Alternatives to F-gas Refrigerants

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MA Toxics Use Reduction Institute
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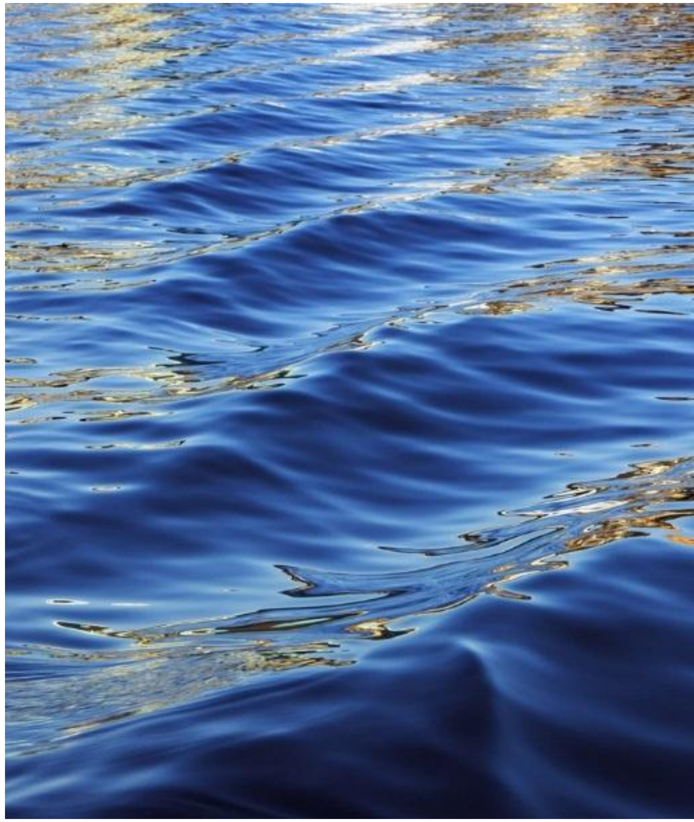
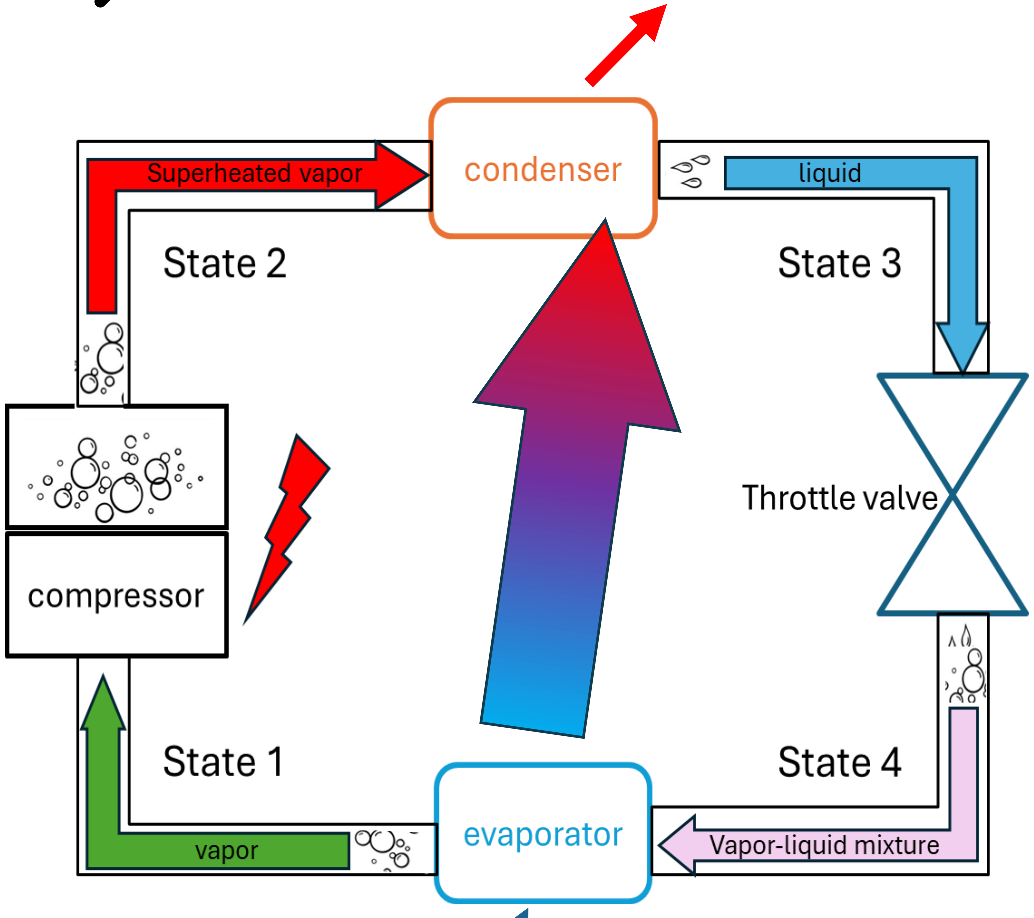


How Refrigerant gases work?

Refrigerant gases work under a vapor compression cycle → Releasing heat by condensation to heat sink



Absorbing heat by evaporation from heat source

Cooling Capacity (CC): The amount of heat a system can remove per unit of time (e.g., kW or BTUs per hour).
Higher CC means a faster heat transfer rate.

Efficiency: How effectively the system uses energy to cool (e.g., Coefficient of Performance, CoP; Seasonal Energy Efficiency Ratio, SEER).
Higher efficiency leads to lower operating costs.

Key Factors:

- ***Refrigerant properties****.
- Equipment design.
- Temperature differences
- Application.

* Drop-in substitutes require similar thermodynamic properties to the refrigerant being replaced.

F-gas Refrigerants

- Introduction of Hydrofluoroolefins (HFOs) and Hydrochlorofluoroolefins (HCFOs):
  - Hydrofluorocarbons (HFCs) substitute to reduce Global Warming Potential (GWP).
  - Intended to be climate-friendly refrigerants due to shorter atmospheric lifetime.
- *Unintended consequences:*
  - *Some high-GWP HFCs are still used in new refrigerant blends.*
  - *PFAS pollution: HFOs produce TFA.*

- ***While PFAS remediation costs amount to several trillion USD*, US market value forecasts for HFOs and PFAS are 2-3 billion and about 30 billion USD, respectively.***

* U.S. Chamber of Commerce (2022): PFOS and PFOA Private Cleanup Costs at Non-Federal Superfund Sites.
Ling (2024) https://doi.org/10.1016/j.scitotenv.2024.170647

The '*average GWP*' blend strategy still uses high GWP HFCs, despite having a weighted average GWP lower than regulatory thresholds.

SNAP approved refrigerant	Composition			GWP	Main applications
	Chemical name	CAS No	% w/w		
HFC-32	Difluoromethane	75-10-5	100	675	Only retrofitting of industrial process chillers
HCFO-1233zd	1-Chloro-3,3,3-trifluoropropene	2730-43-0	100	6	Cold storage, industrial HVACR and ice rinks
HFO-1234ze(E)	1,3,3,3-tetrafluoro-(1E)-propene	29118-24-9	100	6	Commercial; residential; replaces HFC-134a
HFO-1234yf	2,3,3,3-Tetrafluoropropene	754-12-1	100	4	Mobile air conditioning; replaces HFC-134a
R-454A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	65	4	Chillers <90 Kg of charge and cascade systems.
	Difluoromethane (HFC-32)	75-10-5	35	675	
R-454B (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	67	4	Industrial chillers; replaces R-410a blend
	Difluoromethane (HFC-32)	75-10-5	32	675	
R-454C (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	78.5	4	Commercial; residential; heat pumps; replaces R-410a blend
	Difluoromethane (HFC-32)	75-10-5	21.5	675	
R-455A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	75.5	4	Commercial; residential; mobile; replaces HFC-134a
	Difluoromethane (HFC-32)	75-10-5	21.5	675	
	Carbon dioxide (R-744)	124-38-9	3	1	
R-457A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	70	4	Commercial; residential
	Difluoromethane (HFC-32)	75-10-5	18	675	
	1,1-difluoro ethane (HFC-152a)	75-37-6	12	124	
R-516A (blend)	2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	77.5	4	Commercial; residential; replaces HFC-134a
	1,1-difluoro ethane (HFC-152a)	75-37-6	14	124	
	1,1,1,2-tetrafluoroethane (HFC-134a)	811-97-2	8.5	1430	

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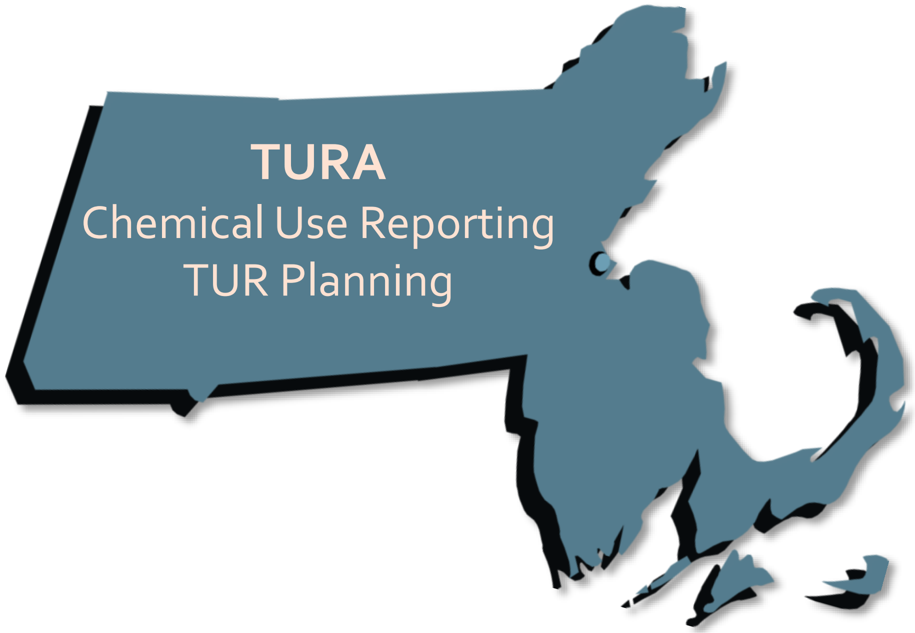
TURI, PFAS and F-Gases

Toxics Use Reduction Act: Helps Massachusetts companies and communities ***reduce the use of toxic chemicals*** while **promoting competitive advantage** of Massachusetts businesses



TURA listed "**Certain PFAS NOL**" category on list of toxic or hazardous substances

- Where are PFAS used?
- Identify and develop safer alternatives

PFAS category includes many polymers, non-polymers and F-gases

- Many PFAS used in clean energy systems

Concern with potential for HFOs to be a regrettable substitute for HFCs as refrigerants and blowing agents

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Hydrofluoroolefins (HFOs) life cycle

HFO manufacturing

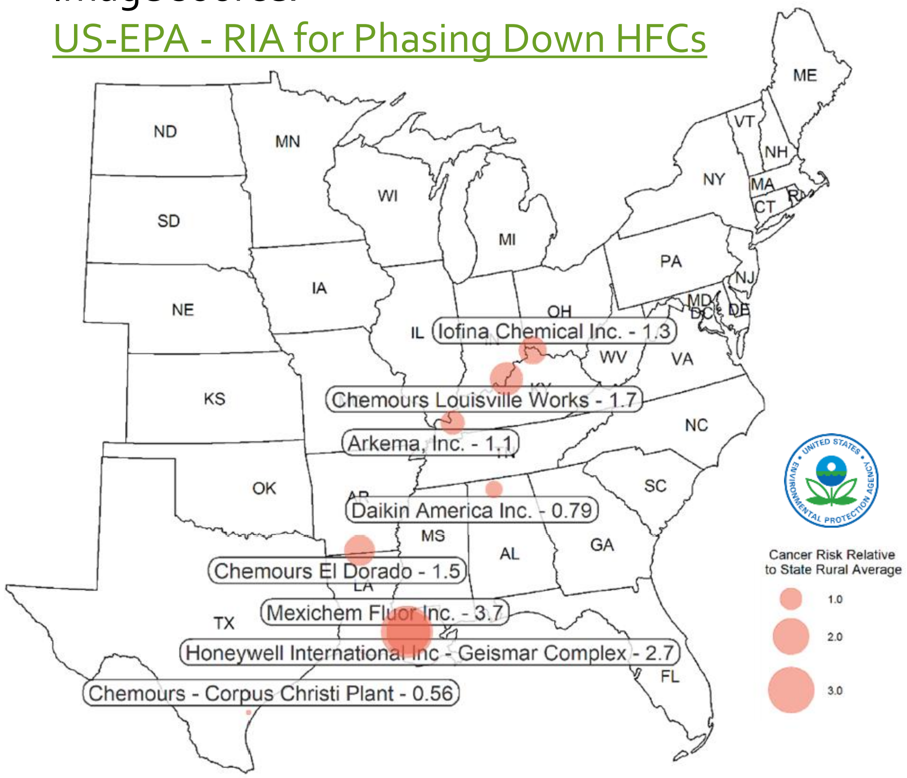
CMR precursors are required.

Proximity to manufacturing sites increases exposure risk to hazardous chemicals (CTC, PCE, HF, toxic HFCs).

Cancer Risk within 1 mile of HFC Facilities

Image source:

US-EPA - RIA for Phasing Down HFCs



Utilization

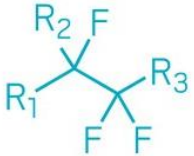
HFOs are the new generation of low-GWP F-gases to replace HFCs.

Some high-GWP (>150) HFCs are still used in new blends:

- HFOs require HFCs to reduce their flammability.
- HFCs require HFOs to reduce GWP.

Are HFCs and HFOs gases considered PFAS?

✓Yes & ✗No



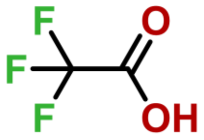
OECD, 2021 **US EPA, 2021**

R_1, R_2, R_3 = nonhydrogen atoms

Image source:

Hogue (ACS C&EN, 2022): How to define PFAS.

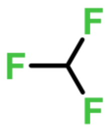
Environmental fate



TFA

HFOs mostly form Trifluoroacetic acid (TFA).

- G. Salierno (2024): HFOs byproducts might potentially produce HFC-23. Only takes 1.1% HFO conversion into HFC-23 for a GWP 150+ contribution.



HFC-23

GWP 14800

- Potential creation of unknown PFAS by *operando* Polymerization.

Reproduced from Mahle technical messenger report

Figure 3: Polymerization: refrigerant bottle

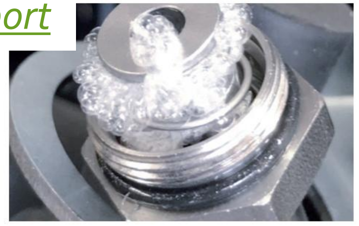
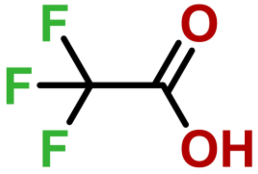


Figure 1: Polymerized refrigerant in connecting piece

TFA is increasing in our diet and blood



TFA

Trifluoroacetic acid
Chemically resistant and long lasting

Due to HFO emissions, TFA exposure dramatically increased.
Now, we are exposed over threshold globally.

RIVM (2022)
Chronic rat toxicity (feeding)
Dose response: Male liver weight vs dose
Relevant potency factor: TFA is 0.002 x toxic as PFOA

Corresponds to a ***water threshold value of 2.2 µg/L***
Exceeded in an increasing number of areas

ECHA REACH Dossier (2024)
Han Wistar Rabbits
embryo-fetal developmental toxicity <180 mg/kg/day
Category 1B: Presumed human reproductive toxicant

Drinking water (*median*)[1,2]

- Germany: 1.5 µg/L
- 19 countries: 0.23 µg/L
- Michigan[3]: 0.22 µg/L
- Wilmington (NC)[4]: up to 110 µg/L

Barely under threshold

Beer (median) 6.1 µg/L[2]

Orange juice (mean 34 µg/L)[5]

Apple juice (mean 6.2 µg/L)[5]

Way over advisory levels: 2-10 µg/L (EU)

Bread *(13 – 420 µg/Kg; median: 165 µg/Kg)*[6]

Human Blood (ng/L):

- Wilmington (NC)[4]: 17
- Indiana[7]: 6.0
- Global[8]: 9.0

TFA NOAEL
60-70 µg/L

1. Neuwald et al. *Environ. Sci. Technol.* **2022** *56* (10), 6380-6390
2. Scheurer & Nödler. *Food Chemistry*, *351*, 129304.
3. Ecology Center, Healthy Stuff Lab. Ann Arbor, MI. October 2023. ecocenter.org
4. Cheng et al. Environ. Sci. Technol. 2025 59 (43), 23125-23135
5. Van Hees et al. https://cdnmedia.eurofins.com/european-east/media/uxcnaa2c/eurofins_tfa_tfms_juice_24_final.pdf
6. The forever chemical in your daily bread report
7. Zheng et al.: Environ. Sci. Technol. 2023, 57 (42), 15782–15793.
8. Zhi et al.: Environ. Sci. Technol. 2024, 58 (49), 21393–21410.

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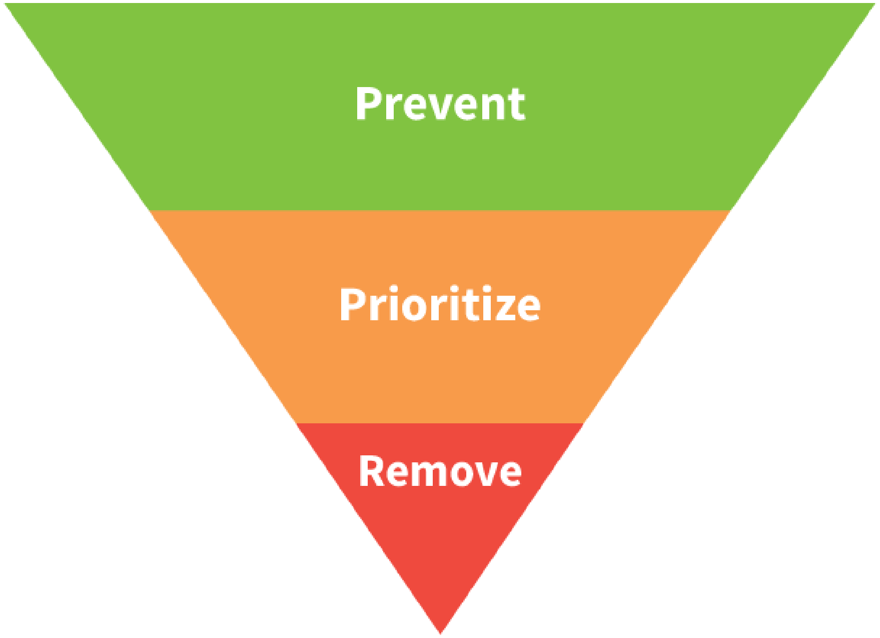
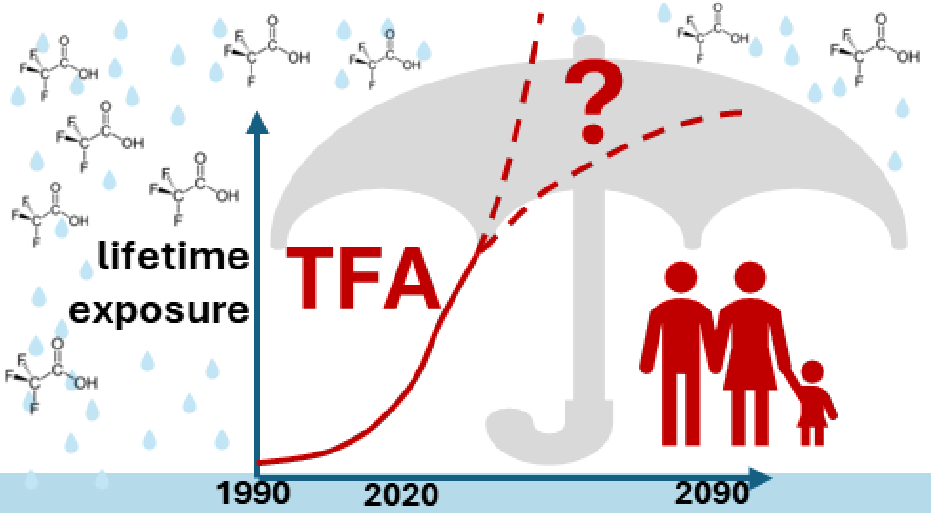
Solutions to the TFA problem



- Transition to alternatives to fluorinated refrigerants:
  - identify non-essential uses
  - focus transition on TFA-precursors produced in greatest volume and with highest TFA yields
- Define TFA as a PFAS,
  and integrate in PFAS reduction strategy
- Minimize gas emissions (better management of fluorinated refrigerants)



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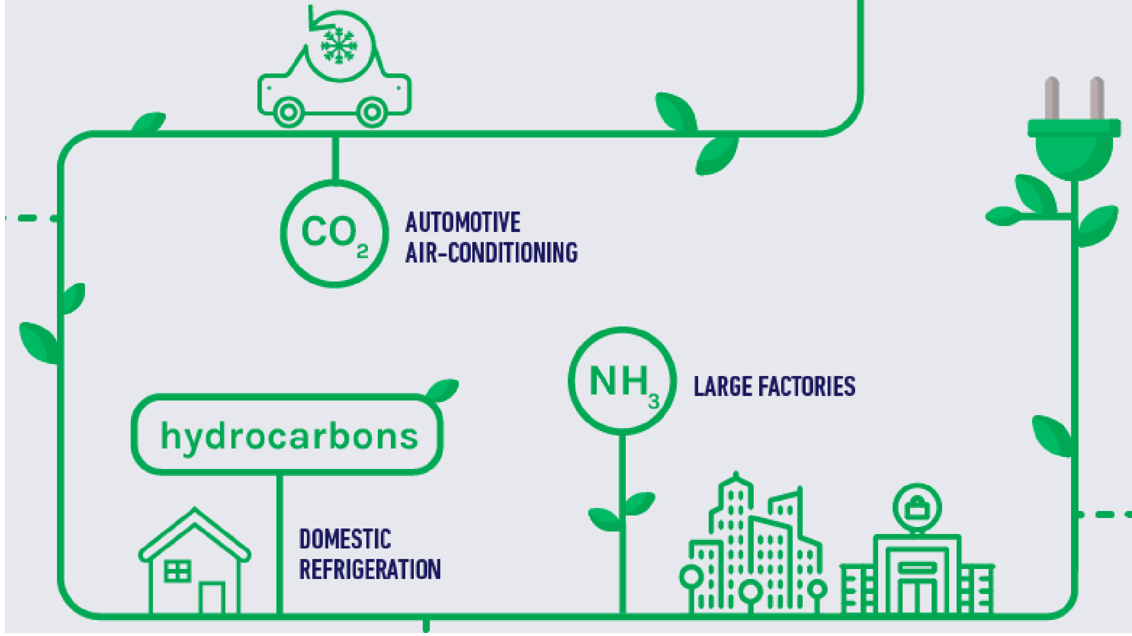

HFOs are potentially regrettable substitutions.

Non F-gases have appropriate market readiness:

- *New CO2 designs offer operational cost savings*
  Wide adoption in supermarkets, cold warehouses

- *Equipment design & safety standards mitigate HC flammability*:
  - 500 g HC charge allowed indoors (US)
  - 500 g HC charge allowed indoors (Europe; heat pumps)

EPA ENERGY STAR Certified HC-based equipment:

- 600+ household fridges
- 700+ Lab Grade Refrigerators

- Ammonia (NH3) is the preferred industrial refrigerant and is not used for domestic applications. *Ultra Low Charge (ULC)* NH3 *systems* reduce but not completely eliminate acute toxicity and eutrophication related liabilities.

***Solid-state technologies* (Peltier; magnetocaloric) offer a refrigerant-free cooling solution.**

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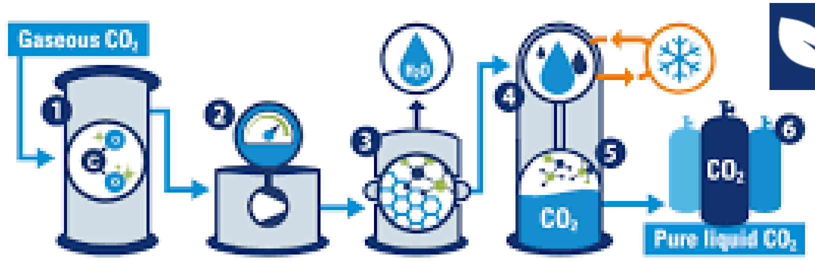
Cleaner production of refrigerant gases

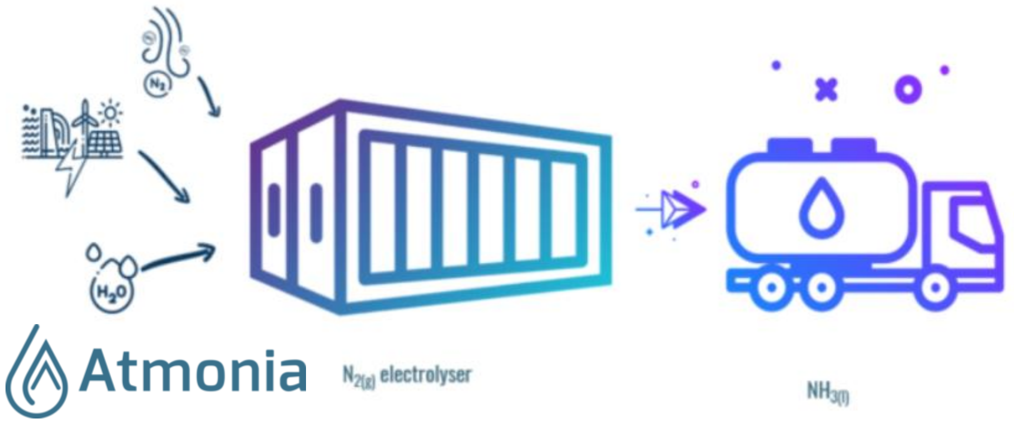
CO_2, NH_3, and HCs have a much lower impact during manufacturing and use.

CO_2: Captured and reused, a promising refrigerant due to its low environmental impact.

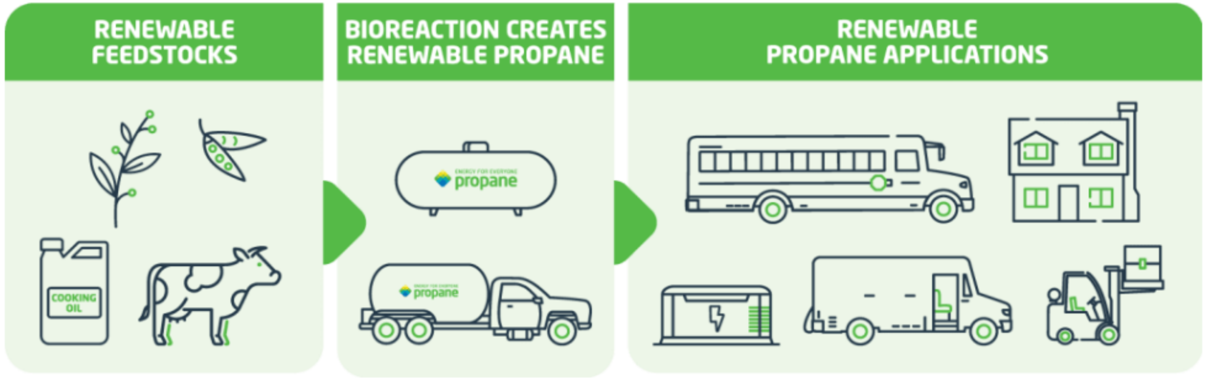
Ammonia: Novel technology uses water, air, and renewable energy for zero-emission production, as opposed to the traditional carbon-intensive Haber-Bosch process.

Propane*: 100% renewable propane, made from bio-based waste, could cut fossil reliance.





* Other hydrocarbons can be produced in the same way.



U.S. DEPARTMENT of ENERGY

https://afdc.energy.gov/fuels/propane-renewable

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ASSESSMENT OF AVAILABLE
LOW-GLOBAL WARMING POTENTIAL
ALTERNATIVES TO F-GAS REFRIGERANTS

https://www.turi.org/publications/assessment-of-alternatives-to-f-gas-refrigerants/

TURI Safer Refrigerants Webinar

April 13, 2025

- Gabriel Salierno (TURI): AA report highlights
- Prof. Dr. Ian Cousins (Stockholm University): PFAS concerns around F-gases.
- Morgan Vanzo (NASRC): State legislations and workforce training.

https://www.youtube.com/watch?v=S8unGzkamUM

Refrigerant Options & Trade-Offs

Feature	F-Gases (HFCs / HFOs)	Hydrocarbons (R-290, R-600a)	Carbon Dioxide (R-744)	Ammonia (R-717)
GWP	HFCs: Very High (up to 14,800) / HFOs: Low (1-10)	Very Low (3-30)	1 (Baseline)	Zero
Efficiency (CoP)	High	High	Best for cold storage and cold climates	Highest
Flammability	HFCs: Non-flammable / HFOs: Mildly flammable	Flammable	Non-flammable	Midly-flammable
Toxicity	Low acute toxicity / Arrhitmia	Low toxicity	Non-toxic	Toxic
Operating Pressure	Moderate	Low to Moderate	High	Low to Moderate
System Requirements	Drop-in compatible (some retrofit possible)	New sealed equipment	New equipment; transcritical design	Strict leaking controls
Key Hazards	High GWP (HFCs); PFAS concerns; TFA formation	Fire hazard	High pressure; asphyxiation	Acute toxicity; corrosion; eutrophication
Regulatory Status	Phasing down (AIM Act: 85% reduction by 2036)	Approved with use conditions	Emerging; approved for new equipment	Restricted to industrial use with safety protocols

Drop-in retrofitting substitutes vs. New equipment purchase

- ***Retrofitted HVACR equipment generally*** exhibits lower efficiency than the newer models, ***contributing to avoidable indirect emissions.***
- HFOs and HFCs/HFOs blends are currently used as a substitute for phasing out HFCs.
- ***Rising F-gas costs and production limitations threaten the availability of drop-in substitutes.***
- Generally lower initial investment.
- Payback period typically 0.7 years.*

- ***Feasibility is translating into wider adoption.***
- More companies manufacturing equipment based on non-fluorinated refrigerants.
- Successful implementation in supermarkets, cold storage, and mobile refrigeration.
- ***Market share growing faster in the EU, given more stringent F-gas policy.***
- Generally higher initial investment.
- Payback period <1 to 3 years.*

* https://www.epa.gov/sites/default/files/2016-03/documents/table_rules_of_thumb.pdf

Financial feasibility of new purchases improves/equalizes when considering energy savings opportunities from modern equipment.

https://www.turi.org/publications/assessment-of-alternatives-to-f-gas-refrigerants/

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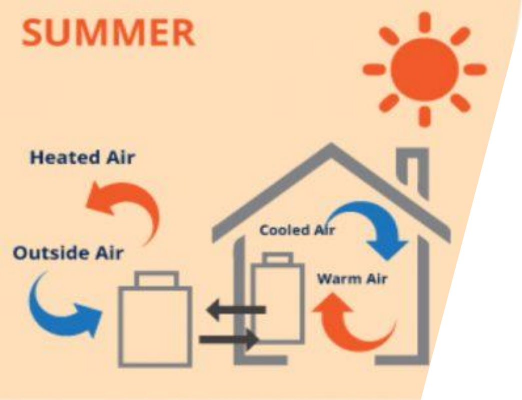

A few examples of heat pumps working with non-F-gases

Brand	Models	Refrigerant	Applications
Vaillant	aroTHERM Plus	R290 (propane)	Residential heating and hot water
Itomic	CHP-80Y, CHP-15H	CO2 (R744)	Supermarkets, apartment buildings
Enerblue	Silver Line	R290 (propane)	Commercial (hospitals, data centers, exhibition centers)
Frick	SmartPAC	Ammonia (R717)	Industrial (hot water production)
Euroklimat	VHERA Series	R290 (propane)	Commercial (air-conditioned buildings)
LG	THERMA V R290 Monobloc	R290 (propane)	Residential and small commercial heating and cooling
Viessmann	Vitocal	R290 (propane)	Residential heating and cooling
SANCO$_2$	Heat Pump Water Heater	CO2 (R744)	Residential hot water heating
LYD	Water to Water Heat Pump	R600a (isobutane)	Industrial heat recovery heat pump

This information does not constitute an endorsement or recommendation of any HVACR product, service, or provider.

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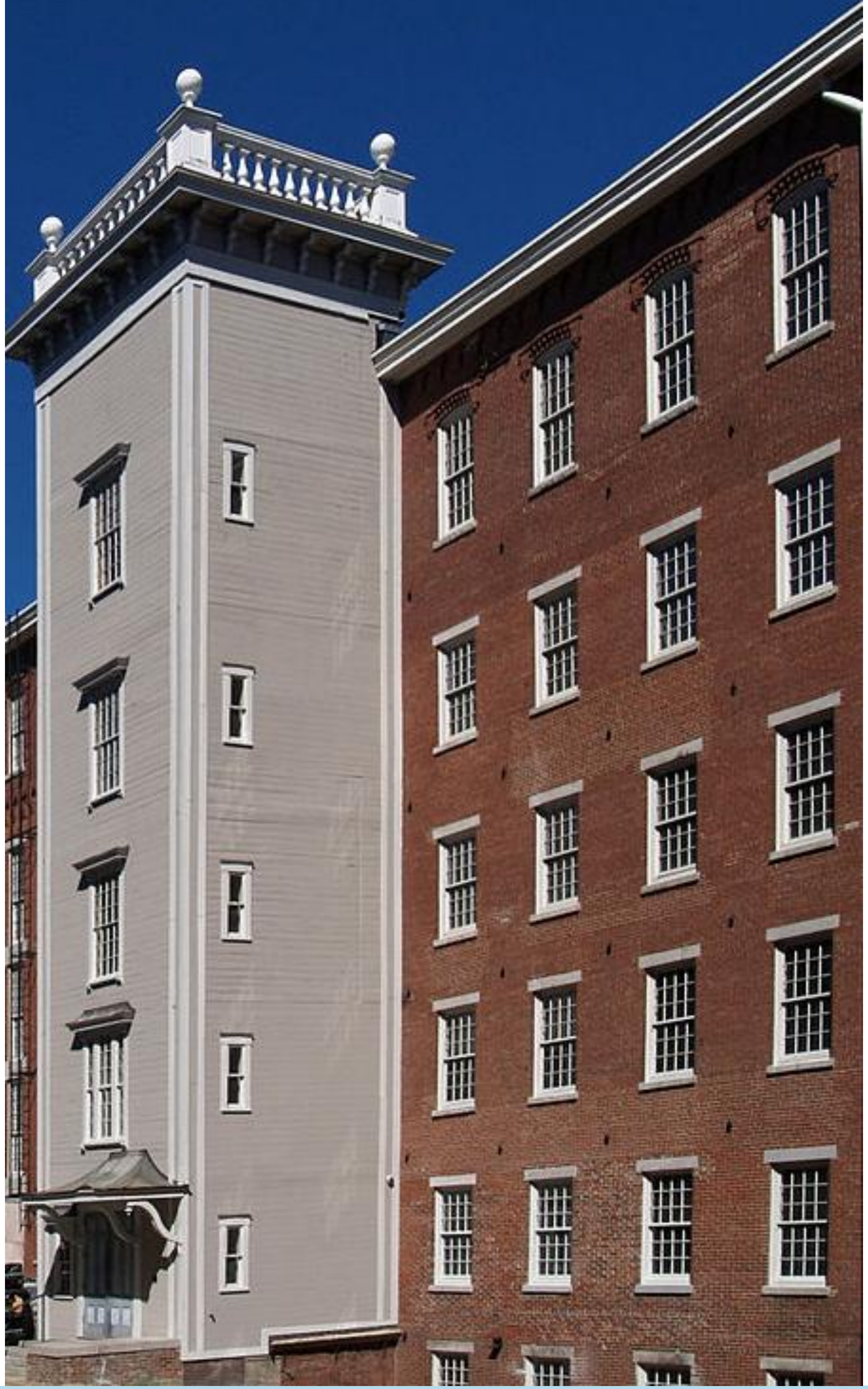
Incentives and opportunities

Program	Type	Incentive	Eligibility	Link
MassDEP Commercial Refrigeration Grant	Grant	Up to $200,000	MA retail food, nonprofits; ultra-low-GWP systems (CO_2, propane)	mass.gov/refrigeration-grant
MassCEC HVAC Training Network	Training Grant	Up to $1.2M per college	Community colleges; heat pump & HVAC technician training	masscec.com/hvac-training-network
MassCEC Climate-Critical Workforce Grants	Training Grant	Up to $800,000	Training providers; career pathways in HVAC, building efficiency	masscec.com/workforce
MassCEC Equity Workforce Grants	Training Grant	Up to $1.2M	Organizations serving EJ communities, low-income, underrepresented populations	masscec.com/workforce

State	Program	Link
RI	Clean Heat RI	cleanheatri.com
NY	Building Solutions	nyserda.ny.gov
NY	Clean Heat for All	nyserda.ny.gov
CA	F-gas Reduction Incentive Program (FRIP)	fripfunding.com
CA	FRIP Workforce Development Initiative	nasrc.org
WA	Refrigerant Management Program	ecology.wa.gov



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