Refrigerants: Past, Present and Future…

Presented to the St. Louis Chapter of AEE

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for the US Department of Energy

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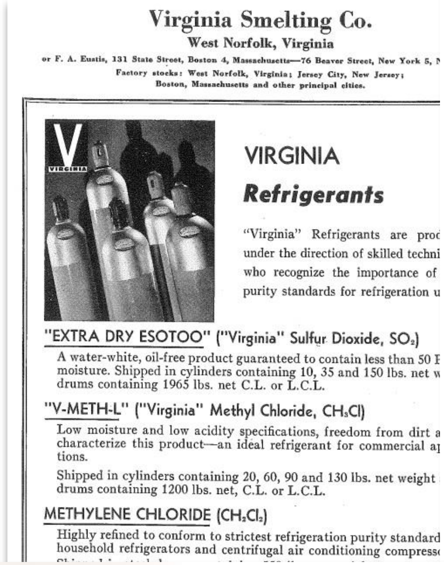
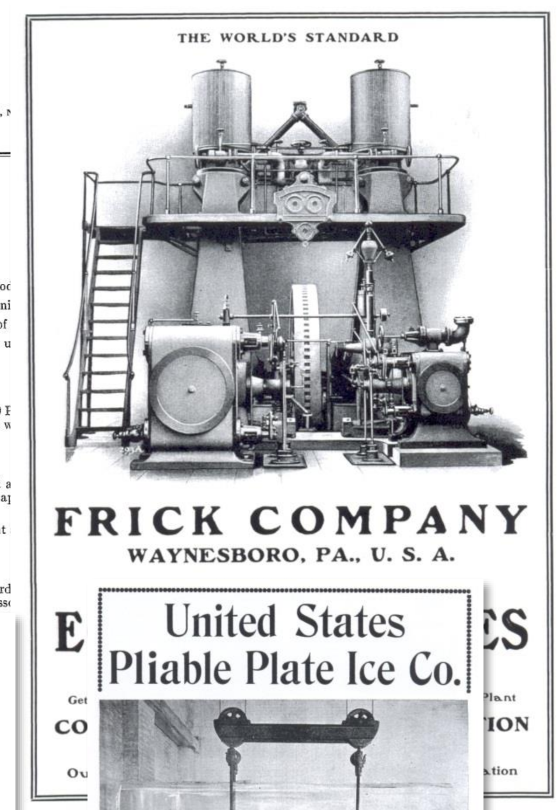
Synopsis

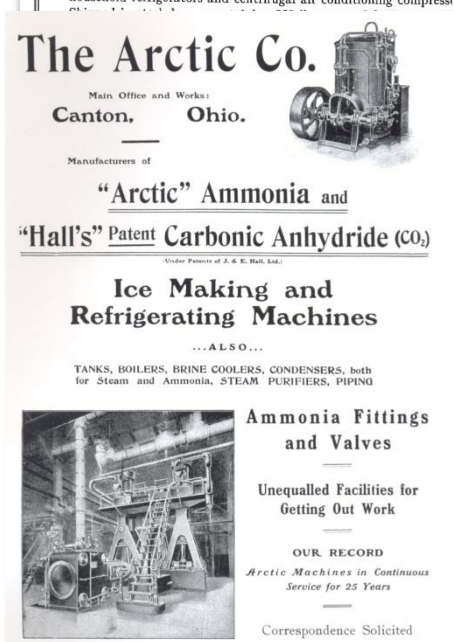
- Motivation
  - History of refrigerants
  - Regulations (Montreal Protocol, EPA SNAP)
- Existing refrigerants
- Alternative refrigerants
  - HFOs and blends, “natural” refrigerants
- Research
  - ORNL
  - AHRI/ASHRAE/DOE

Brief History of Refrigeration

- Early applications
  - Ice making, brewing, shipping, meat packing
- Common refrigerants in early refrigeration systems
  - Ether
  - Carbon dioxide (CO_2)
  - Ammonia (NH_3)
  - Sulfur dioxide (SO_2)
  - Methyl chloride (CH_3Cl)
  - Chosen for their availability, not necessarily for safety



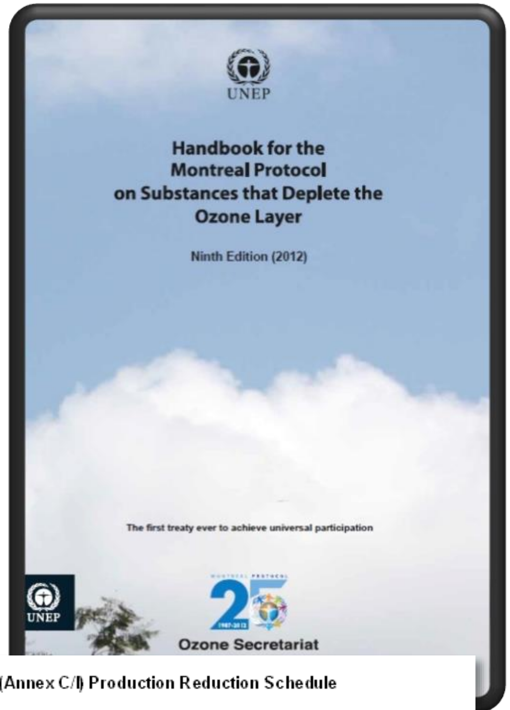




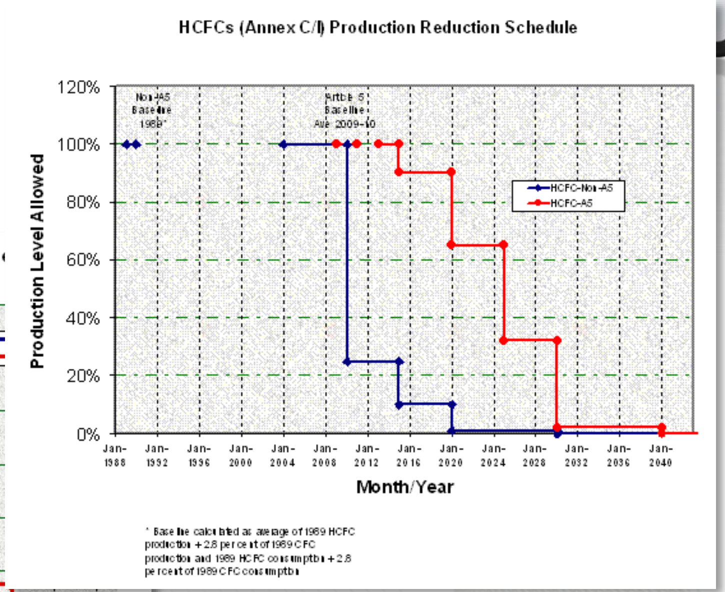
Brief History of Refrigeration

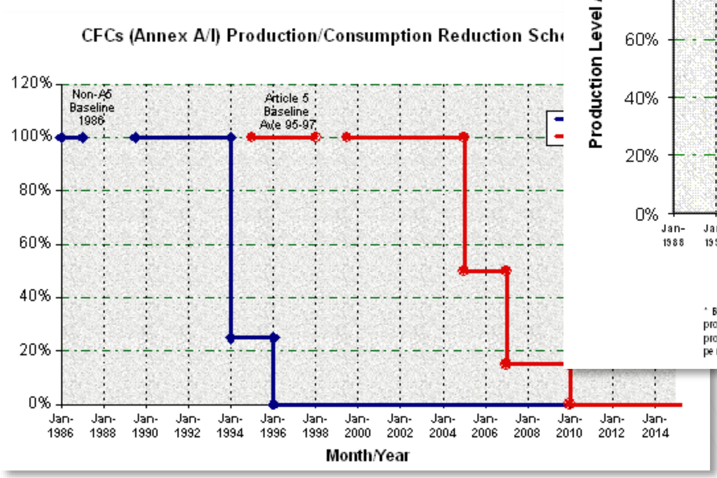
- Thomas Midgley, Jr. (1889-1944)
  - Mechanical Engineer by training
  - Employed by General Motors
    - GM owned Frigidaire
  - 1920s-30s:
    - Beginning of refrigeration machinery operated in proximity to general public
    - Common refrigerants were toxic (sulfur dioxide, methyl chloride, ammonia)
    - A “safety refrigerant” was desired
    - Developed dichlorodifluoromethane (CCl_2F_2) – “Freon” or R-12
      - Subsequently leading to a whole family of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants

Refrigerants and the Ozone



- Chlorine in upper atmosphere can break down atmospheric ozone
  - A single chlorine atom is able to react with 100,000 ozone molecules before it is removed from the catalytic cycle
- Significant source of chlorine:
  - CFCs and HCFCs
- Montreal Protocol (1987):
  - Phase-out of CFCs and HCFCs

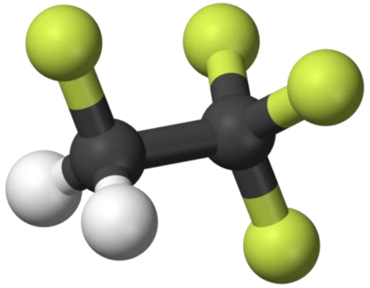




Current Refrigerants

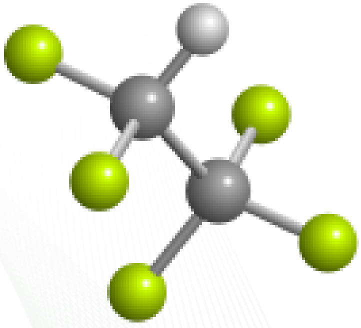
R-32

- In response to CFC and HCFC phase-out, refrigerant manufacturers developed chemicals with no Ozone Depleting Potential (ODP)



R-134a

- Hydrofluorocarbons (HFCs)
  - Contains no chlorine
    - Poses no threat to ozone
    - ODP = 0
  - However, they are potent greenhouse gasses (as are CFCs and HCFCs)
    - Several thousand times more potent than CO_2



R-125

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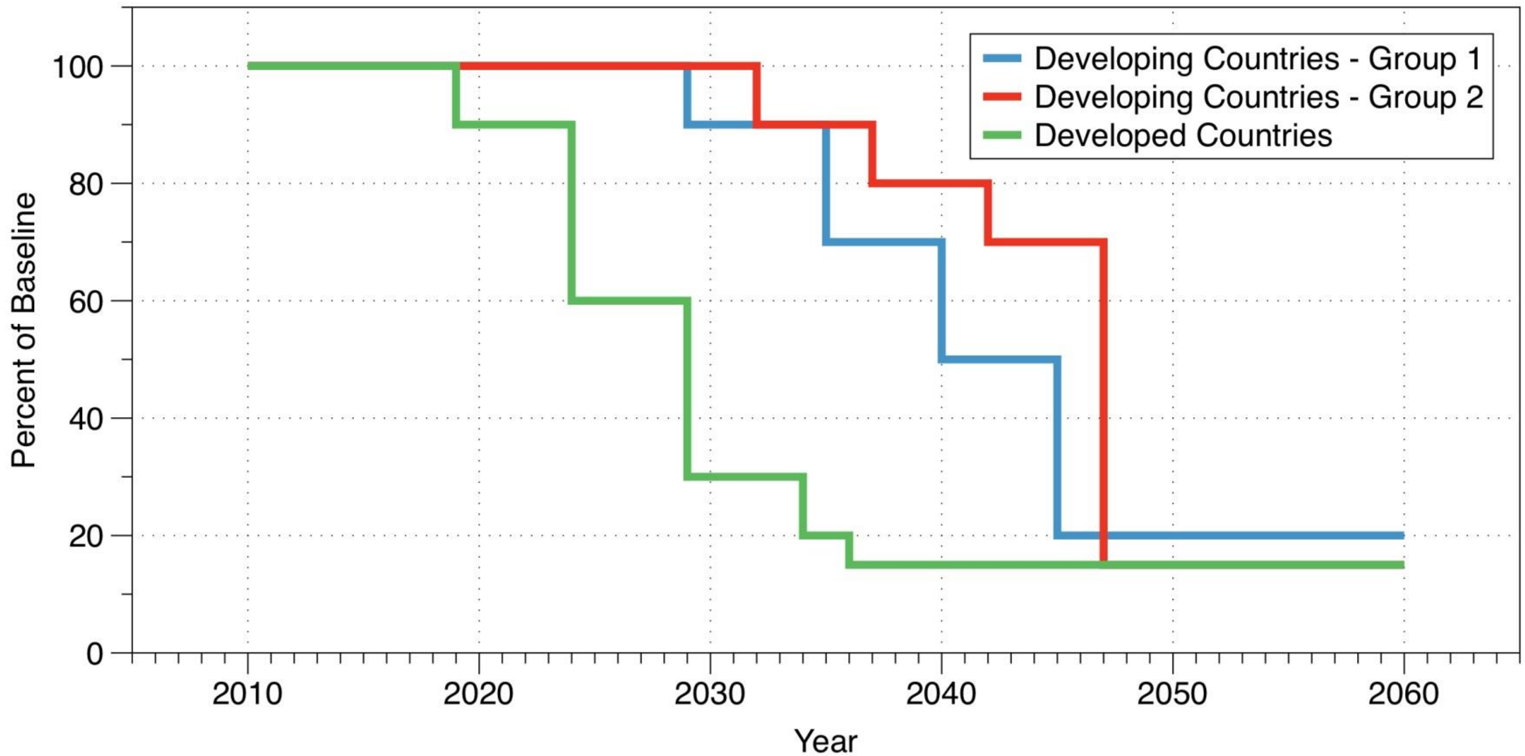
Global Warming Potential (GWP)

- Global Warming Potential (GWP)
  - Represents how a given mass of a chemical contributes to global warming over a given time period compared to the same mass of carbon dioxide
  - Carbon dioxide's GWP is by definition equal to 1.0
  - GWP values for common HFC refrigerants used today:

Refrigerant	GWP
CO_2	1
R-134a	1400
R-404A	3900
R-407A	2100
R-410A	2100

Kigali Amendment to Montreal Protocol

- Proposed HFC phase-out schedule
  - Reduce greenhouse gas emissions



Source: UNEP (2016)

EPA SNAP
(Significant New Alternatives Policy)

- Identify acceptable substitutes for ozone-depleting and high global warming potential substances
  - https://www.epa.gov/snap

- Residential and Commercial Air Conditioning
  - R-134a and R-410A are viable options
  - Potential future options?

- Commercial Refrigeration
  - Targeted bans on high-GWP refrigerants
    - Example: R-404A and R-507 are unacceptable in new supermarket systems effective 1 January 2017
  - Potential future options?

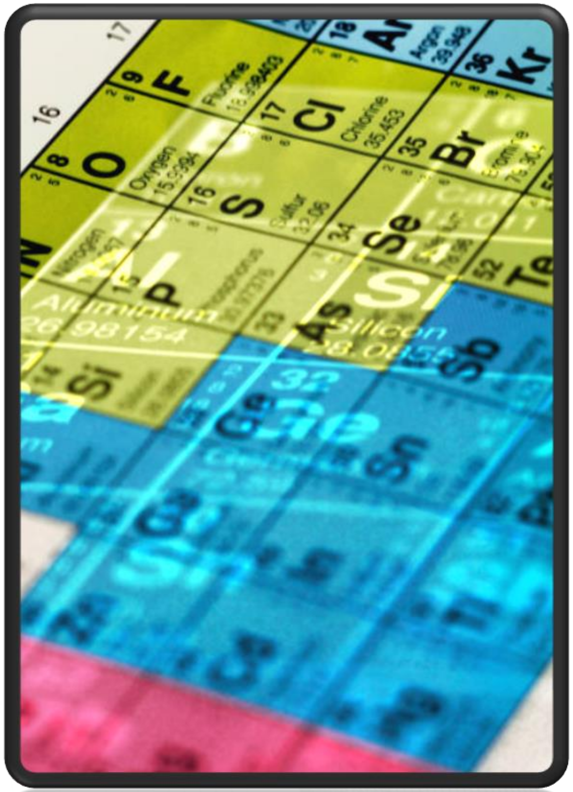
EPA SNAP Ruling and Court Cases

- EPA Rule 20: Protection of ***Stratospheric Ozone***: Change of Listing Status for Certain Substitutes under the SNAP Program
- Two refrigerant manufacturers sued EPA
  - Contend that EPA overstepped its authority
  - HFCs do not contain chlorine and are not ozone depleting
  - Federal Circuit Court ruled against the EPA
- Other refrigerant manufacturers and organizations sought to appeal the decision
  - Appeal was lost
  - Recently, US Supreme Court announced it will not review the case

Next Generation Refrigerants

- Hydrofluoro-olefins (HFOs)
  - Fluorinated propene isomers
    - R-1234yf ($CF_3CF = CH_2$)
    - R-1234ze(E) ($CF_3CH = CHF$)
  - GWP < 4
  - Mildly flammable

- "Natural" Refrigerants
  - What's old is new again?
  - CO_2, hydrocarbons, ammonia
  - Very low global warming potential
  - Toxicity, flammability, efficiency?



Refrigerant Cost

- Retail price of HFO-1234yf is about 10 times more than current price of bulk HFC-134a
  - R-134a: ~$5/lb
  - R-410A: ~$6/lb
  - R-404A: ~$7/lb
  - R-1234yf: ~$67/lb
  - Price of HFO blends will be high
  - Long term price (in about 10 years) is likely to be 2-3x current R-134a cost (Sherry et al. 2017)
- Hydrocarbon refrigerants
  - Propane and Isobutane: ~$6 to $8 per pound

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Refrigerant Options for Air Conditioning

Today	Future		
Refrigerant	**Alternative**	**GWP**	**Safety Classification**
R-22 GWP=1760 A1	R-444B	295	A2L
	R-449A	1282	A1
	R-454A	238	A2L
	R-454C	146	A2L
	R-457A	139	A2L
R-134a GWP=1924 A1	R-450A	547	A1
	R-451A	133	A2L
	R-451B	146	A2L
	R-513A	573	A1
	R-515A	403	A1
	R-1234yf	1	A2L
	R-1234ze(E)	1	A2L
R-410A GWP=1924 A1	R-32	677	A2L
	R-446A	461	A2L
	R-447A	572	A2L
	R-447B	714	A2L
	R-452B	676	A2L
	R-454B	467	A2L
	R-459A	461	A2L

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	R-1234ze		A2L
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	R-446A		A2L
	R-447A		A2L
	R-447B		A2L
	R-452B		A2L
	R-454B	467	A2L
	R-459A	461	A2L

Few non-flammable options

Generally higher GWP

Acceptable in all equipment

Refrigerant Options for Air Conditioning

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R-22 (GWP=1760)	R-444B	295	A2L
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	R-451B	146	A2L
	R-513A	[illegible]	A1
	R-515A	[illegible]	A1
	R-1234yf	[illegible]	A2L
	R-1234ze(	[illegible]	A2L
R-410A (GWP=1924)	R-32	[illegible]	A2L
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	R-447B	714	A2L
	R-452B	676	A2L
	R-454B	467	A2L
	R-459A	461	A2L

Numerous mildly flammable options

Generally lower GWP

Limited to smaller systems?

Refrigerant Options for Air Conditioning

- Hydrocarbon Options
  - Higher flammability
  - Suitable for small equipment

Refrigerant	GWP	Safety Classification
R-290 (propane)	3	A3
R-600a (isobutane)	3	A3
R-441A	3	A3

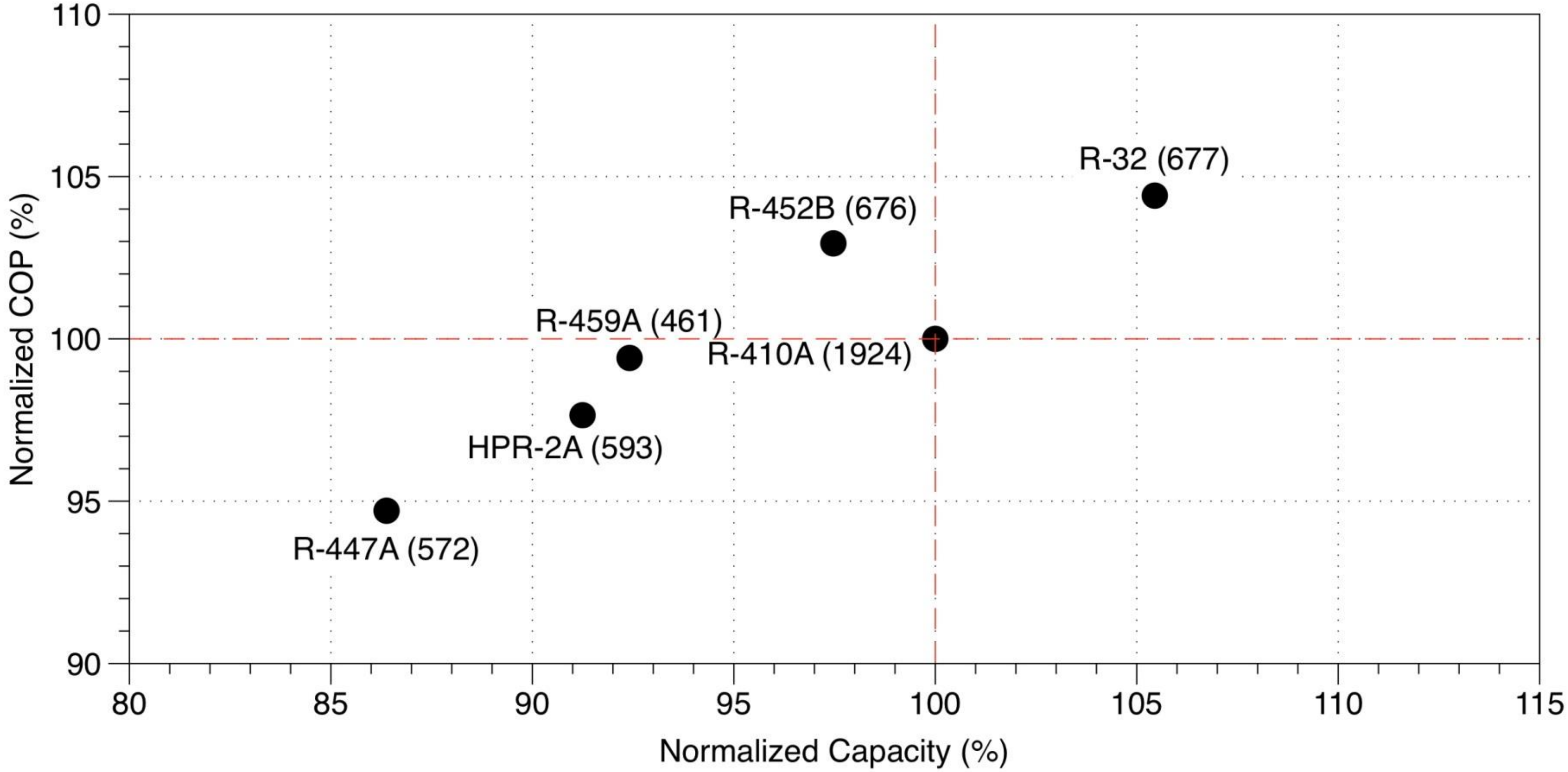
Evaluation of Alternative Refrigerants in Mini-Split and Rooftop AC Units

- Mini Split
  - Capacity: 1.5 tons
  - Refrigerant: R-410A
  - EER: 12.0

- Rooftop AC
  - Capacity: 11 tons
  - Refrigerant: R-410A
  - EER: 10.7

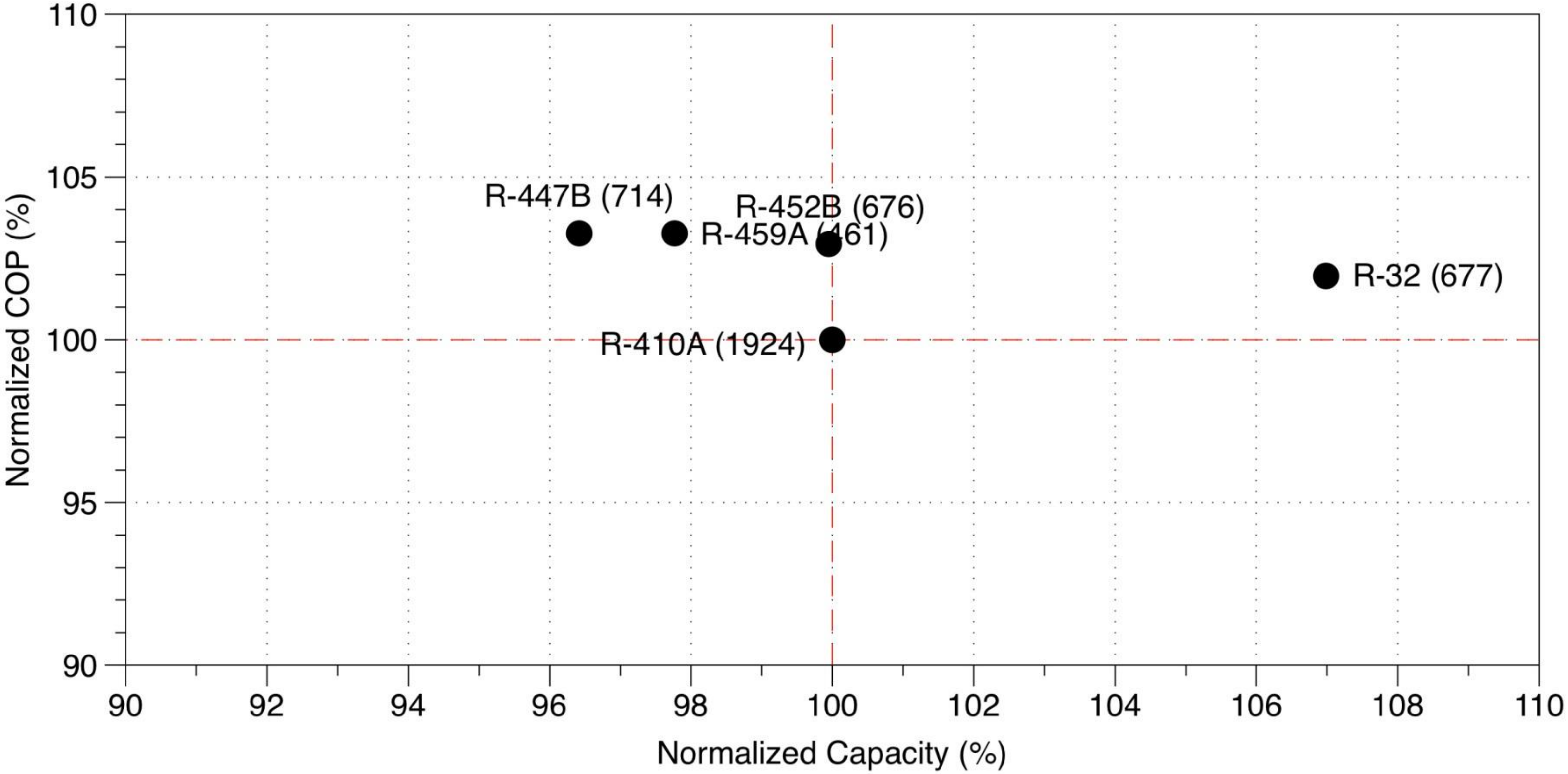
Mini-Split Evaluation: Alternatives for R-410A

- AHRI Conditions: 95°F outdoor, 80°F indoor



Rooftop AC Evaluation: Alternatives for R-410A

- AHRI Conditions: 95°F outdoor, 80°F indoor



Refrigerant Options for Commercial Refrigeration

Today	Future			
Refrigerant	**Alternative**	**GWP**	**Toxicity**	**Flammability**
R-404A (GWP=3943) A1	R-448A (N40)	1273	A	1
	R-449A (XP40)	1282	A	1
	R-449B	1296	A	1
	R-452A (XP44)	1945	A	1
	R-452C	2019	A	1
R-134A (GWP=1300) A1	R-450A (N13)	547	A	1
	R-513A (XP10)	573	A	1
	R-451A	133	A	2L
	R-451B	146	A	2L

Refrigerant Options for Commercial Refrigeration

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Refrigerant	Alternative	GWP	Toxicity	Flammability
R-404A (GWP=3943)	R-448A (N40)	1273	A	1
	R-449A (XP40)	1282	A	1
	R-449B	1296	A	1
	R-452A (XP44)	1945	A	1
	R-452C	2019	A	1
R-134A (GWP=1300)	R-450A (N13)	547	A	1
	R-513A (XP10)	573	A	1
	R-451A	133	A	2L
	R-451B		A	2L

Non-toxic

Nonflammable

Moderate GWP
Long-term solution?

Refrigerant Options for Commercial Refrigeration

Today	Future			
Refrigerant	**Alternative**	**GWP**	**Toxicity**	**Flammability**
R-404A (GWP=3943)	R-448A (N40)	1273	A	1
	R-449A (XP40)		A	1
	R-449B		A	1
	R-452A (XP44)		A	1
	R-452C		A	1
R-134A (GWP=1300)	R-450A (N13)		A	1
	R-513A (XP10)	[illegible]	A	1
	R-451A	133	A	2L
	R-451B	146	A	2L

Non-toxic

Mildly flammable

Lower GWP

Safety?

Refrigerant Options for Commercial Refrigeration

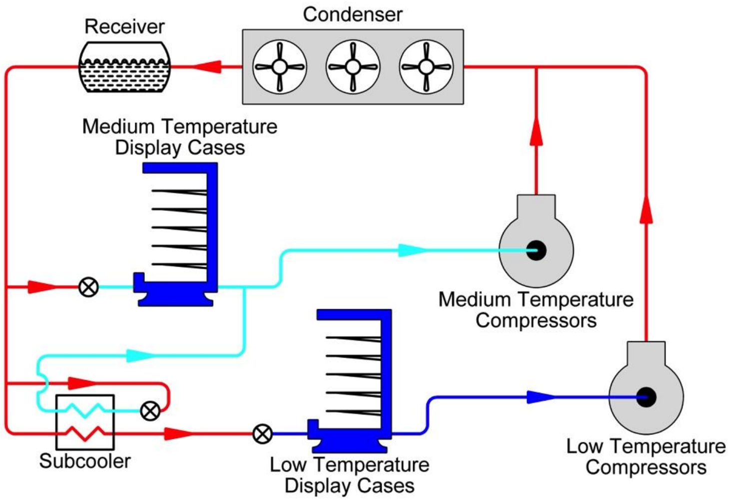
- "Natural" refrigerant options
  - Flammability, toxicity, efficiency?

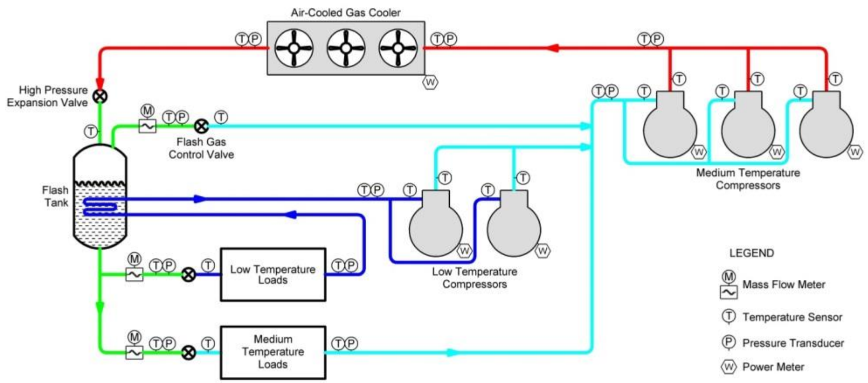
Refrigerant	GWP	Toxicity	Flammability
Propane (R-290)	3	A	3
Isobutane (R-600a)	3	A	3
Ammonia (R-717)	0	B	2L
CO_2 (R-744)	1	A	1

Evaluation of Alternative Refrigerants for Commercial Refrigeration

- HFC System
  - LT Capacity: 5 tons
  - MT Capacity: 15 tons
  - Refrigerant: R-404A

- Transcritical CO_2
  - LT Capacity: 2.5 tons
  - MT Capacity: 9.6 tons
  - Refrigerant: R-744





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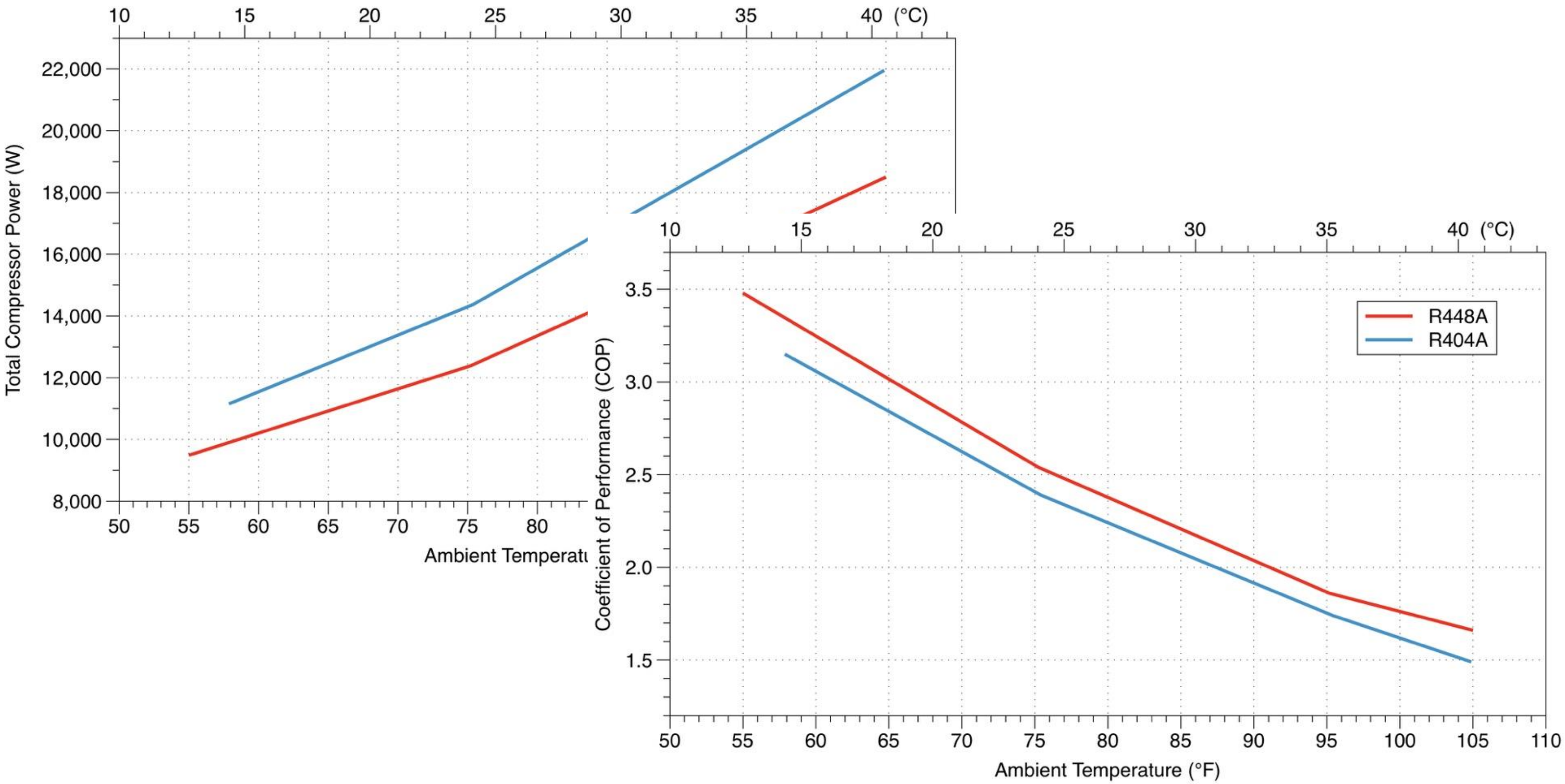
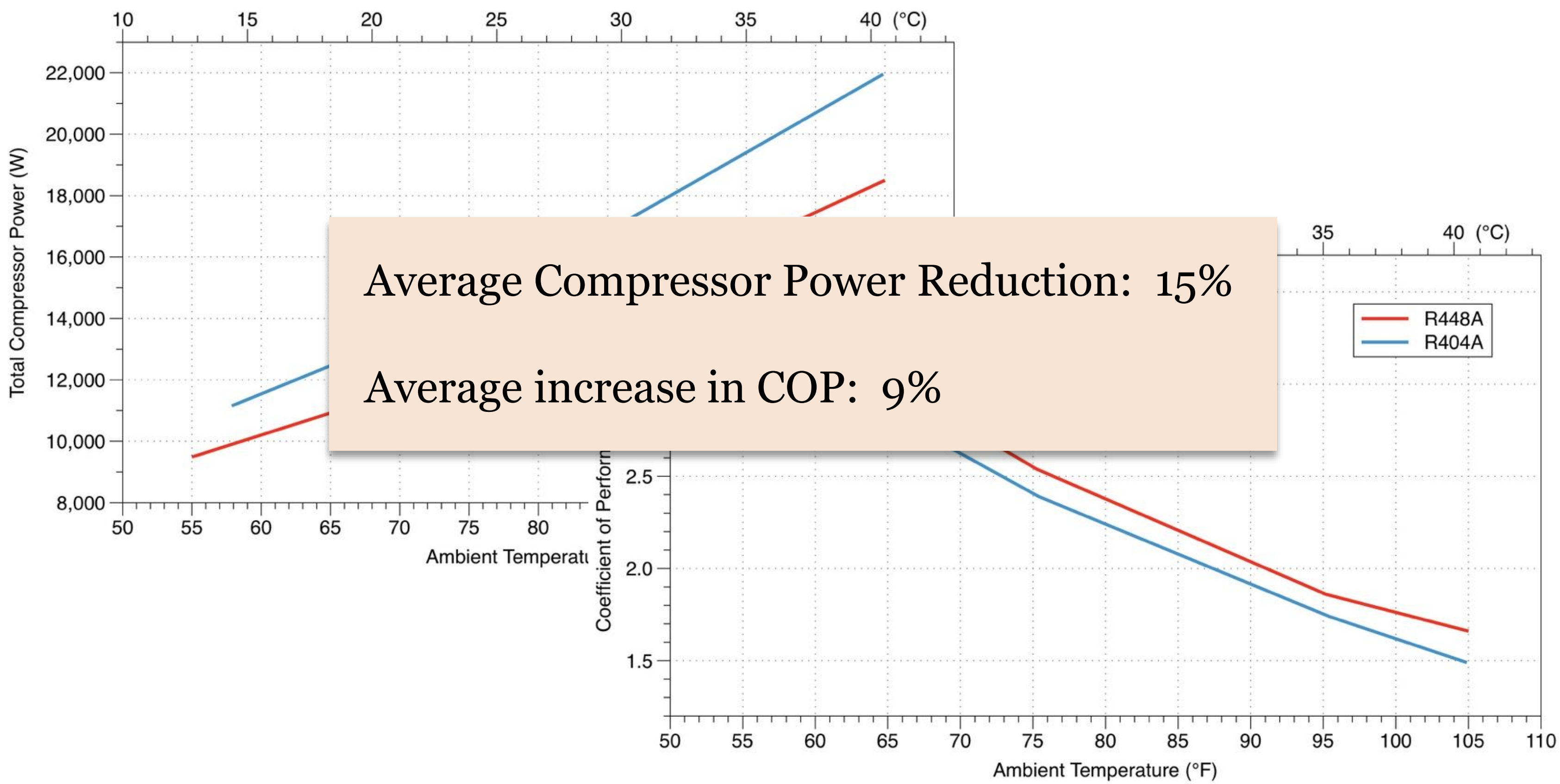
Commercial Refrigeration Evaluation: Alternatives for R-404A

- R-404A vs. R-448A:



Commercial Refrigeration Evaluation: Alternatives for R-404A

- R-404A vs. R-448A:

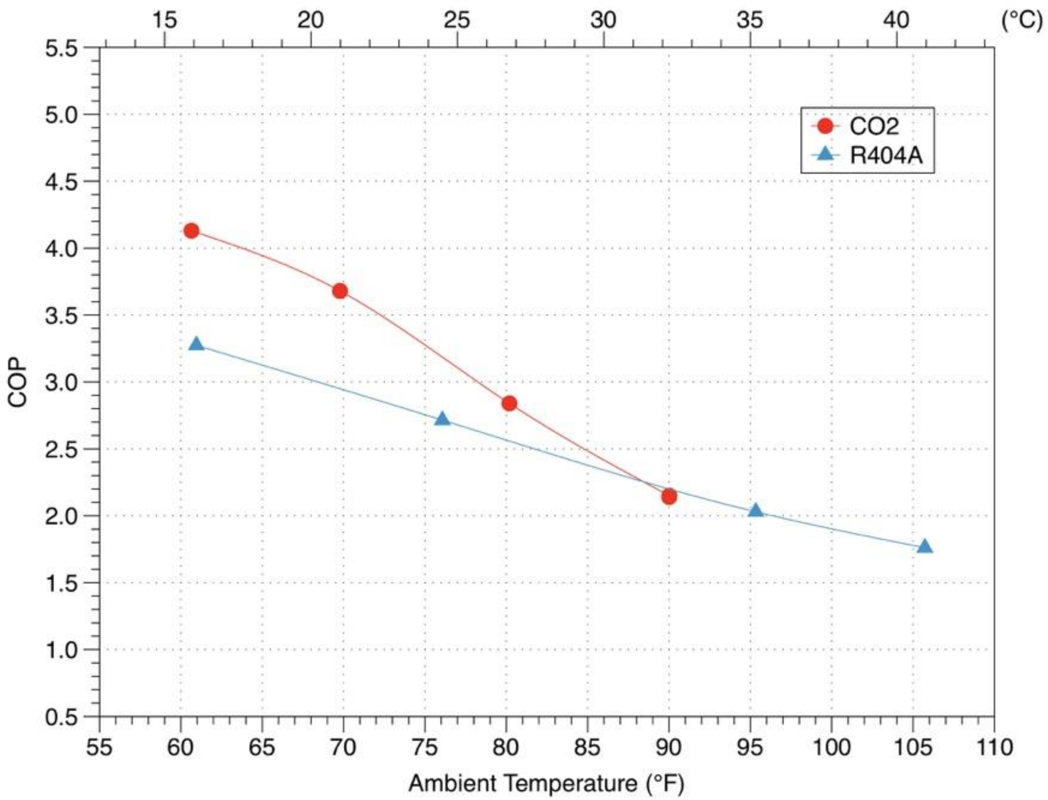


Average Compressor Power Reduction: 15%

Average increase in COP: 9%

Commercial Refrigeration Evaluation: Transcritical CO_2 Booster System

- Comparison of R-404A and CO_2 Systems:



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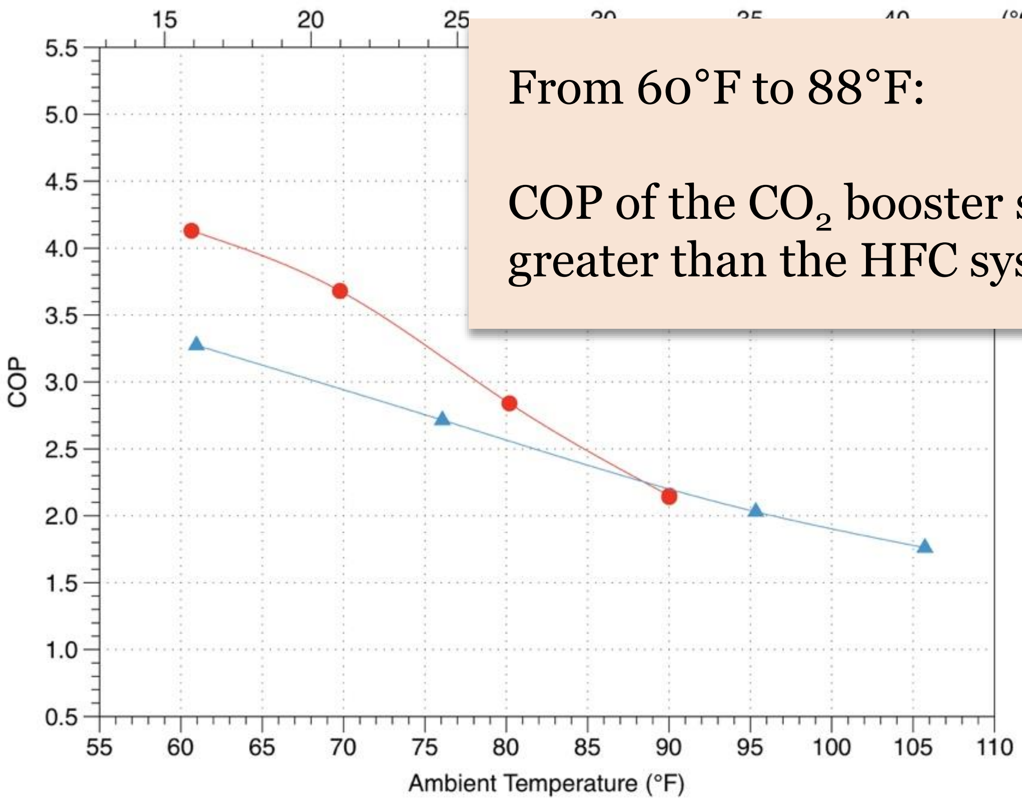
Commercial Refrigeration Evaluation: Transcritical CO_2 Booster System

- Comparison of R-404A and CO_2 Systems:



From 60°F to 88°F:

COP of the CO_2 booster system is 15% greater than the HFC system

Refrigerant Research

- Efficiency of equipment with new refrigerant options
  - Research results to inform system design
- Flammability concerns
  - Likelihood and severity of ignition event
  - Byproducts of combustion
    - Hydrogen fluoride or carbonyl fluoride
    - Both extremely toxic
  - Research results to inform codes and standards

Coordinated Research Efforts: Flammable Refrigerants

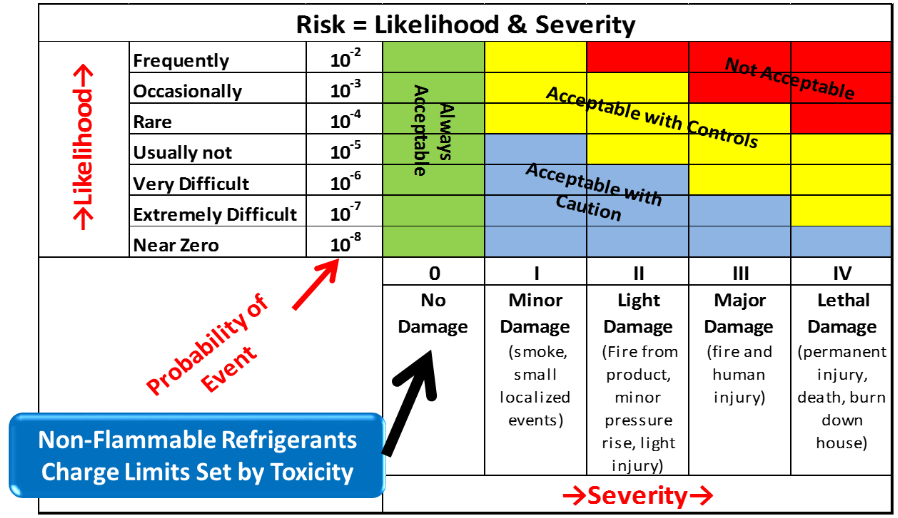
- Air Conditioning, Heating & Refrigeration Institute (AHRI)
  - $1.0M
- American Society of Heating, Refrigerating & Air-Conditioning Engineers (ASHRAE)
  - $1.3M
- U.S. Department of Energy (USDOE)
  - $3.0M
- California Air Resources Board (CARB)
  - $0.3M

ASHRAE-Funded Research

- **1806-RP**: Flammable Refrigerants Post-ignition Simulations and Risk Assessment Update
- **1807-RP**: Guidelines for Flammable Refrigerant Handling, Transporting, Storing and Equipment Servicing, Installation and Dismantling
- **1808-RP**: Servicing and Installing Equipment Using Flammable Refrigerants: Assessment of Field-made Mechanical Joints
- These projects are on-going, with results anticipated to be released by early to mid 2019.

1806-RP Flammable Refrigerants Post-ignition Simulations and Risk Assessment Update

- **Background**
  - AHRI has sponsored several Risk Assessments to quantify the PROBABILITY of an ignition event occurring.
  - Need to understand the SEVERITY of the event to fully understand the risk of using flammable refrigerants.
  - Experimental/empirical work on SEVERITY was recently undertaken in AHRTI 9007.

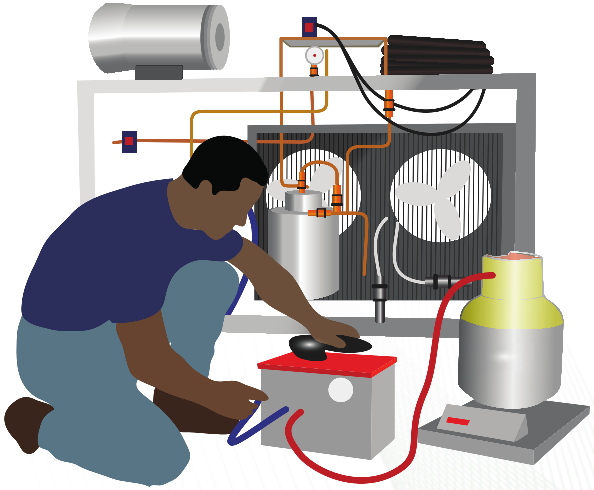


  - Such experimental work is very expensive and time-consuming.
- **Objective**
  - Develop further understanding of the SEVERITY of flammable refrigerant events through computer-based simulations using computational fluid dynamics (CFD).
  - Update the Risk Assessments with this new information.

1807-RP Guidelines for Flammable Refrigerant Handling, Transporting, Storing and Equipment Servicing, Installation and Dismantling

- **Background**
  - Lack of information on issues associated with handling Class A2L, A2, and A3 refrigerants.
  - Several countries outside the U.S. are adopting the use of flammable refrigerants.
    - Their specific requirements for safe handling and use are unknown to the U.S. industry.
  - Such information can be valuable in establishing standards and guidelines for use in the U.S.

- **Objective**
  - Characterize current international and domestic best practices for safe use of flammable refrigerants.
  - Leverage this information to recommend guidelines for safe use of flammable refrigerants.
  - Recommend appropriate testing to validate these guidelines.

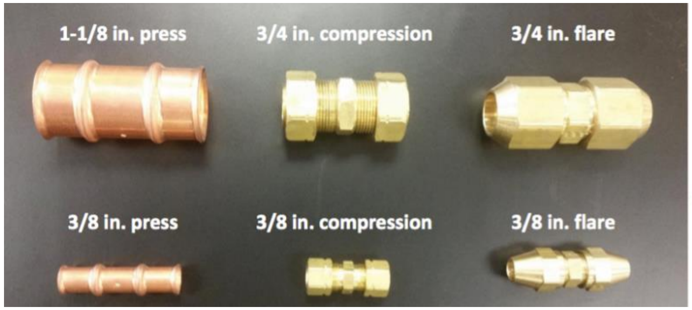


UNEP (2010)

1808-RP

Servicing and Installing Equipment using Flammable Refrigerants: Assessment of Field-made Mechanical Joints

- **Background**
  - Need to assess the robustness of field-made joints used to connect refrigerant piping and system components.
  - Are they suitable for use with flammable refrigerants?



50x of each fitting type-size tested (300 total)

+ 25x brazed joints as a baseline

- **Objective**
  - Characterize and quantify the leak-tightness of various types of field-made joints.
  - Account for mechanical and human factors.
    - Effect on consistency of leak-tightness
  - Identify types of field-made joints that are suitable for use with flammable refrigerants.
    - Incorporate into ASHRAE Standards 15 and 15.2, as well as other relevant codes and standards.

Summary of Refrigerant Research

- Many proposed HFO refrigerant blends perform similarly to current HFC refrigerants:
  - Comparable efficiency
  - Slightly lower capacity
- Many proposed HFO refrigerant blends show good performance at high ambient conditions
  - Slightly higher efficiency
  - Comparable or slightly higher capacity
- Flammability of many alternative refrigerants is an issue
  - Maximum safe refrigerant charge
  - Safe equipment design
  - Safe handling, servicing and transportation practices

Discussion

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