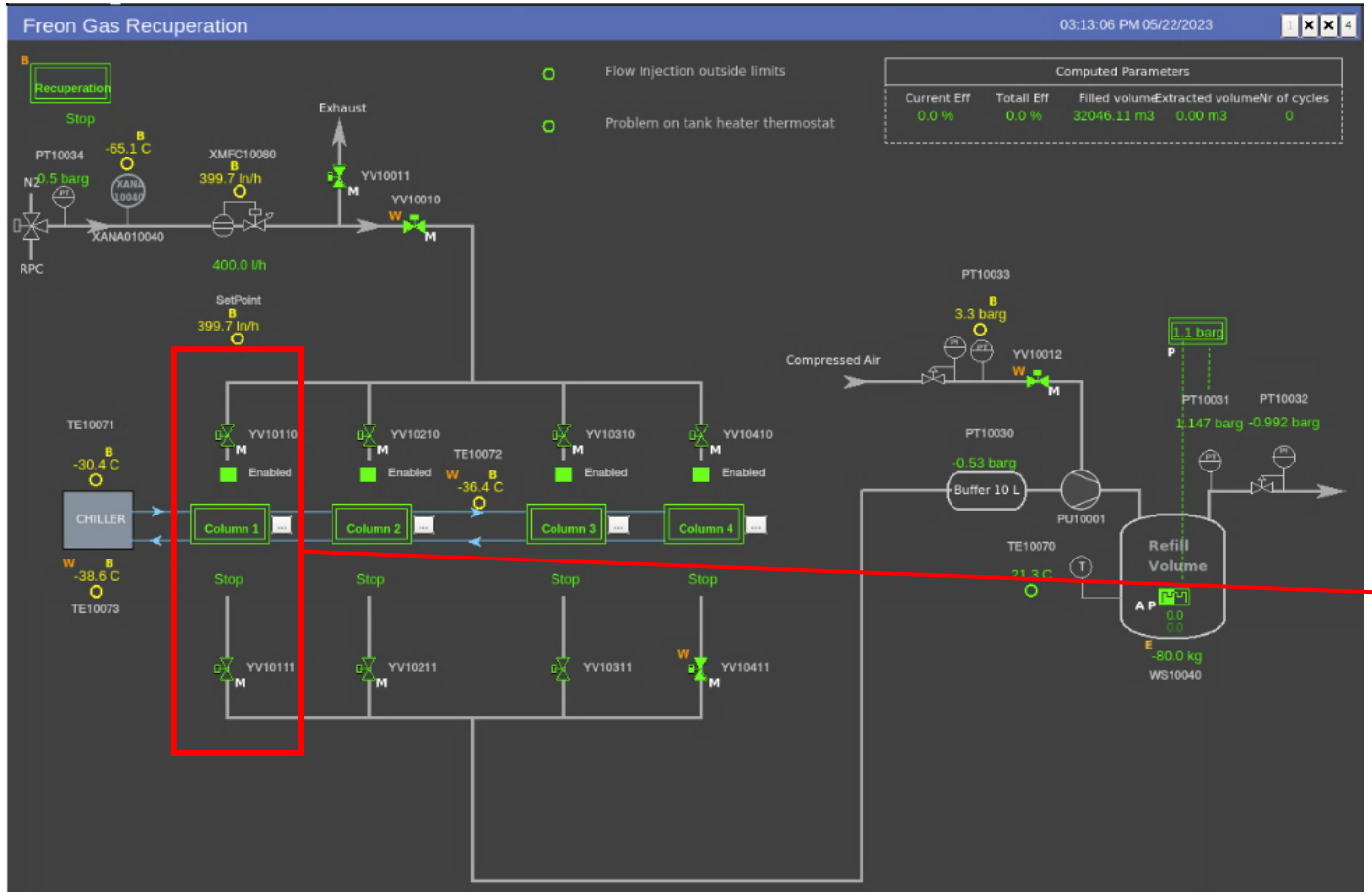
R134a recuperation: 1st plant installed

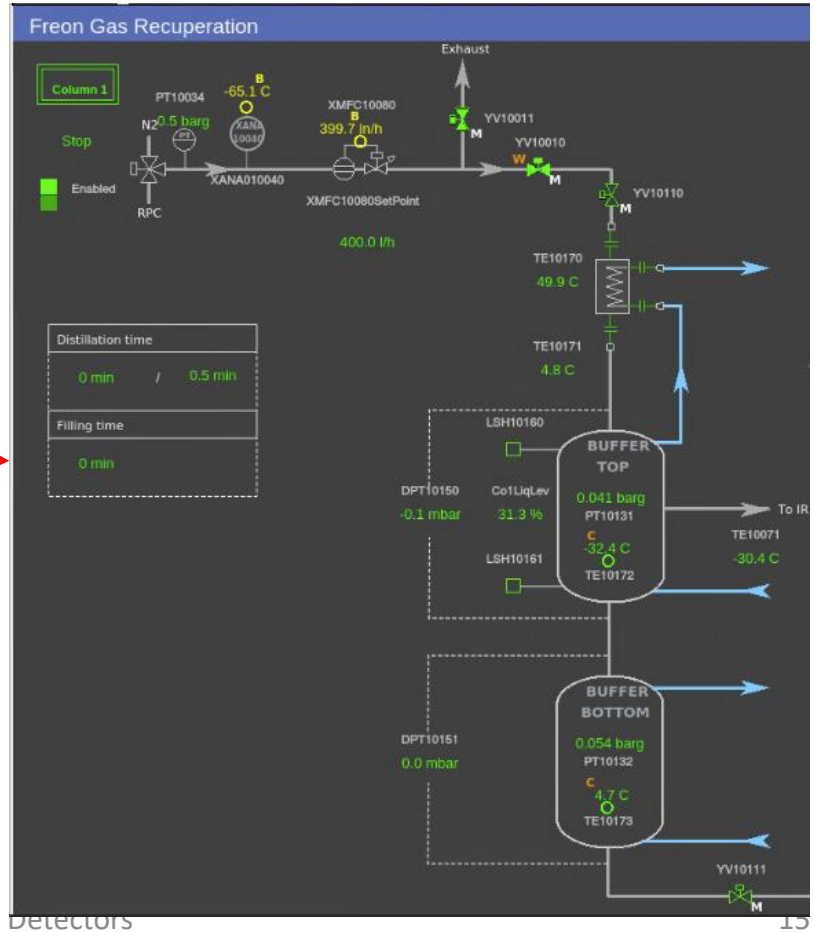
View of R134a recuperation plant installed at CMS. Fully operational since May 2024



R134a recuperation: 1st plant installed

View of software controls



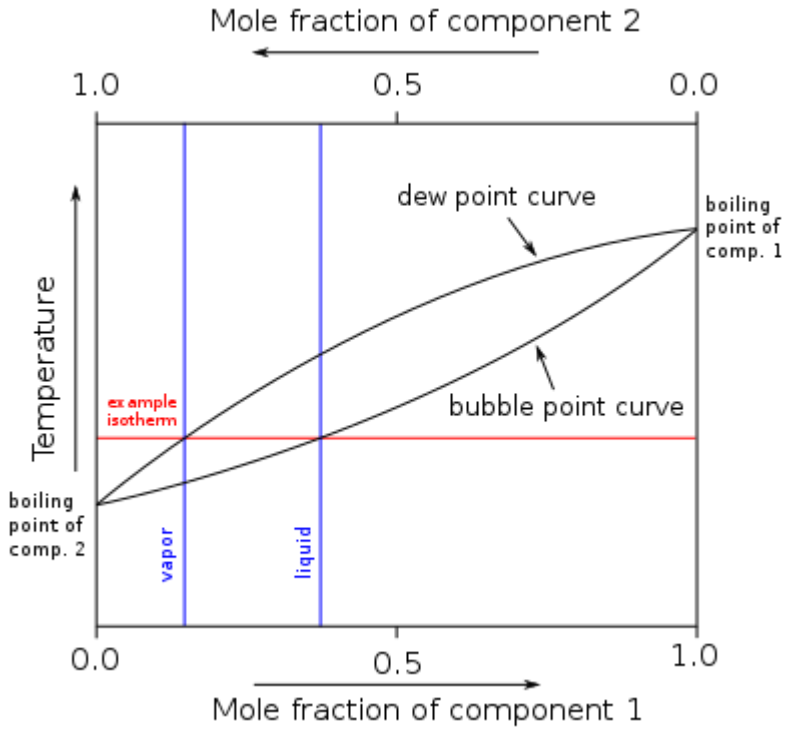


R134a-iC4H10 azeotrope

Technical challenge: separation of an azeotropic mixture

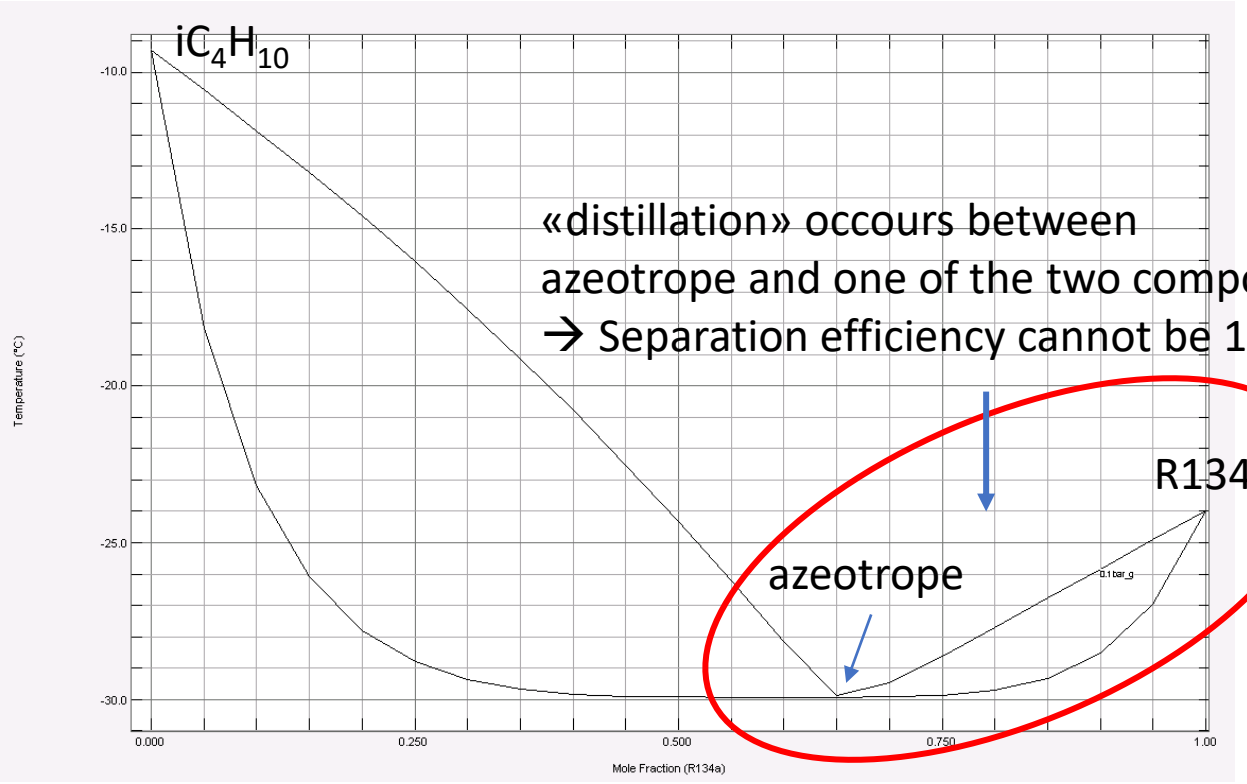
Ideal mixture:

Two boiling termeratures (component1 and component2)
No other min or max for vapour and liquid curves

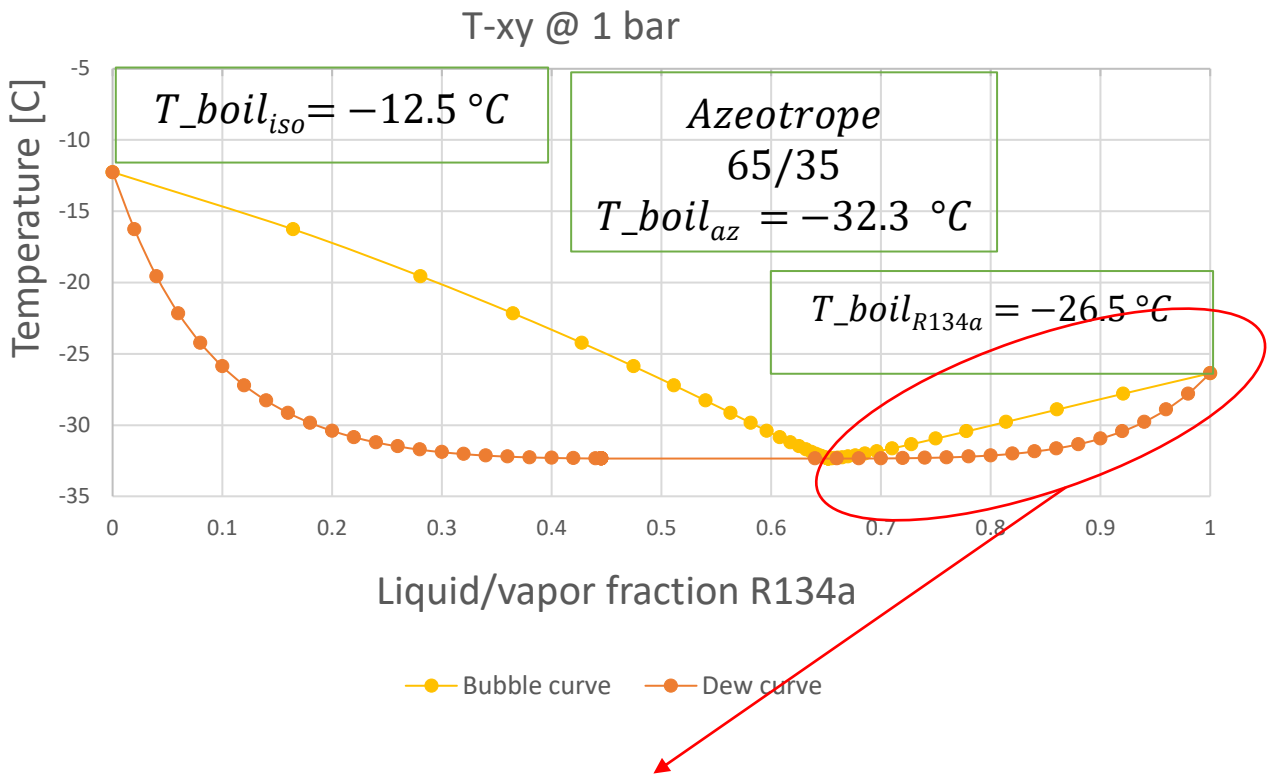


Azeotropic mixture:

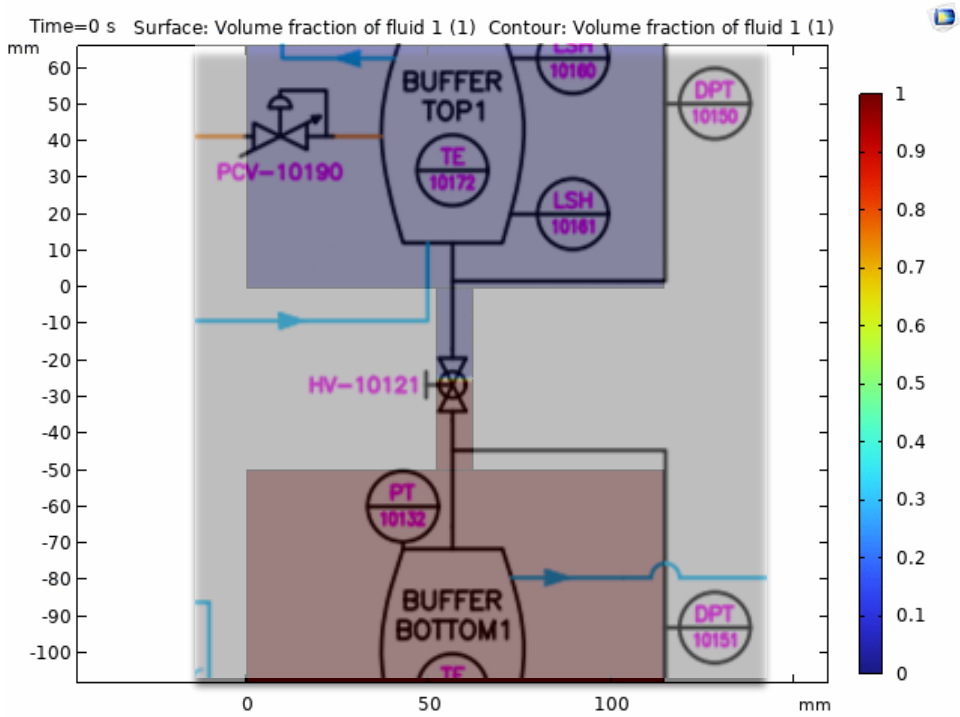
In the boiling temperature vs composition plot is present a min or a max



R134a-iC4H10 azeotrope



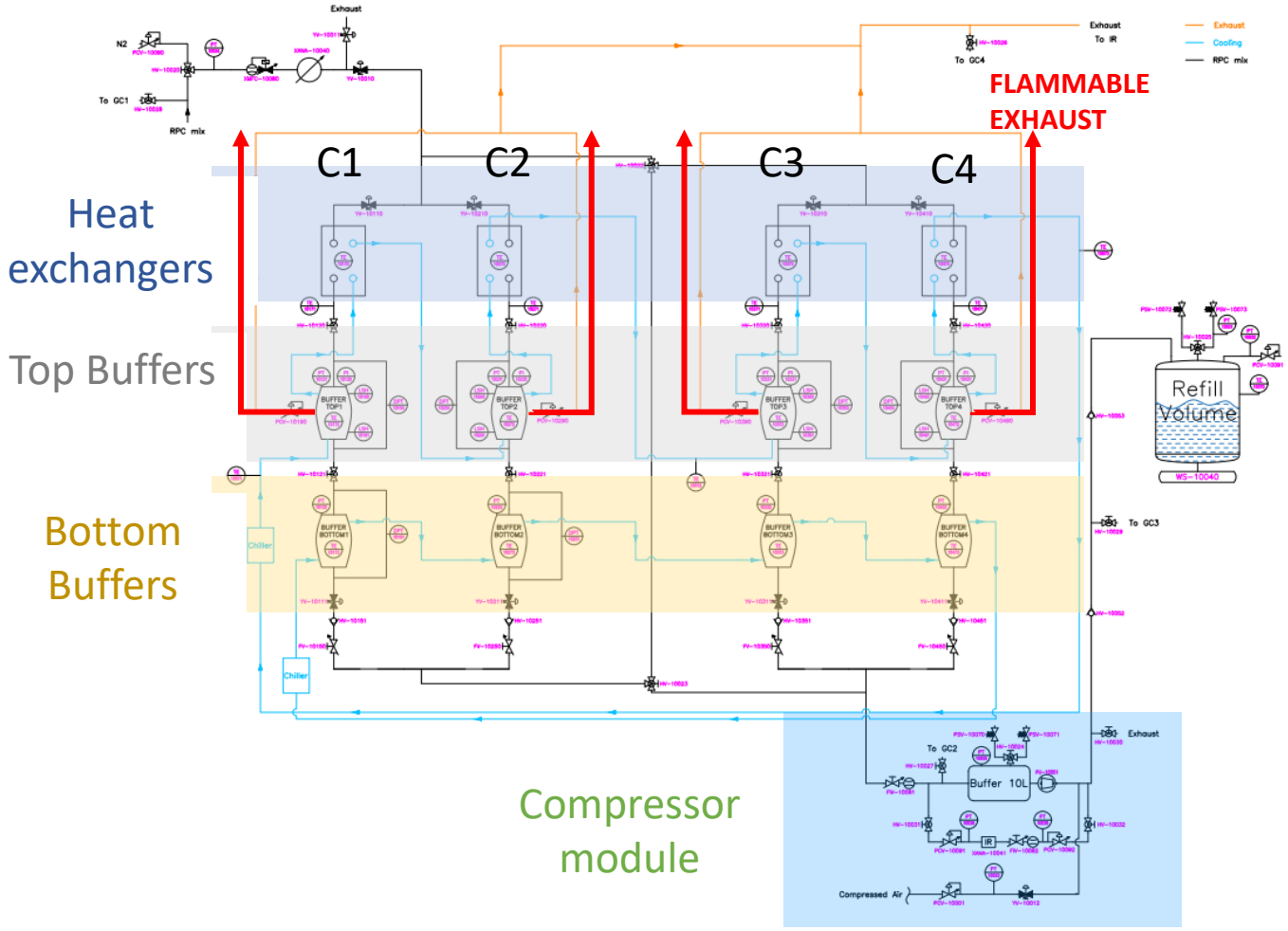
Azeotrope → mixture that exhibits the same concentration in the vapor phase and the liquid phase. This contrasts with ideal solutions with one component typically more volatile than the other



Thermodynamic simulation

Slow heating of liquified azeotrope (orange curve)
and subsequent return in the cold buffer
allows to enrich the liquid of R134a and the vapor phase of iC_4H_{10}

R134a recuperation: operational parameters



Optimal configuration:

- **Filling rate** → 200 l/h up to 600 l/h
- **Chiller Temp.** → -38°C
- **Cold buffers pressure** →

  C1&C2: 10 mbar

  C3&C4: 35 mbar
- **Bottom buffer T** → 20°C
- **Emptying rate** → 600 l/h («air» equivalent)

80% of recuperation efficiency

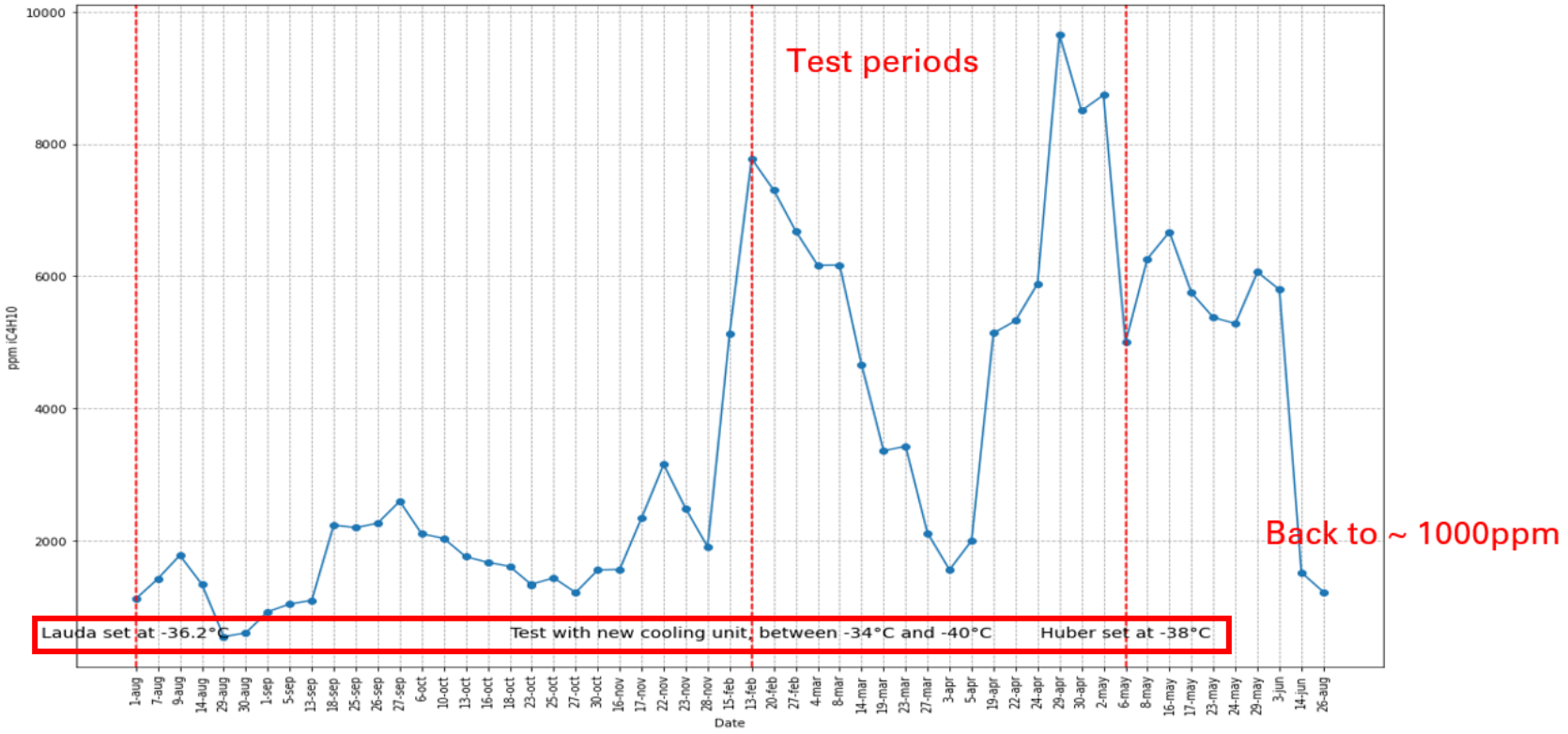
R134a recuperation: from commissioning to operation

Many parameters/conditions tested: examples

Temperatures: cold and warm buffers

At high feed flow (> 600 l/h) the efficiency decreases: more R134a is lost at the exhaust due to lower heat exchange
For the same reason, the efficiency increases decreasing chiller Temperature

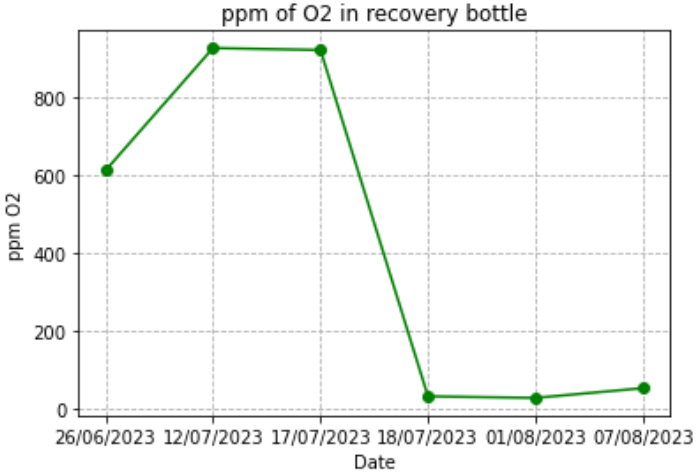
Just after the replacement of the chiller unit, 4 months of tuning were needed



R134a recuperation: from commissioning to operation

Air concentration

Presence of air (in particular Oxygen) in the recuperated R134a is indication of problems with the compressor

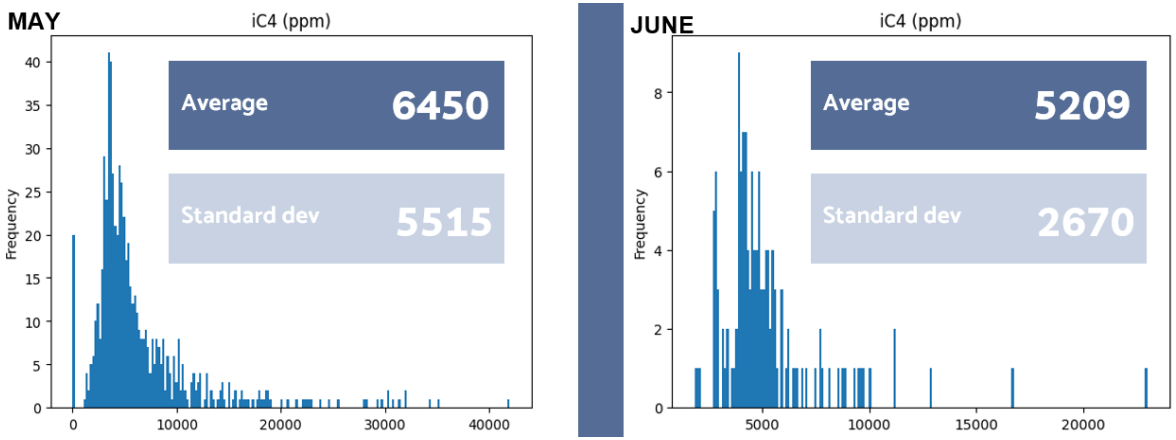


Compressor type currently in use has a lifetime of only 500 hours (after which a maintenance with replacement of internal joints is needed)
Market survey for finding new compressor model is ongoing, but not easy:
it has to

- be compatible with R134a
- work both with R134a in gas and liquid phases
- work with potentially flammable mixture
- have flow capacity > 1000 nl/h (R134a)

iC4H10 concentration

The iC4H10 concentration and its standard deviation are indicators of the effectiveness of the separation process (example in plot previous slide)



Before (may) and after (June) the modification for splitting the four extraction lines for each separation module

R134a recuperation: from commissioning to operation

iC4H10 concentration

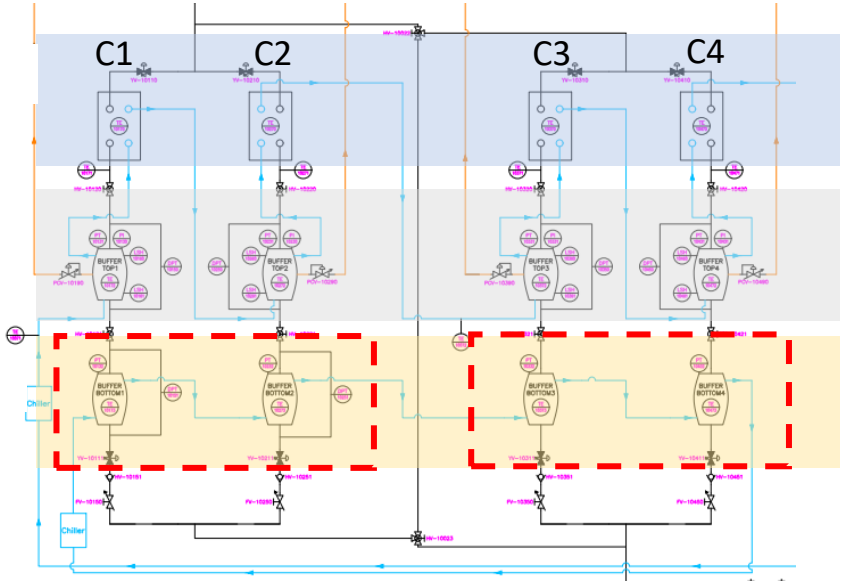
Effects of the cold and warm buffer dimensions

Column	Avg. iC4H10 (ppm)
C1	7000
C2	9400
C3	4070
C4	4100

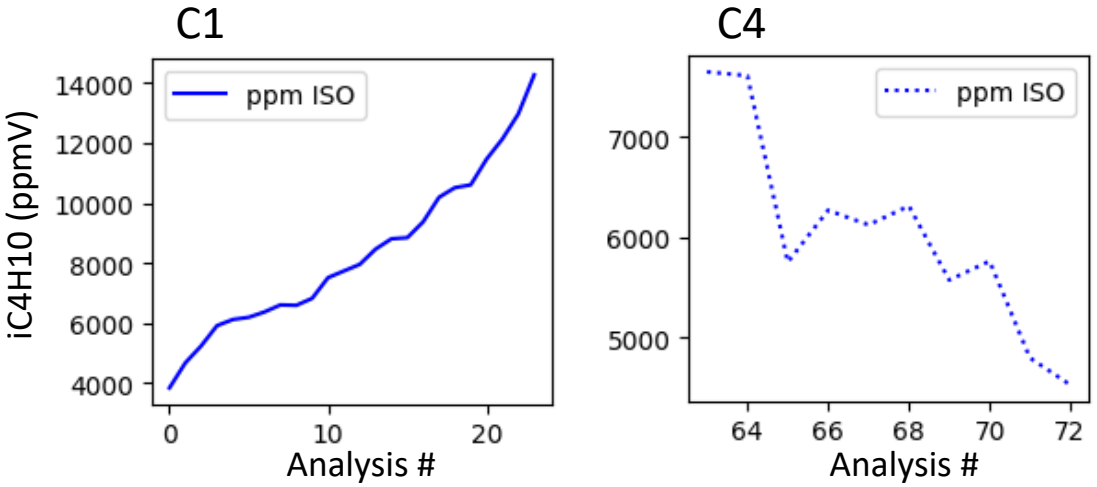
Heat exchangers

Top Buffers
h 30 cm

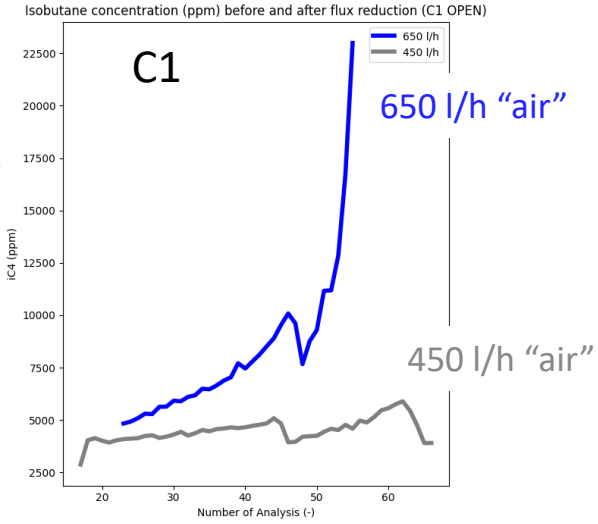
Bottom Buffers
C1-2 h 10 cm
C3-4 h 20 cm



Different behaviour probably due to different buffers size



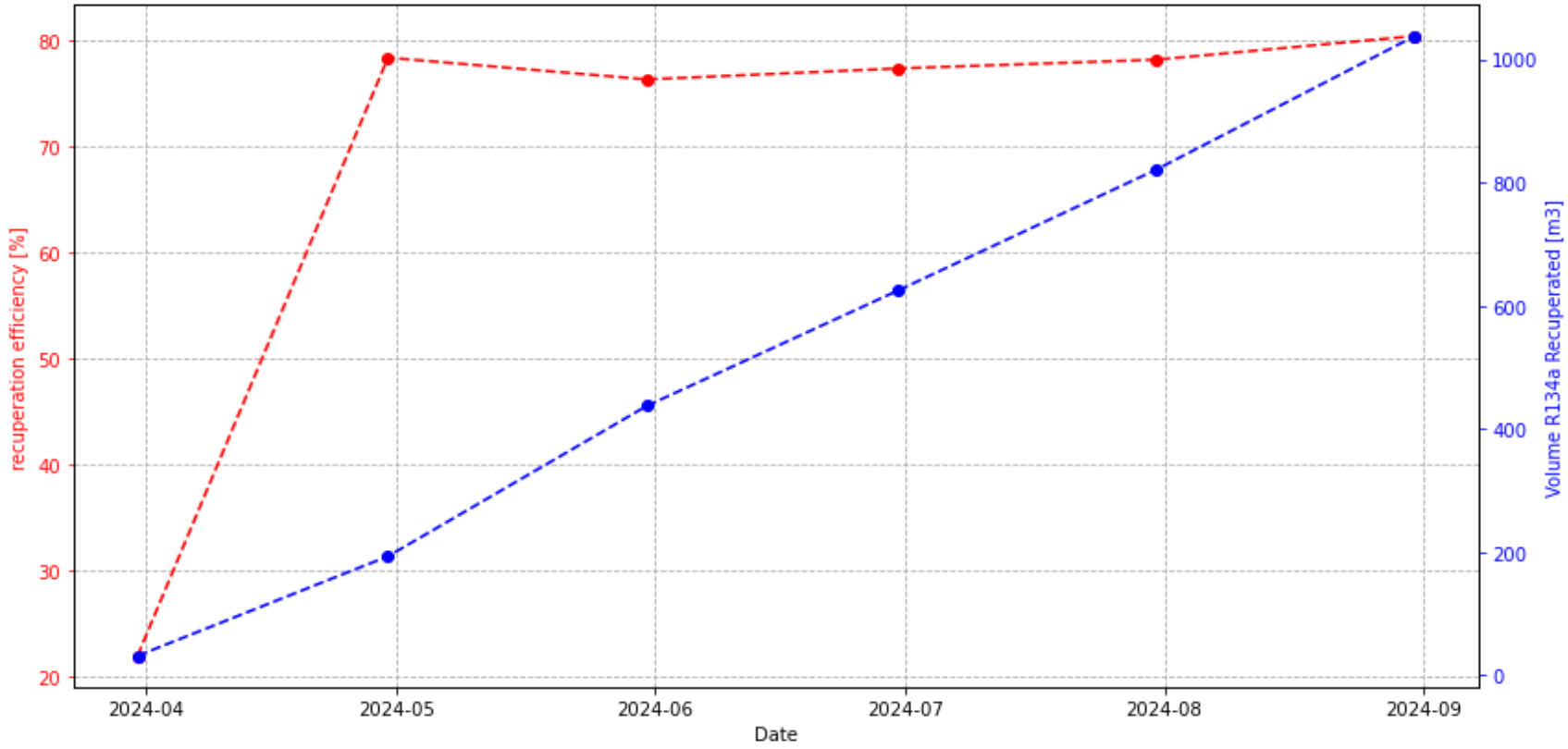
Effects of the extraction flow



R134a recuperation: from commissioning to operation

Where we are:

- From may 2024 achieved design performance
- At mixer level used 50% recuperated and 50% fresh R134a
- Not enough gas at the input of the recuperation plant to go beyond this value



Gas Recuperation: costs vs benefits

Positive effects –R134a examples:

R134a recuperation for CMS-RPC

95.2% R134a in gas mixture ~ 700 l/h ~ 12t/year ~ 130 kCHF/year (at current price)

With 80% or recuperation efficiency (and considering the reduced flow coming back from the detector)

→ 12 t/year R134a saved ~ **-130 kCHF/year** ~ **-18000 tCO2e/year**

allowing to maintain constant operational cost and GHG emissions despite the increase in fresh flow required to cope with the increase of luminosity

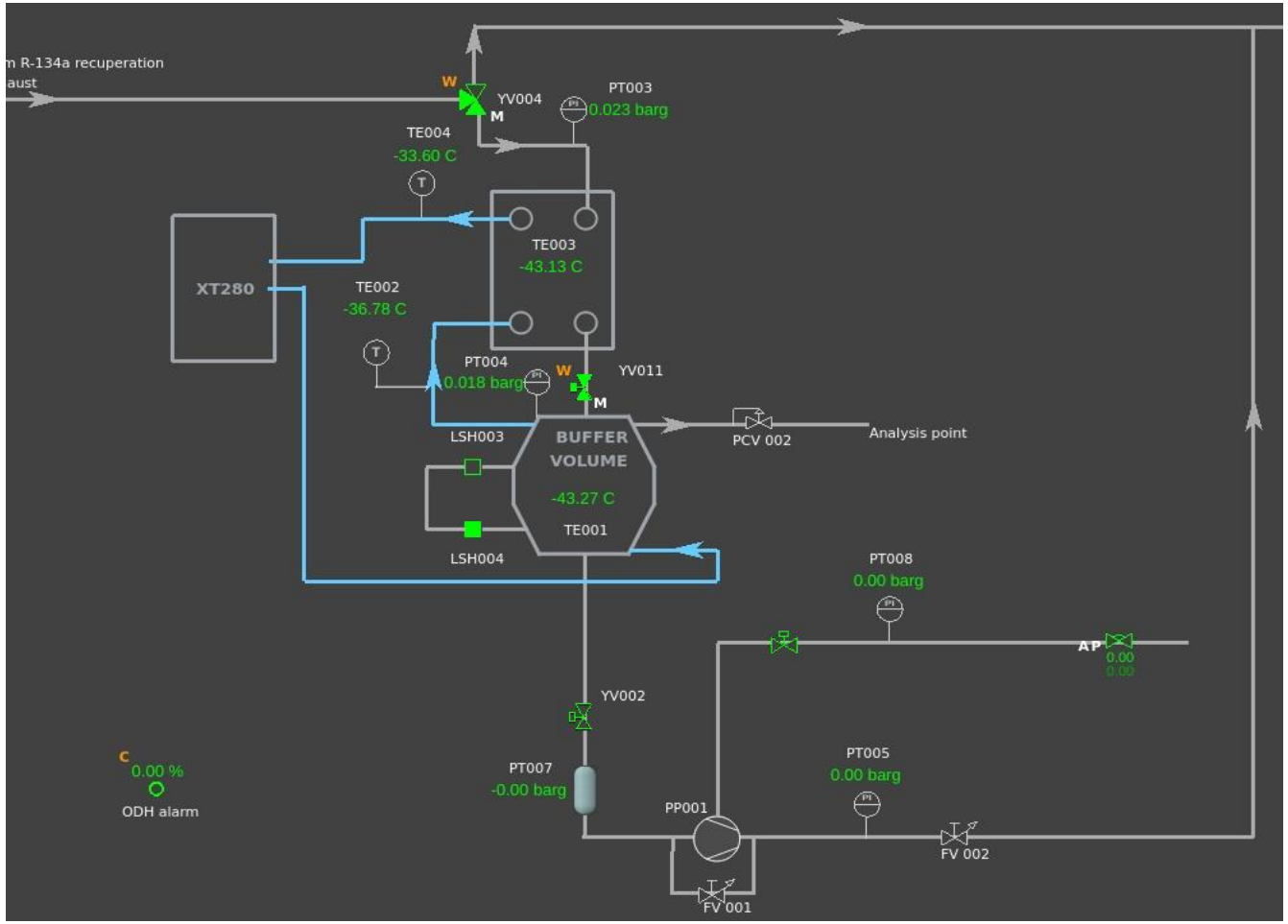
Detector operation is less subject to market crisis affecting price and availability.

Indeed, the availability of recuperated gases can mitigate difficult situations when there is a shortage of fresh gas.

In 2022 when there was a major disruption of CF4 availability in Europe: the CMS-CSC detectors could be operated and therefore participate to the CMS data taking only thanks to the usage of recuperated CF4.

R&D for an SF6 recuperation plant

Installed at P5/CMS. It is NOT an SF6 recuperation prototype.
Preliminary tests to evaluate feasibility and study properties of R134a-SF6 mixture at different concentration than usual



This system receives the mixture exhausted from the R134a recuperation plant

R&D for an SF6 recuperation plant

From RPC gas system to R134a recuperation

	[%]	nl/h
R134a	93.2	373
iC4H10	4.5	18
SF6	0.3	1.2
N2	2	8

From R134a recuperation to SF6 test

	[%]	nl/h
R134a	73	74.6
iC4H10	18	18
SF6	1	1.2
N2	8	8

From R134a recuperation back to RPC gas system mixer

	[%]	nl/h
R134a	99.9	300
iC4H10	0.1	0.3
SF6	0	0
N2	0	0

R&D for an SF6 recuperation plant

Two tests performed

-40 °C

	[%]	nl/h	Recup[%]
R134a	21	6.7	9
iC4H10	51	16.4	91
SF6	**3**	**0.82**	**68**
N2	25	8	100

-45 °C

	[%]	nl/h	Recup[%]
R134a	14	2.2	3
iC4H10	35	5.8	32
SF6	**5**	**0.8**	**65**
N2	47	8	100

60 % recuperation seems to be achievable

Next step is the test of separation membranes for removing N2 from gas stream

Still a long way (few years before we will have a final plant)

However, in 1 year of operation (and considering leaks) at recuperation will arrive

→ 56 kg SF6 (~2 kCHF)

→ Equivalent to 1350 tCO2e

So, it is mainly for reducing GHG emissions

Conclusions

GHGs usage in particle detectors

F-gas regulation

- Due to the environmental risk, “F-gas regulations” started to **limit the GHGs usage** (EU case)
- **availability** and **price** are today critical for old F-gases

Gas recirculation and recuperation systems

GHGs usage can be limited thanks to **gas recirculation and recuperation systems** (**useful not only for GHGs but also for any expensive gases**)

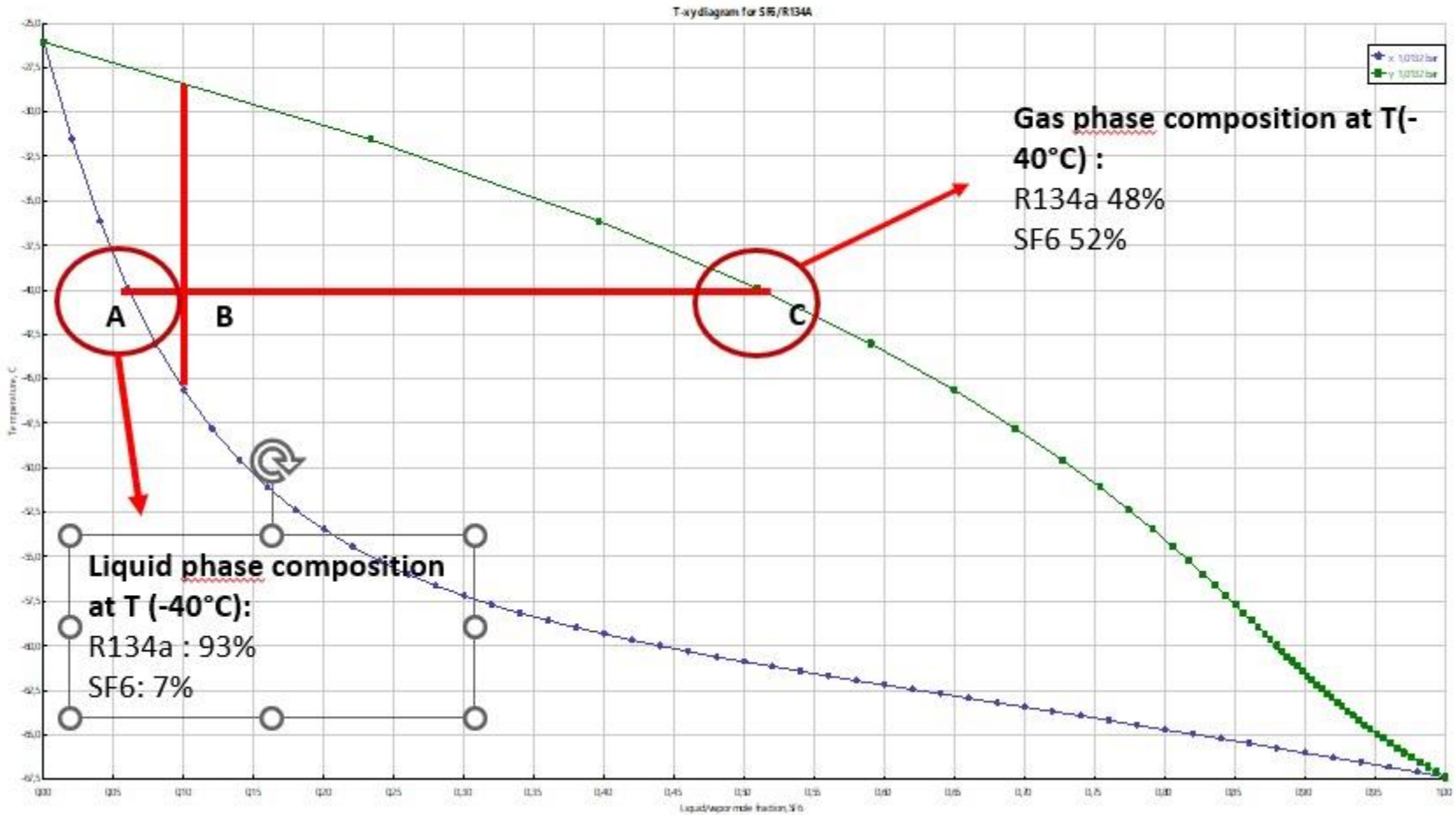
Two examples discussed:

R134a

- Operational at CMS
- Cost effective (> 100 kCHF/year saved)
- GHG emissions reduced by about 50%

SF6

- In R&D phase
- Probably not cost effective (considering current SF6 price)
- GHG emissions reduced by about 10%

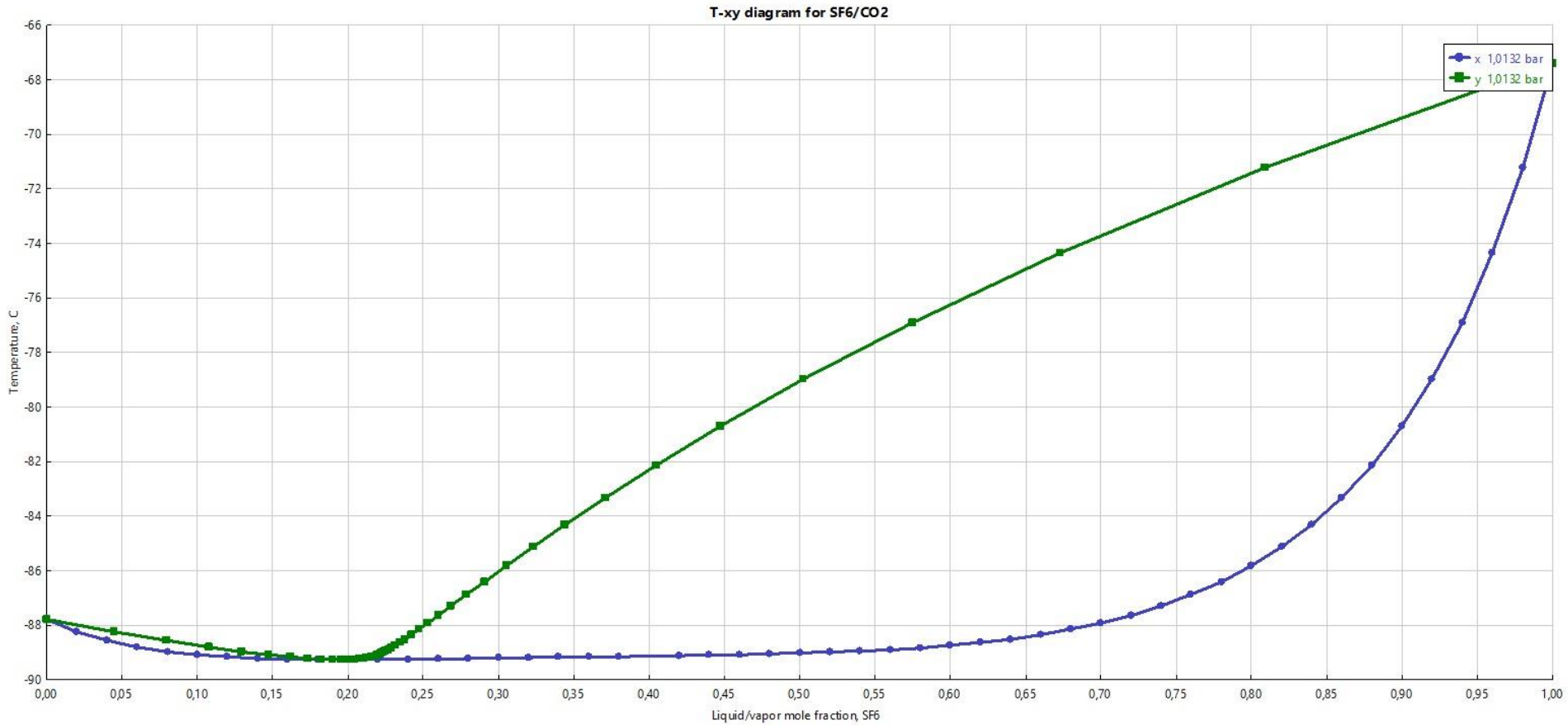


If we enter in the system with 10 % SF6, 90% R134a at a temperature of -40°C
Liquid phase is bigger than gas phase.

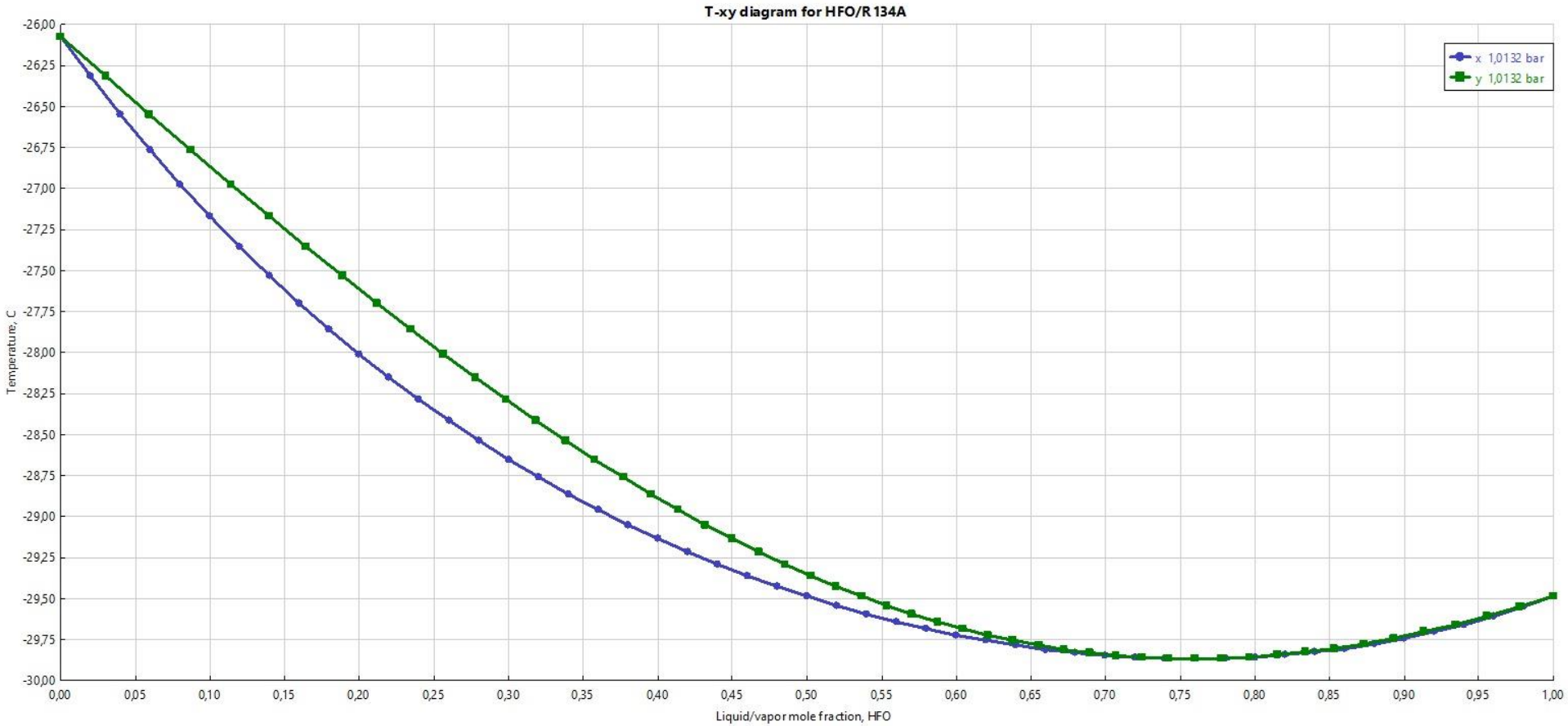
Liquid phase = $\frac{BC}{AC} = 91.1\%$

Gas phase = $\frac{AB}{AC} = 8.9\%$

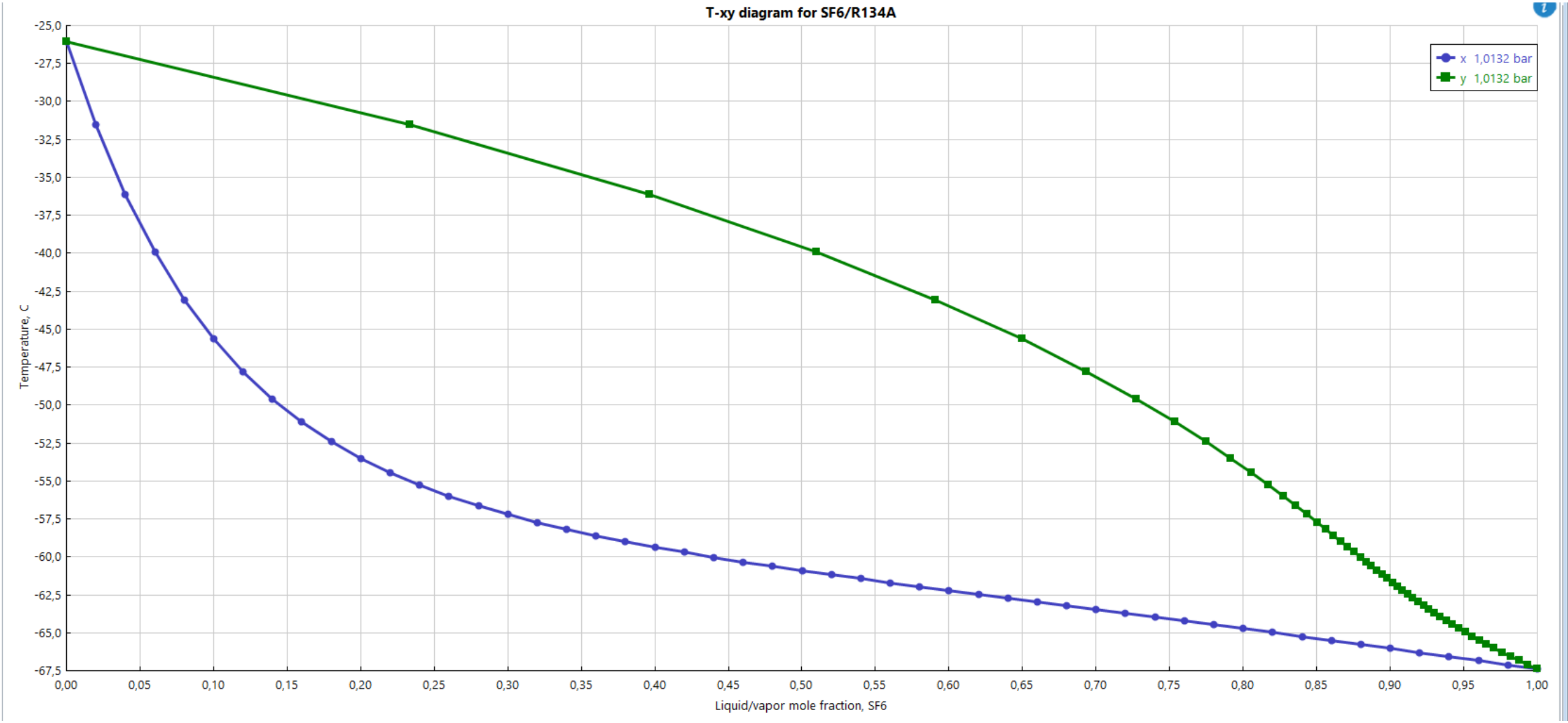
SF6-CO2


T-xy diagram for SF6/CO2
x 1,0132 bar
y 1,0132 bar
Temperature, C
Liquid/vapor mole fraction, SF6
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
0,00
0,05
0,10
0,15
0,20
0,25
0,30
0,35
0,40
0,45
0,50
0,55
0,60
0,65
0,70
0,75
0,80
0,85
0,90
0,95
1,00

HFO-R134a


T-xy diagram for HFO/R 134A
x 1,0132 bar
y 1,0132 bar
Temperature, C
-26,00
-26,25
-26,50
-26,75
-27,00
-27,25
-27,50
-27,75
-28,00
-28,25
-28,50
-28,75
-29,00
-29,25
-29,50
-29,75
-30,00
0,00
0,05
0,10
0,15
0,20
0,25
0,30
0,35
0,40
0,45
0,50
0,55
0,60
0,65
0,70
0,75
0,80
0,85
0,90
0,95
1,00
Liquid/vapor mole fraction, HFO

gas recirculation systems for labs


T-xy diagram for SF6/R134A
x 1,0132 bar
y 1,0132 bar
Temperature, C
-25,0
-27,5
-30,0
-32,5
-35,0
-37,5
-40,0
-42,5
-45,0
-47,5
-50,0
-52,5
-55,0
-57,5
-60,0
-62,5
-65,0
-67,5
0,00
0,05
0,10
0,15
0,20
0,25
0,30
0,35
0,40
0,45
0,50
0,55
0,60
0,65
0,70
0,75
0,80
0,85
0,90
0,95
1,00
Liquid/vapor mole fraction, SF6