REFRIGERANTS

By :-

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- History
- Classification
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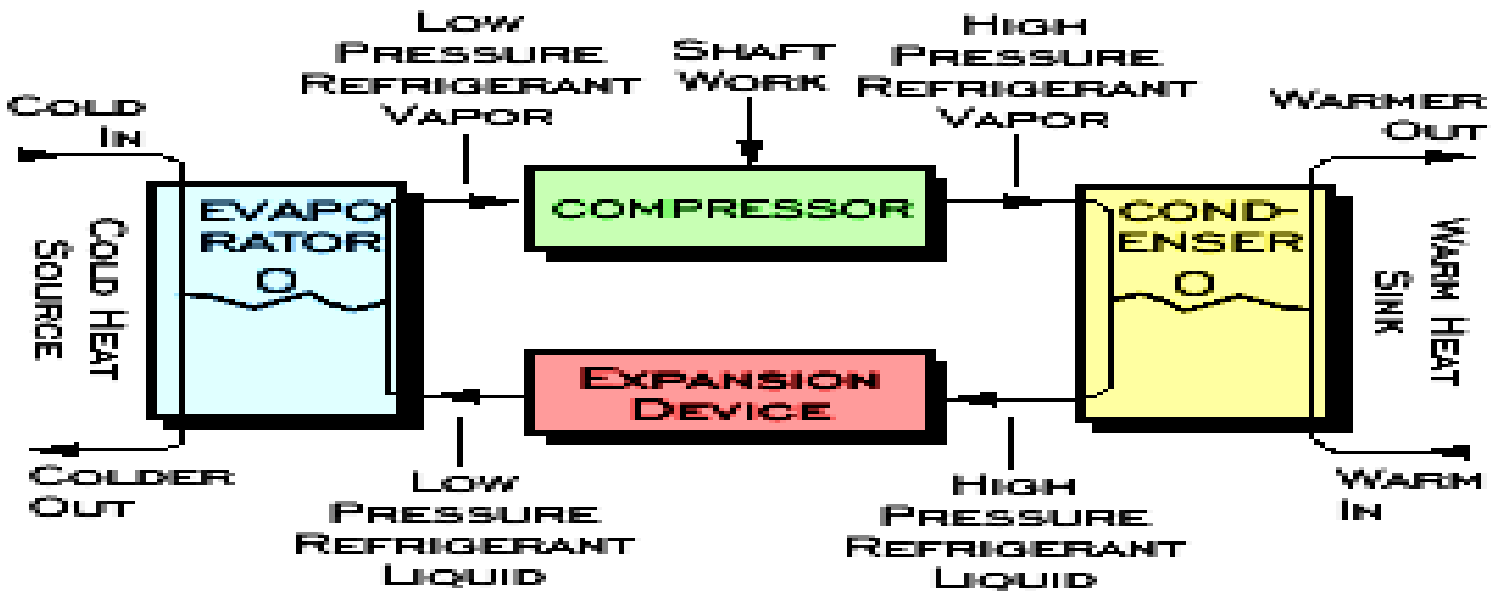
REFRIGERANT:-

“ Refrigerant acts as a transportation medium to move heat absorbed in the evaporator to the condenser where it is rejected ”.



HISTORY OF REFRIGERANTS :-

Natural refrigerants:-

1) Ice blocks
2) Using nocturnal cooling
3) Use of evaporation

Artificial refrigerants :-

1) In 1835, Jakob Perkins use ethyl ether as the refrigerant (b.p= 30'c). (if air mixed forms an explosive gas).
2) In 1874, Raowl Piolet designs the first sulphur dioxide based system. (forms H_2SO_4 when gets moisture).
3) In 1885, Fraunz Windhausen builds the first to use co_2 in Germany. (high operating pressure).
4)In 1920, iso-butane based domestic refrigerator (highly flammable), General Electric first introduce "Kelvinator " refrigerator.

5) In 1930, Introduction of CFC_s .

CLASSIFICATION OF REFRIGERANTS

Based on Working Principle :-

REFRIGERANTS

PRIMARY REFRIGERANTS

1) Used directly as working fluids.
2) Undergo phase change.
   Eg, R134a, R404a

SECONDARY REFRIGERANTS

1) Liquids that are used to transport energy.
2) Not undergo any phase change.
   Eg. Water , brines.

REFRIGERANT SELECTION CRITERIA:-

i. Thermodynamic and Thermo-physical properties

ii. Environmental and safety properties, and

iii. Economics

BASED ON CHEMICAL PROPERTIES

REFRIGERANTS

PURE FLUIDS

SYNTHETIC

1) CFC_S — R 12 OR FERON 12
2) $HCFC_S$ — R134a
3) HFC_S — R23

NATURAL

1) ORGANIC (HC)
2) INORGANIC
   - a) NH_3
   - b) CO_2
   - c) H_20

CRYOGENIC

NON CRYOGENIC

MIXTURE

1) AZEOTROPIC
2) ZEOTROPIC

BASED ON SAFETY :-

Toxicity

Class A

- No Toxicity indication <= 400 ppm
  EG. CO_2 , R 22

Class B

- Toxicity < 400 ppm
  EG. NH_3

Flammability
(at 21°C and 101 kPa)

Class 1

Do not show flame propagation .

Class 2

Lower flammability limit more than 0.10 kg/m3 and a heat of combustion of less than 19 kJ/kg

Class 3

Lower flammability limit of less than or equal to 0.10 kg/m3 and a heat of combustion greater than or equal to 19 kJ/kg.

NOMENCLATURE
(synthetic) (DU PONT CORP.)

All refrigerants are designated by R followed by a number

R xyz

Where,

X+1 = Number of carbon atoms
Y -1 = Number of hydrogen atoms
Z = Number of fluorine atoms

The balance indicates number of **Cl** atoms

Ex: **R 22**

X = 0 ⇒ No. of Carbon atoms = 0+1 = 1
Y = 2 ⇒ No. of Hydrogen atoms = 2-1 = 1
Z = 2 ⇒ No. of Fluorine atoms = 2

The balance = 4 – no. of (H+F) atoms = 4-1-2 = 1 ⇒ No. of Chlorine atoms = 1

∴The chemical formula of R 22 = $CHClF_2$

	Safety group	
Higher Flammability	A3	B3
Lower Flammability	A2	B2
	A2L*	B2L*
No flame Propagation	A1	B1
	Lower Toxicity	Higher Toxicity

*A2L and B2L are lower flammability refrigerants with a maximum burning velocity of $\leq$ 10 cm/s

R 152a burns at 23 cm/s and R 32 burns at 6.27 cm/s

Classification of a few refrigerants

Classification	Denomination	Composition or chemical formula	Safety classification
		(mass percentage)	
INORGANIC COMPOUND			
R717	ammonia	NH_3	B2
R718	water	H_2O	A1
R744	carbon dioxide	CO_2	A1
ORGANIC COMPOUND			
Hydrocarbons			
R170	ethane	CH_3CH_3	A3
R290	propane	$CH_3CH_2CH_3$	A3
R600a	isobutane	$CH(CH_3)_2CH_3$	A3
Halocarbons			
Chlorofluorocarbons (CFCs) and Bromofluorocarbons (BFCs)			
R11	trichlorofluoromethane	CCl_3F	A1
R12	dichlorodifluoromethane	CCl_2F_2	A1
Hydrochlorofluorocarbures (HCFC)			
R22	chlorodifluoromethane	$CHClF_2$	A1
R141b	1,1-dichloro-1-fluoroethane	CH_3CCl_2F	A2
R142b	1-chloro-1,1-difluoroethane	CH_3CClF_2	A2
Hydrofluorocarbons (HFCs)			
R32	difluoromethane	CH_2F_2	A2
R125	pentafluoroethane	CHF_2CF_3	A1
R134a	1,1,1,2-tetrafluoroethane	CH_2FCF_3	A1
R143a	1,1,1-trifluoroethane	CH_3CF_3	A2
R152a	1,1-difluoroethane	CH_3CHF_2	A2
Azeotropic mixtures			
R502		R22/R115 (48.8/51.2)	A1
R507		R125/R143a (50/50)	A1
Zeotropic mixtures			
R404A		R125/R143a/R134a	A1

INORGANIC REFRIGERANTS:

Designated by number 7 followed by their molecular weight.

NH_3= 17, R 717
Ex :- **CO_2, H_2O, NH_3.**

•**CO_2**

1. Zero ODP & GWP is 1.
2. Non Flammable, Non toxic.
3. Drawback - Operating pressure (high side) : 80 bars.
4. Low efficiency

•**Ammonia**

1. Toxic.
2. Flammable (16 – 28% concentration).
3. Not compatible with copper (cuperic oxide)

•**Water**

1. Used in absorption system .
2. Cannot be used under higher working pressure.

MIXTURES

1) Azeotropic mixture : 500 series,

• A stable mixture of two or several refrigerant .
• vapor and liquid phases retain identical compositions over a wide range of temperatures.

Examples : R-500 : 73.8% R12 and 26.2% R152

R-502 : 8.8% R22 and 51.2% R115

2) Zeotropic mixture : 400 series,

•Composition in liquid phase differs to that in vapor phase.
•Do not boil at constant temperatures unlike azeotropic refrigerants because of dff. Boiling points.

Examples :R404a : R125/143a/134a (44%,52%,4%)

R407c : R32/125/134a (23%, 25%, 52%)

NATURAL REFRIGERANTS :-

Hydrocarbon

⇒ Their efficiency is good

⇒ With no ODP and very small GWP values

⇒ Compatible with lubricating oils

⇒ Extraordinary reliability.

⇒ Highly flammable

Examples: R170, Ethane, C_2H_6
R290 , Propane C_3H_3
R600, Butane, C_4H_{10}
R600a, Isobutane, C_4H_{10}
Blends of the above Gases

SYNTHETIC REFRIGERANTS

CFCs:

- Combination of **CARBON+CHLORINE+FLUORINE.**
- Also commonly know as **FREONS.**
- High **ODP=1** and high **GWP.**
- **CHLORINE** has an excellent anti-wear characteristic.
- As **ODP** & **GWP** is high so it got banned.
- Few examples are:
  - R-11
  - R-12
  - R-13 and many more.

CFCs:

REFRIGERANT	CHEMICAL NAME	APPLICATION
R-11	Trichloromonofluoromethane	Centrifugal chillers
R-12	Dichlorodifluoromethane	Reciprocating & rotatory equipment
R-13	Monochlorotrifluoromethane	Low stage cascade system
R-13B1	Bromotrifluoromethane	Low to medium temp. application
R-113	Trichlorotrifluoroethane	Low capacity chillers
R-114	Dichlorotetrafluoroethane	High capacity chillers
R-500	Refrig. 152A/12	Reciprocating compressor
R-502	Refrig. 22/115	Reciprocating equipments
R-503	Refrig. 23/13	Commercial refrigeration

HCFCs:

- Combination of **HYDROGEN+CHLORINE+FLUORINE+CARBON.**
- Low **CHLORINE** content than CFCs.
- It has **ODP=0.05** & **LESS** but not zero.
- Low **GWP** value than CFCs.
- **NON-FLAMMABLE** & environment acceptable.
- Few examples are:
  - R-123 **ODP=0.02**
    BP= -28'C
    Critical Temperature=183.68'C
  - R-22 **ODP=0.05**
    BP= -40.81'C
    Critical Temperature=96.15'C

HCFCs:

REFRIGERANT	CHEMICAL NAMES	APPLICATION
R-22	Monochlorodifluoromethane	Commercial A.C
R-123	Dichlorotrifluoroethane	chillers
R-124	Chlorotetrafluoroethane	Medium chillers
R-401A	R-22 + R-152a + R-124	Medium temp. system
R-401B	R-22 + R-152a + R-124	Transport refrigerator
R-402A	R-22 + R-125 + R-290	Ice machine
R-402B	R-22 + R-125 + R-290	Super market refrigeration

HFCs:

- Combination of **HYDROGEN+FLUORINE+CARBON.**
- **NON-FLAMMABLE, RECYCLABLE, LOW TOXICITY.**
- Minimum **EMISSION** and maximize **ENERGY-EFFICIENT.**
- Its **ODP=0** and **LOW GWP.**
- Require **POE** oil for the lubrication purpose.
- Few examples are:
  - R-410A **ODP=0**
    BP= -48.5'C
    Critical Temperature=72.8'C
  - R-134A **ODP=0**
    BP= -26.06'C
    Critical Temperature=101.08'C

HFCs:

REFRIGERANT	CHEMICAL NAMES	APPLICATION
R-23	Trifluoromethane	Low temp. refrigeration
R-134A	Tetrafluoroethane	Automative system & commercial ref.
R-404A	R-125 + R-143a + R-134a	Medium & low temp.
R-407C	R-32 + R-125 + R-134a	R 22 replacement
R-410A	R-32 + R-125	Residential A.C
R-507	Refrig. 125/143a	Commercial ref.

POE’s

- Synthetic refrigeration lubricant is used with all HFC refrigerants such as R407A and R407C.
- Used in Centrifugal, Screw, Scroll, reciprocating types Compressors.
- They provide maximum protection and lubrication at higher compressor temperatures.

Refrigerant Acids:-

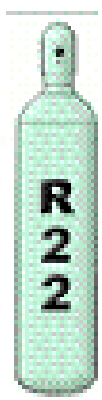
- HFC’s & POE’s are used widely.
- It causes formation of oil sludge's due to low stability.
- It leads to seize the compressors & further burn out.
- Do preventive maintenance to check inorganic acids.

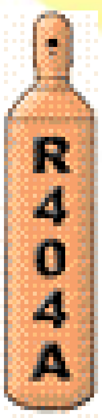
COLOR CODES OF REFRIGERANTS

- Easy recognize gas cylinder
- Different refrigerant has different color coding
- Few examples are given below:

  R-22 – LIGHT GREEN
  R-134A – LIGHT SKY BLUE
  R-404A – ORANGE

- The name label of the gases are given on the cylinder.





PROPERTIES OF REFRIGERANTS

Thermodynamic properties

- Boiling point :- It should have low boiling point.
- Freezing point :- It should have low freezing point.
- Evaporative pressure :- It should be above atmospheric pressure.
- Condensing pressure :- It should have low condensing pressure.
- Latent heat of vaporization :- It should have high latent heat of vaporization.
- Critical pressure and temperature :- It should be above the condensing pressure and temperature.
- Thermal conductivity :- It should have high thermal conductivity.
- Co-efficient of performance :- COP has direct effect on running cost of refrigeration cycle so higher the COP lower will be the running cost.

Thermodynamic Properties

Refrigerants	R 12	R 22	R 134a	R 404a	R 407a	NH_3	H_2O	CO_2
B.P (^oC)	-28.8	-40.81	-26.2	-46.4	-45	-33	100	-78.3
F.P (^oC)	-157.7	-160	-96.66	------	-------	-77.7	0	-56.6
Latent heat of vaporization (KJ/kg)	166.95	233.75	215.9	143.68	235.57	1371.2	2.25 7	571.3
Critical temp. (^oC)	112	96.15	100.95	72.07	82.2	132.4	374	30.98
Critical pressure (bar)	41.15	49.9	40.6	37.32	45.15	8.88	217. 7	77.77
Specific heat (KJ/mol.K)	.074	.057	.08754	1.03	1.520	6.91	4.18	.0374
COP(@ 35'C)		3.677	3.701	3.586	3.603			

Chemical properties

- **Toxicity** :- It should be non toxic. It should not be harmful for humans.
- **Corrosiveness** :- It should not be corrosive and should not have any effect on materials used in equipments.
- **Flammability** :- It should be inert and should not catch fire when subjected to high temperature.
- **Miscibility with oil** :- It should not react with lubrication oil.
- **Chemical stability & inertness** :- It should be chemically stable for operating ranges of temperature.

Physical properties

- Specific volume :- It should be low in vapour state.
- Viscosity :- It should have low viscosity.
- Leakage Detection :- It should have less tendency to leak & if it leaking it should have a pungent smell so that the leakage can be detected easily.

Refrigerants	R 12	R 22	R 134a	R 404a	R 407a	NH_3	H_2O	CO_2
Viscosity(c p)	.1076	.1256	.012	.001	.1	.276	1	.137

Other properties

- Handling & Maintenance :- It should be easy & safe to handle.
- Cost & Availability :- It should be readily available at LOW cost.
- Performance of the System:- It should have high COP & LOW power requirement.

OZONE DEPLETION:

- Ozone layer gets depleted by the action of CFCs.

- The greatest concentration of ozone are found from 12 km to 50 km above the earth forming a layer in the stratosphere which is called the ozone layer.

- Few examples are given in details:
  - R-12 **ODP** is “1”
  - R-22 **ODP** is “0.05”
  - R-134a **ODP** is “0”

CFC + IRRADIATED WITH UV RAYS → FREE CHLORINE

Cl + OZONE → ClO + OXYGEN

ClO + O → Cl + OXYGEN

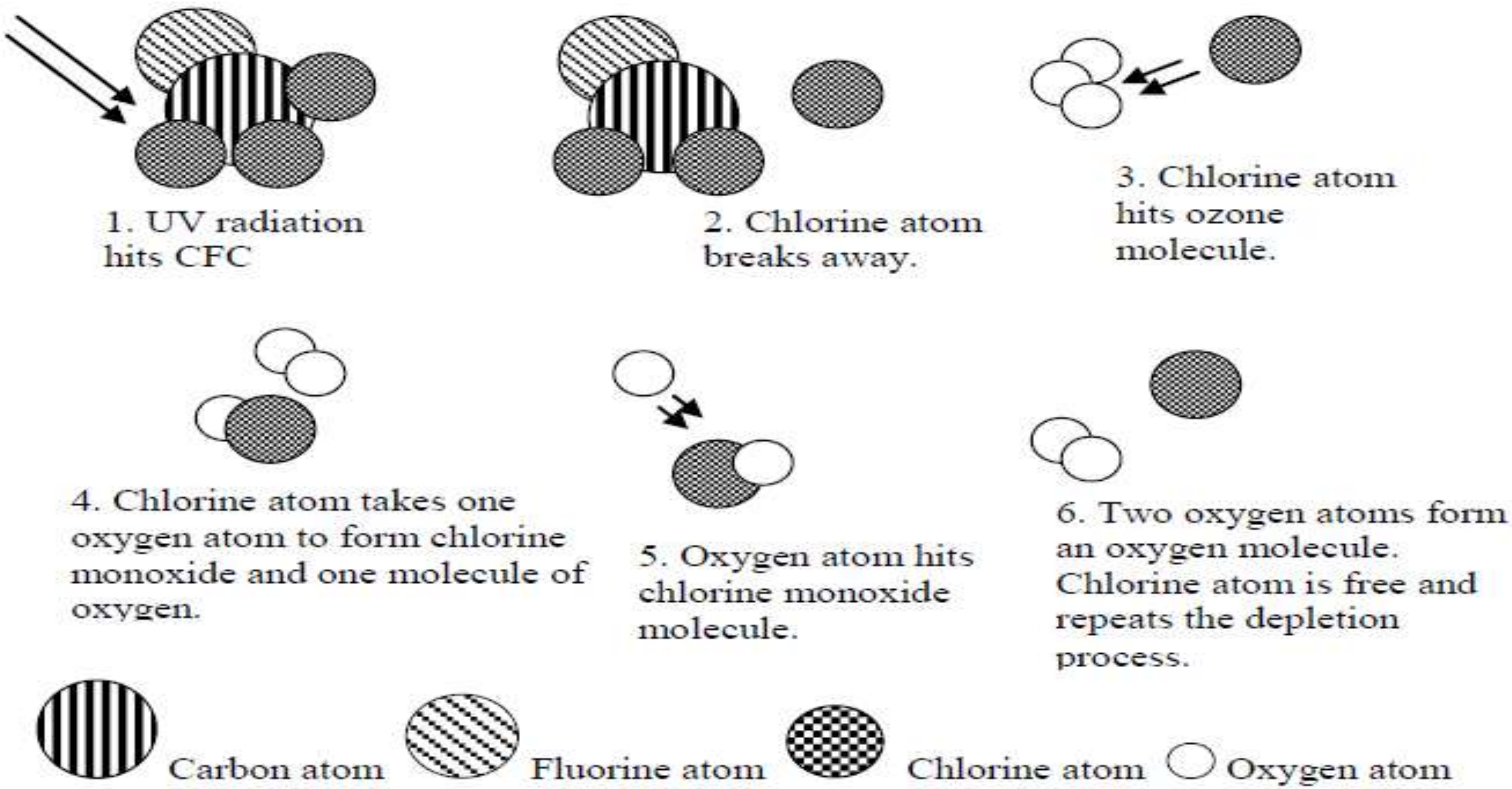


Figure 4.4. Graphical Representation of the Reactions Involved in Ozone Depletion

GLOBAL WARMING POTENTIAL

- Measurement of global warming
- Done in relation with CO2,where co2 has GWP 1
- Lower the value of GWP better the refrigerant
- Few examples are given below:
  - R-11 - High chlorine content
    GWP is 4000
  - R-22 - Low chlorine content
    GWP is 1700
  - R-134A- No chlorine content
    GWP is 1300

MONTREAL PROTOCOL :-

=> SIGNED IN 1987 UNDER THE 'UNEP', AFTER MUCH DISCUSSIONS

=> MORE THAN 170 COUNTRIES HAVE RATIFIED

=> INDIA RATIFIED ON SEPT 17,1992

=> ONE OF MOST SUCCESSFUL EXAMPLE OF INTERNATIONAL COOPERATION IN UN HISTORY

ozone depleting substance	developed countries	developing countries
CFCs	phased out end of 1995	total phase out by 2010
halons	phased out end of 1993	total phase out by 2010
HCFCs	total phase out by 2020	total phase out by 2040

TEWI

- Total Equivalent Warming Impact
- TEWI = direct emission (c)+ indirect (e).
- The refrigerants have been rated according to their LCCP(Life cycle climate performance).
- LCCP= TEWI + GWP(ID)+ GWP(D).

CONCLUSION

- Don't treat the today's refrigerants with yesterday's techniques.
- CFC's replaced by refrigerants blends.
- R & D of the refrigerants is in the field of environmental acceptability.
- TEWI, the factor used to decide the overall capability of a refrigerant.

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