Introduction to Refrigerants - Part II

Sameer Khandekar
Sir M. Visvesvaraya Chair Professor
Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur (UP) 208016 INDIA
Webpage: home.iitk.ac.in/-samkhan/

ME340A: Refrigeration and Air Conditioning
Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur 208016 India

In this lecture…

- Comparison between refrigerants.
- Alternate refrigerants.
- Flammability and Toxicity.
- Contemporary trends.

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Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

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Indian Institute of Technology Kanpur
Kanpur 208016 India

1 Comparison of refrigerants

Why coose/repalce one with another?

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Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

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Indian Institute of Technology Kanpur
Kanpur 208016 India

Comparison between different refrigerants

- Synthetic refrigerants were commonly used for RAC/cold storage applications such as R 11, R 12, R 22, R 502 (CFC 12+R 22) and NH_3.
- Of these, R 11 was primarily used with centrifugal compressors in air conditioning applications. R 12 was used primarily in small capacity refrigeration and cold storage applications, while the other refrigerants were used in large systems such as large AC/CS.
- Among these refrigerants, except ammonia, all the others are synthetic and are 'non-toxic' and 'non-flammable'.
- However, these refrigerants have to be phased out due to their Ozone Depletion Potential (ODP).

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Kanpur 208016 India

Comparison between different refrigerants

- The synthetic replacements for the older refrigerants are: R-134a (HFC-134a) and blends of HFCs, which are generally non-toxic and non-flammable.
- However, compared to the natural refrigerants the synthetic refrigerants offer lower performance and they also have higher Global Warming Potential (GWP).
- Hence, these synthetic refrigerants also need eventual replacement.

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Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

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Comparison between different refrigerants

- The most commonly used natural refrigerant is ammonia. This is also one of the oldest known refrigerants. It has excellent thermodynamic, thermophysical and environmental properties.
- However, it is toxic and is not compatible with some of the common materials of construction such as copper, which somewhat restricts its application.
- Other natural refrigerants that are being suggested are hydrocarbons (HCs) and carbon dioxide (R-744). Though these refrigerants have some specific problems, they are being studied widely and their prominence is again increasing very rapidly.

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Comparison between different refrigerants

- The depletion of stratospheric ozone layer was attributed to Cl and Br containing chemicals such as Halons, CFCs, HCFCs etc.
- Since ozone layer depletion could lead to catastrophe on a global level, global community is aiming to phase out the OD substances.
- In addition to ozone layer depletion, most of the conventional synthetic refrigerants also cause significant global warming.
- Search for suitable replacement continues! → low ODP, low GWP

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Alternate refrigerants

- The alternate refrigerants can be classified into two broad groups:
  - Non-Ozone depleting synthetics based on Hydro-Fluoro-Carbons (HFCs) and their blends and Unsaturated Olefins
  - Coming back to natural refrigerants
    - Ammonia, Carbon dioxide, Hydrocarbons and their blends

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Replacement chart/ general properties

Refrigerant	Application	Substitute suggested Retrofit(R)/New (N)
R 11(CFC) NBP = 23.7°C h_{fg} at NBP=182.5 kJ/kg T_{cr} =197.98°C Cp/Cv = 1.13 ODP = 1.0 GWP = 3500	Large air conditioning systems Industrial heat pumps	R 123 (R,N) R 141b (N) R 245fa (N) n-pentane (R,N)
R 12 (CFC) NBP = -29.8°C h_{fg} at NBP=165.8 kJ/kg T_{cr} =112.04°C Cp/Cv = 1.126 ODP = 1.0 GWP = 7300	Domestic refrigerators Small air conditioners Water coolers Small cold storages	R 22 (R,N) R 134a (R,N) R 227ea (N) R 401A,R 401B (R,N) R 411A,R 411B (R,N) R 717 (N)

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Replacement chart/ general properties

R 22 (HCFC) NBP = -40.8°C h_{fg} at NBP=233.2 kJ/kg T_{cr} =96.02°C Cp/Cv = 1.166 ODP = 0.05 GWP = 1500	Air conditioning systems Cold storages	R 410A, R 410B (N) R 417A (R,N) R 407C (R,N) R 507,R 507A (R,N) R 404A (R,N) R 717 (N)
R 134a (HFC) NBP = -26.15°C h_{fg} at NBP=222.5 kJ/kg T_{cr} =101.06°C Cp/Cv = 1.102 ODP = 0.0 GWP = 1200	Used as replacement for R 12 in domestic refrigerators, water coolers, automobile A/Cs etc	**No replacement required** High global warming potential * Highly hygroscopic

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R 717 (NH_3) NBP = -33.35°C h_{fg} at NBP=1368.9 kJ/kg T_{cr} =133.0°C Cp/Cv = 1.31 ODP = 0.0 GWP = 0.0	Cold storages Ice plants Food processing Frozen food cabinets	**No replacement required** * Toxic and flammable * Incompatible with copper * Highly efficient * Inexpensive and available
R 744 (CO_2) NBP = -78.4°C h_{fg} at 40°C=321.3 kJ/kg T_{cr} =31.1°C Cp/Cv = 1.3 ODP = 0.0 GWP = 1.0	Cold storages Air conditioning systems Simultaneous cooling and heating (Transcritical cycle)	**No replacement required** * Very low critical temperature * Eco-friendly * Inexpensive and available

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Replacement chart/ general properties

Refrigerant	Application	Substitute suggested Retrofit(R)/New (N)
R718 (H_2O) NBP = 100.°C h_{fg} at NBP=2257.9 kJ/kg T_{cr} =374.15°C Cp/Cv = 1.33 ODP = 0.0 GWP = 1.0	Absorption systems Steam jet systems	**No replacement required** * High NBP * High freezing point * Large specific volume * Eco-friendly * Inexpensive and available
R600a (iso-butane) NBP = -11.73°C h_{fg} at NBP=367.7 kJ/kg T_{cr} =135.0°C Cp/Cv = 1.086 ODP = 0.0 GWP = 3.0	Replacement for R 12 Domestic refrigerators Water coolers	**No replacement required** * Flammable * Eco-friendly

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Frequently used Refrigerants

Refrigerant	Chemical formula	Atmospheric lifetime (years)	GWP	ASHRAE safety group	ODP
R22	$CHClF_2$	12	1810	A1	0.05
R134a	$C_2H_2F_4$	14	1430	A1	0
R290	$CH_3CH_2CH_3$	12	3.3	A3	0
R404a	44±2% C_2HF_5 52±1% $C_2H_3F_3$ 4±2% $C_2H_2F_4$	40	3920	A1	0
R407c	23±2% CH_2F_2 25±2% C_2HF_5 52±2% $C_2H_2F_4$	16	1774	A1	0
R600a	$CH(CH_3)_2CH_3$	12	3	A3	0

GWP Global Warming Power
ODP Ozone Depletion Power
A1 no flame propagation, **A3** highly flammable

Pure substances proposed under various test programs and in ASHRAE 34

Refrigerant	Replacing	Safety class	GWP 100 Year (IPCC5)
HFC32	R410A	A2L	677
HC290 (propane)	R22, R404A, R407C	A3	
HC600a (isobutane)	R134a	A3	
R717 (ammonia)	R22, R407C	B2L	
R744 (carbon dioxide)	R404A, R410A	A1	1
R1233zd(E)	R123	A1	1
R1234yf	R134a	A2L	<1
R1234ze(E)	R134a	A2L	<1
HC1270	R22, R407C	A3	
R1336mzz(Z)	R123	A1	2
R1130(E)*	R123	B2	<1

** 1130(E) is pending official ASHRAE 34 approval*

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Environmental impact of refrigerants

What is ODP and GWP?

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Environmental effects of refrigerants

- Depletion of the ozone layer in the stratosphere.
- Global warming:
  - *Refrigerants directly contributing to global warming when released to the atmosphere*
  - *Indirect contribution based on the energy consumption of among others the compressors* (*CO_2 produced by power stations*)

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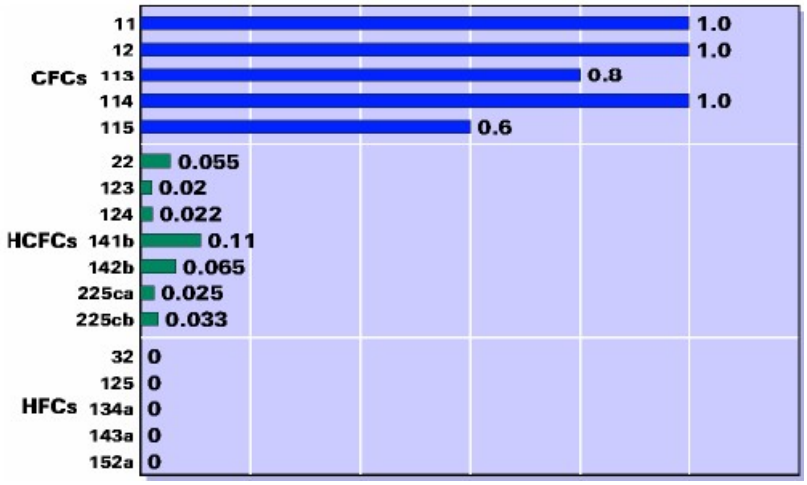
Ozone depletion potential (ODP)



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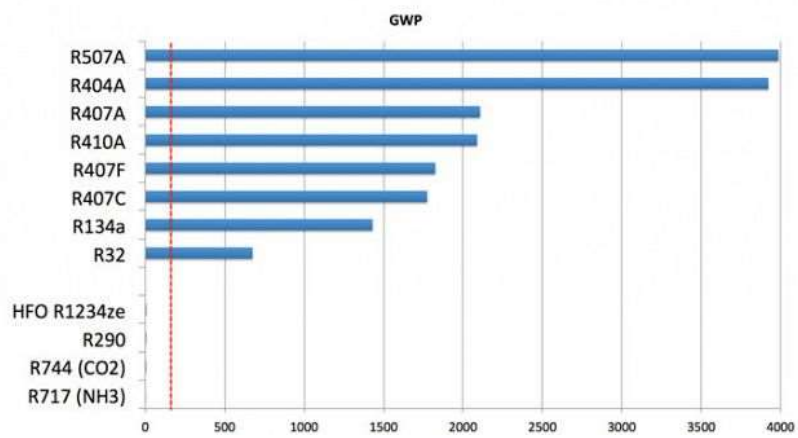
Global warming potential (GWP)



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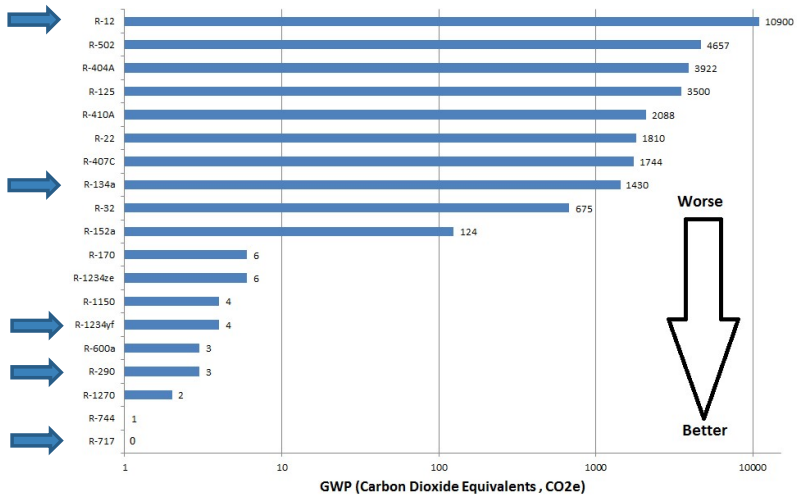
Global warming potential (GWP)



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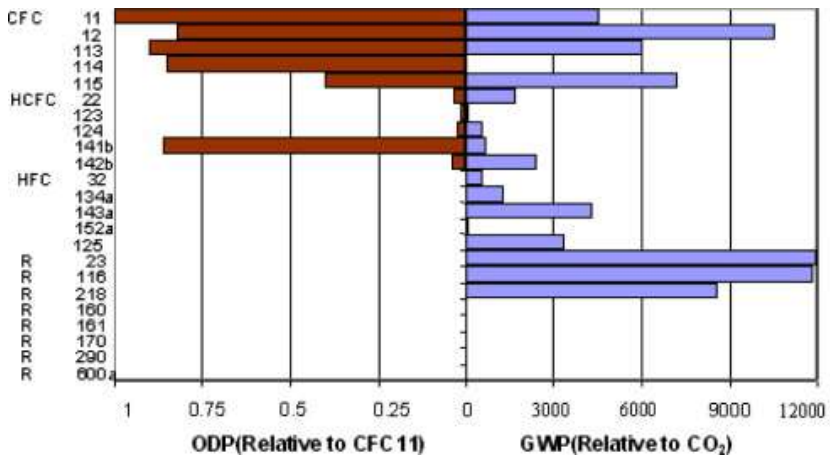
ODP/GWP



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Carbondioxide as refrigerant

- Non Flammable
- Non toxic
- Inexpensive and widely available
- Its high operating pressure provides potential for system size and weight reducing potential.

Drawbacks:

- Operating pressure (high side) : 80 bars
- Low efficiency

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Hydrocarbon refrigerants

- Used since the 1880's → natural → Zero ODP and negligible GWP
- Good substitutes for CFC's, HCFC's, and HFC's.
- Compatible with copper, miscible with mineral oil, lubricating oils
- Retrofitting of existing systems is relatively cheap.
- Energy saving: up to 20%
- When HC's burn they produce carbon and steam; when synthetic refrigerants burn they all produce highly toxic fumes.
- Proving to be good for Domestic Refrigeration and Air Conditioning and also for Mobile Air Conditioning Systems (MACS)
- Commercial/Industrial Refrigeration and Air Conditioning

Drawback :

- Flammable

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Ammonia – A natural refrigerant

- Ammonia is produced in a natural way by human beings and animals; 17 grams/day for humans.

Natural production	3000 million tons/year
Production in factories	120 million tons/year
Used in refrigeration	6 million tons/year

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Advantages of using ammonia as refrigerant

- ODP = 0; GWP = 0
- Excellent thermodynamic properties small molecular mass, large latent heat, large vapor density and excellent heat transfer characteristics.
- High critical temperature (132°C): highly efficient cycles at high condensing temperatures
- Its smell causes leaks to be detected and fixed before reaching dangerous concentration
- Relatively low price

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Some drawbacks of ammonia as refrigerant

- Toxic
- Flammable (16 – 28% concentration)
- Not compatible with copper
- Temperature on discharge side of compressor is higher compared to other refrigerants.

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Properties of ammonia

Concentration (ppm)	Effect
5	Noticeable by smell
25	Irritation noticeable
50	Irritation of nose, mouth and throat; acclimatization after a while
500	Immediate irritation of mucous membranes, respiration difficult
3500	Lethal after a short period of exposure
20000	Causes blisters and chemical burns
Lower explosion limit	16 % by volume in air
Higher explosion limit	25 % by volume in air
Ignition temperature	650 C
Ignition energy required	.01 to 1 Joule

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Refrigeration properties of ammonia

- Evaporation enthalpy 0°C — 1262 KJ/KG
- Pressure at 0°C — 4.9 bar
- Pressure ratio 0/35°C — 3.15
- COP 0/35°C — 6.77
- Discharge temperature 0/35°C — 81°C
- Volumetric refrigerating capacity — 3800 KJ/m^3
- Volumetric refrigerating capacity of R134a 2000 KJ/m^3

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Energy efficiency – reciprocating compressor

Performance: t-evap = -10 °C; t-cond = 35 °C				
Refrigerant	Refrigerating capacity	Shaft power	COP	1/COP
[-]	[kW]	[kW]	[-]	[%]
R717 (NH_3)	425.8	112.9	3.771	100.0
R22	380.3	121.3	3.135	120.3
R134a	218.8	74.7	2.929	128.7
R404A	352.4	132.6	2.658	141.9
R507	356.7	136.0	2.623	143.8

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Energy efficiency – screw compressor

t-evap = -30 °C; t-cond = 35 °C				
Refrigerant	Refrigerating capacity	Shaft power	COP	1/COP
[-]	[kW]	[kW]	[-]	[%]
R717 (NH_3)	435.9	228.0	1.912	100.0
R22	443.2	228.4	1.940	98.6
R134a	221.5	139.4	1.589	120.3
R404A	394.7	257.5	1.533	124.7
R507	408.4	262.7	1.555	123.0

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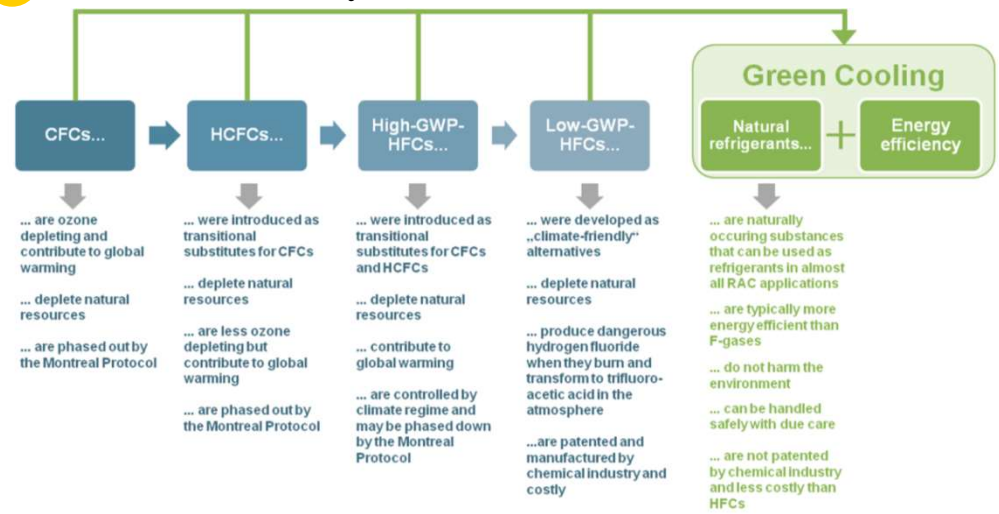
Interim summary



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Interim summary

Different groups of refrigerants and their ozone depletion and global warming potentials (IPCC, 2007)

Substance group	Abbreviation	ODP	GWP	Example (refrigerant/foam blowing agent)
Saturated chlorofluorocarbons	CFC	0.6-1	4750-14,400	R11, R12
Saturated hydrochlorofluorocarbons	HCFC	0.02-0.11	77-2310	R22, R141b
Saturated hydrofluorocarbons	HFC	-	124-14,800	R32, R134a
Unsaturated hydrochlorofluorcarbons	u-HCFC	<0.001	0-10	R1233zd
Unsaturated hydrofluorocarbons	u-HFC	-	<1-12	R1234yf, R1234ze, R1234yz
Natural refrigerants		-	0-3	R744 (carbon dioxide) R717 (ammonia) R290 (propane)

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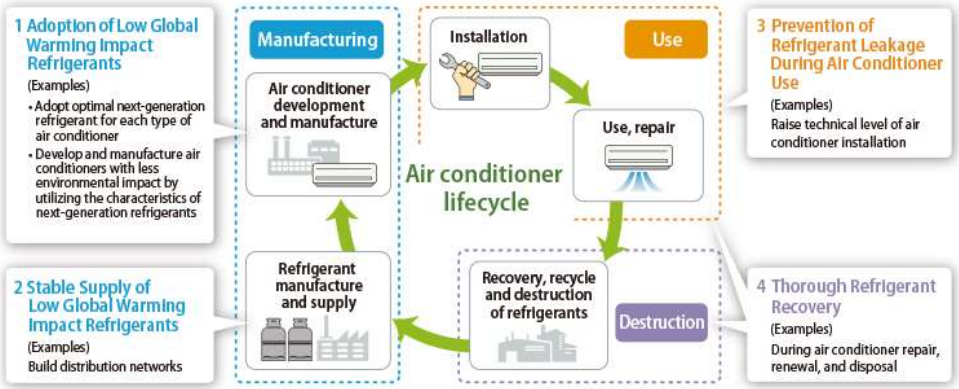
Typical manufacturing cycle/life cycle



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3 Flammability and Toxicity

Classification and more…

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Flammability of refrigerants

- The question of refrigerant flammability is often raised when discussing low GWP refrigerant alternatives for the future.
- Flammability of a refrigerant is its ability to burn or ignite, causing fire or combustion. It is a property of a mixture in which a flame is capable of self-propagating for a certain distance.
- The degree of difficulty required to cause the combustion of a substance needs quantification.
- When the substance is flammable depends on the upper and lower flammability limits and the supplied energy for ignition.
- The consequences of the flammability event depend on the burning velocity, heat released and by-products of combustion.

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Flammability of refrigerants

- Lower flammability limit (LFL, % by volume or g/m^3): minimum concentration of the refrigerant that is capable of propagating a flame through a homogeneous mixture of the refrigerant and air under the specified test conditions at 23.0 °C and 101.3 kPa.
- At a concentration in air lower than the LFL, gas mixtures are too weak to burn. For example, Methane gas has a LFL of 4.4%. If the atmosphere has less than 4.4% methane, combustion cannot occur even if a source of ignition is present.
- Upper flammability limit (UFL) is the highest concentration of a gas or a vapor in air capable of producing a flash of fire in presence of an ignition source (arc, flame, heat). Concentrations higher than UFL are 'too rich' to burn.

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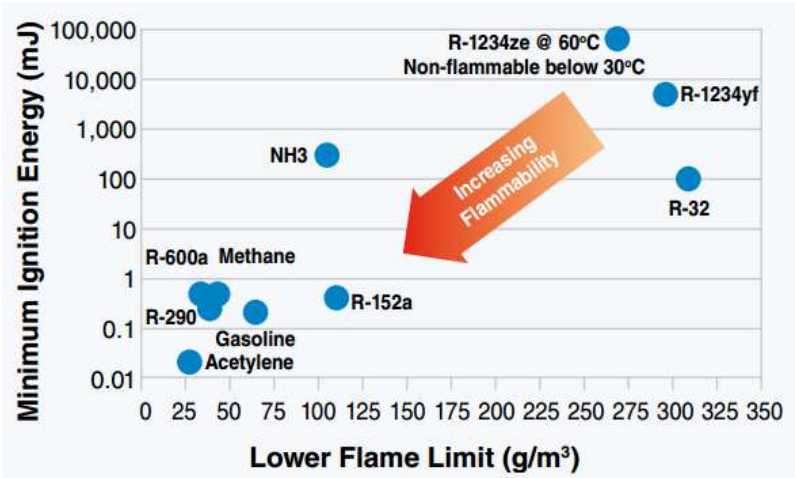
Minimum ignition energy and lower flame limit



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Burning velocity and heat of combustion

- **Burning velocity** is velocity relative to the unburnt gas (normally in cm/s), at which a laminar flame propagates in a direction normal to the flame front, at the concentration of refrigerant with air giving the maximum velocity.
- **Heat of combustion** is the heat evolved from a specified reaction of a substance with oxygen.

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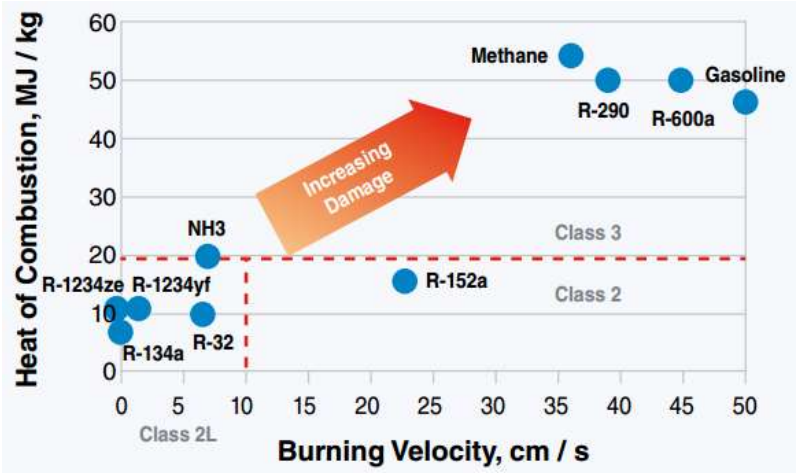
Burning velocity and heat of combustion



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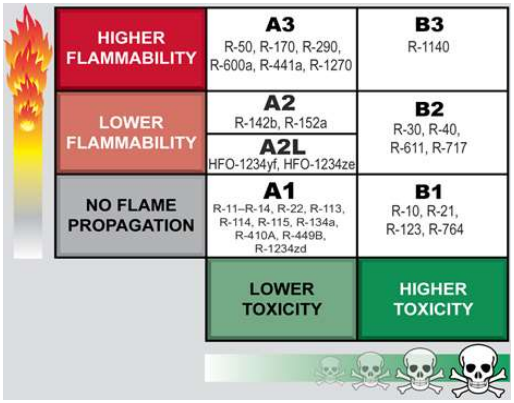
Flammability and Toxicity

- Standards provide limitations and recommended practices on how to properly handle different refrigerants, including flammable ones.
- ASHRAE standard 34 "Designation and Safety Classification of Refrigerants" classifies refrigerants based on their flammability and toxicity characteristics.
- Non-flammable A1 to highly flammable A3, depending on refrigerant's LFL value, heat of combustion and maximum burning velocity



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ME340A: Refrigeration and Air Conditioning
Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur 208016 India

Auto ignition temperature

Approximate auto ignition temperatures

R22	630 °C
R12	750 °C
R134a	740 °C
R290	465 °C (Propane)
R600a	470 °C (Iso-butane)
Oil	222 °C

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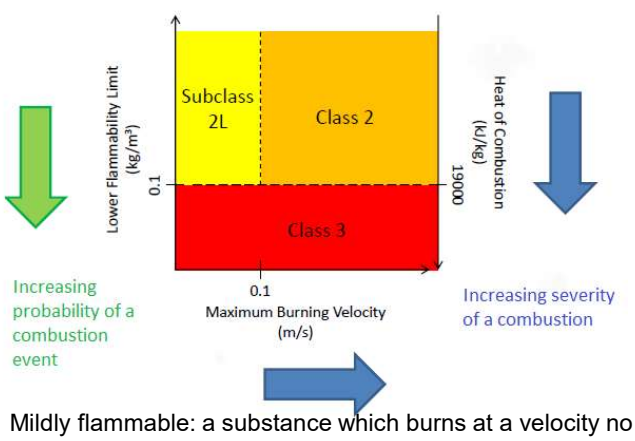
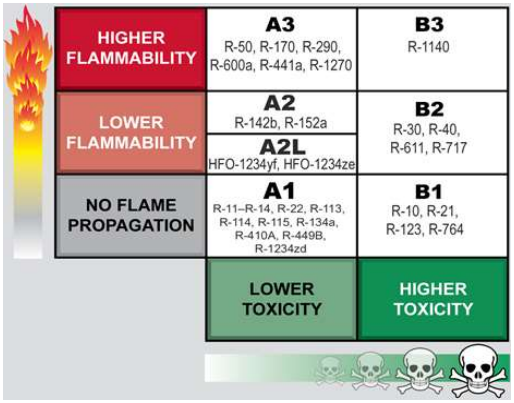
Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur 208016 India

Flammability and Toxicity





Mildly flammable: a substance which burns at a velocity no greater than 10 cm/s. By comparison, Usain Bolt's world record 100-metre time equates to 1043 cm/s, while hydrocarbons burn many times faster.

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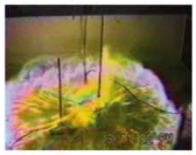
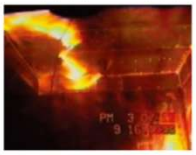
Flammability and Toxicity

Classification	A3	A2	A2L	B2L
Substance	Propane	HFC-152a	HFC-32	Ammonia
Burning velocity	39 cm/sec	23 cm/sec	6.7 cm/sec	7.2 cm/sec
Heat of combustion	46 MJ/kg	16 MJ/kg	9 MJ/kg	19 MJ/kg
Combustion state				

Sameer Khandekar

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ME340A: Refrigeration and Air Conditioning
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Department of Mechanical Engineering
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Kanpur 208016 India

The TEWI factor

- The Total Equivalent Warming Impact (TEWI) rating measures the efficiency of a refrigerant by combining its direct and indirect global warming contribution.
- It is expressed in kg of CO_2.
- TEWI = leakage rate + Recuperation Rate + Indirect emissions due to energy consumption

Sameer Khandekar

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ME340A: Refrigeration and Air Conditioning
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Leakage rate

- Leakage rate is the amount of green house gases released into the atmosphere by the refrigeration system. It is given by the mass of refrigerant emissions in kilograms times the GWP of the refrigerant
- Leakage Rate = Mass of refrigerant leaking from system x GWP of Refrigerant
- Typical leakage rates:
  - Hermetic compressor: 1 - 2%
  - Split units: 6 - 8%
  - Automotive air conditioning: 10 - 20%

Sameer Khandekar

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Department of Mechanical Engineering
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Kanpur 208016 India

Recuperation rate

- Recuperation rate = GWP_{ref} x $Charge_{ref}$ x (1 – recuperation factor)
- Recuperation factor is the percentage of refrigerant recovered when a refrigeration or air conditioning equipment reaches the end of its useful life.

Sameer Khandekar

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ME340A: Refrigeration and Air Conditioning
Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur 208016 India

Indirect emissions

- Indirect emissions are emissions of CO_2 which occur by generation of electricity needed to run the RAC equipment during its lifetime.
- *$CO_{2\ contrib}$ = Machine life x Energy cons. PA x Emission factor*
- The emission factor is the amount of CO_2 released into the atmosphere when fuel is burned to produce one kWh of electricity.

Sameer Khandekar

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ME340A: Refrigeration and Air Conditioning
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Department of Mechanical Engineering
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Example of TEWI calculation

- Chiller unit running on R407c with a charge of 426 kg.
- Average leakage rate pa: 4 kg
- Lifespan of equipment: 25 years
- GWP of R407c: 1610 kg CO_2
- Average power rating of unit: 298.3 kW
- Chiller working on an average of 20 hours per day
- Recuperation factor assumed to be 50 %

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Tel: 7038; e-mail: samkhan@iitk.ac.in

Department of Mechanical Engineering
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Calculation of TEWI

- Leakage Rate = 4 x 1610 x 25 = 128 800 kg CO_2
- Recuperation rate = 1610 x 426 x (1 – 0.5) = 342 930 kg CO_2
- Indirect contribution due to energy consumption =

  = 25 x (298.3 x 20 x 365) x 0.6 = 32 663 850 kg CO_2

  {Emission factor is assumed to be 0.9 for Mauritius}
- TEWI factor for the chiller unit calculated over its lifetime of 25 years :

128 800 + 342 930 + 32 663 850 = 33 135 580 kg CO_2

This implies that the chiller will contribute to the equivalent of 33 135 580 kg of CO_2 over its useful life of 25 years.

- *Direct emissions = 1.4 % of the indirect emissions*

Sameer Khandekar

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Department of Mechanical Engineering
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Conclusions

- In the aftermath of the Montreal protocole HFC's have predominantly replaced CFC's and HCFC's in RAC equipment.
- However, due to their high GWP, HFC's are not a good replacement solution.
- The solution are the natural refrigerants :

  Ammonia, Hydrocarbons and Carbon dioxide
- System need to have low TEWI factor
- High efficiency with ammonia and lower power consumption with hydrocarbons

Sameer Khandekar

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Tel: 7038; e-mail: samkhan@iitk.ac.in

Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur 208016 India

Thanks!

Any questions ?

You can write to me

- samkhan@iitk.ac.in

Sameer Khandekar

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