

A brief review on Development of Refrigerants and their Applications

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Abstract - The refrigerator and air conditioner plays an important role in domestic and industrial field. They have a thoughtful effect on our daily lives. They also contribute to the world's major environmental issues, such as depletion of the ozone layer and global warming. The development of refrigerants is in various stages from the day of its introduction to its recent stage of development is really interesting and it depends on various factors like its harmlessness, ability to last and environmental issues. In this study, we will see various generations of refrigerants from the first day of its use to this new generation of refrigerants which are environment friendly and can be used at the place of some standard refrigerants which are harmful for environment along with their chemical name, normal boiling point, applications, ODP i.e. ozone depletion potential, GWP i.e. global warming potential and their price per kg.

Key Words: Air-conditioning, GWP, ODP, Global warming, Ozone depletion, etc.

1. INTRODUCTION

Refrigerators are an old technology that started a long time ago. Refrigeration involves removing heat from a closed space or object to maintain a lower temperature than the surrounding environment. Nowadays refrigeration has vast applications in various fields like domestic and industrial but in traditional days there were different methods like salting, drying, watering. It has been research out that addition of chemicals such as sodium nitrate or potassium nitrate to water has results in temperature drop.

Refrigerators are substances that are used in refrigeration systems. They get evaporated by taking up heat from the space which is to be cooled, thus producing a cooling effect. There are many reasons such as harmlessness, ability to last and environmental issues, etc behind the history of development of the refrigerants. These are some major trigger for this development.

Knowing the particular thing throughout or having complete knowledge about particular thing makes oneself able and efficient to apply that knowledge for the required applications. In this paper we have briefly described the different types of refrigerators and their important specifications such as its R-number, chemical formula, standard boiling point, application, GWP, ODP, and their kilogram value on the market.. Development stages of refrigerants in brief are given below:

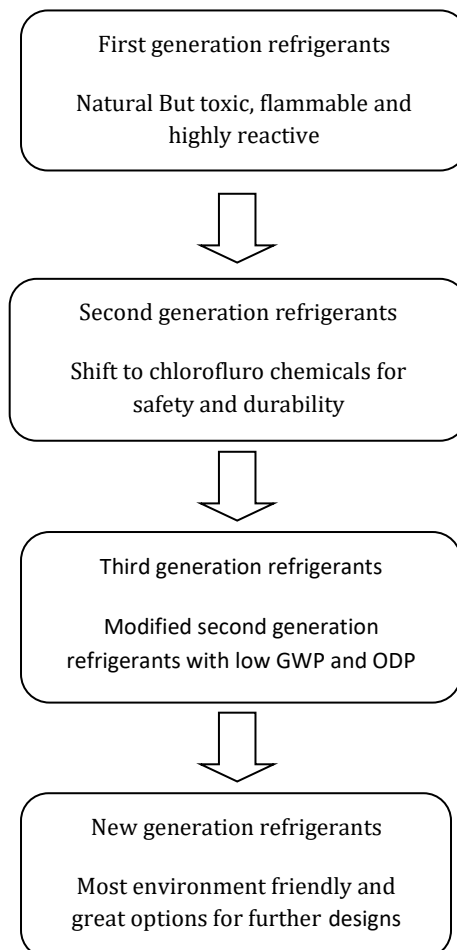


Fig-1: Development stages of refrigerants

2. FIRST GENERATION REFRIGERANTS

First generation refrigerants were used in the 19th century which was just the beginning of the mechanical refrigeration process. Most of the first generation refrigerants are natural like water, carbon dioxide, etc. Water was one of the most used refrigerants at that time.

We can observe from the table first generation refrigerant has very less number of ODP and GWP which means they are not harmful to the environment but with increased development and requirement they failed to meet desired refrigeration effect and hence the second generation of refrigerants came into picture.

Table -1: First generation refrigerants and their applications

First generation refrigerants and their applications								
Sr. no	Name	R-number	Chemical formula	NBP (°C)	Applications	ODP	GWP	Price/kg
1	Carbon dioxide	R-744	CO ₂	-78.46	• Food preservation	0	1	₹ 35
2	Ammonia	R-717	NH ₃	-33.3	• Thermal storage system • HVAC chillers • Heat pump systems	0	0	₹ 65
3	Sulphur dioxide	R-764	SO ₂	-10.0	• Cold storage plants	0	0	₹ 150
4	Ethyl ether	R-610	(C ₂ H ₅) ₂ O	35	• Generally used in refrigerants blends	0	0	₹ 1000
5	Dimethyl ether	R-170	C ₂ H ₆ O	-25	• Generally used in refrigerants blends	0	0	₹ 180
6	Methyl chloride	R-40	CH ₃ CL	-24.2	• Refrigerant of choice in some type of refrigerator and air conditioners	0.02	16	₹ 1200

Carbon dioxide was the effectively used refrigerant for the long time but it is the major contributor to the ozone layer depletion. Refrigeration is not only reason behind its contribution to the ozone depletion but still due to this it was totally supplanted with CFC's. Ethyle eather was also considered as most decent refrigerant due to its less weight and its fluidity at normal temperature. Though all first generation refrigerants were environment friendly, refrigerants were flammable, toxic or both and some were also highly reactive so, using those results in hazardous accidents most of the time. Some first generation refrigerants and their characteristics are discussed below:

second generation refrigerants. CFC is non-toxic, non-flammable as well as less reactive. It is very stable that only UV rays can break it and it suitable for variety of application because of its less reactiveness i.e. it doesn't react with anything.

3. SECOND GENERATION REFRIGERANTS

Key feature of second generation refrigerant is switching to chlorofluoro chemicals for safety and durability as we have seen the scarcity of safety and durability in first generation refrigerants. Chlorofluoro carbons and its variation in hydrocarbon have great impact on flammability and toxicity of refrigerant. Thus CFC's are

Table-2: Second generation refrigerants

Second generation refrigerants and their applications								
Sr. no	Name	R-number	Chemical formula	NBP (°C)	Applications	ODP	GWP	Price/kg
1	Trichloro fluoro methane	R-11	CCL ₃ F	23.71	<ul style="list-style-type: none"> • Considered as safe refrigerant • Used in air conditioning of small buildings, factories, stores, etc. 	1	4000	₹ 550
2	Dichloro difluoro methane	R-12	CCL ₂ F ₂	-29.75	<ul style="list-style-type: none"> • Domestic refrigerators and freezers • Water coolers • Ice makers • Liquid chillers • Transport refrigeration 	1	8500	₹ 550
3	Chloro trifluoro methane	R-13	C ₄₈ H ₄₈ O ₂₀	-81.3	<ul style="list-style-type: none"> • Low temperature refrigeration • Flash freezing and cryogenic processes 	1	11700	₹ 460
4	Chloro difluoro methane	R-22	CHCLF ₂	-40.8	<ul style="list-style-type: none"> • Air conditioners • Heat pumps • AC system • Mini splits 	0.055	1700	₹ 650
5	R-22	R-502	C ₃ HCL ₂ F ₇	-45.3	<ul style="list-style-type: none"> • Low temperature and transport refrigeration 	0.33	5600	₹ 275
6	R-115	R-502	-	-45.3	<ul style="list-style-type: none"> • Low temperature and transport refrigeration 	0.33	5600	₹ 310

Some of the second generation refrigerants are R-11, R-12, etc. R-11 is really a great refrigerant which is mostly used for refrigeration and air conditioning applications. It is also not toxic, flammable and explosive. The only problem associated with second generation refrigerants is that, they are major contributors to the ozone depletion and global warming (We can observe from the Table-2) so, this problem created the need of third generation refrigerants, which are modified second generation refrigerants.

4. THIRD GENERATION REFRIGERANTS

Third generation refrigerants are the refrigerants with the aim of reducing the global warming and ozone depletion potential. This is the new group of refrigerants based on hydrochlorofluoro (HFO) and hydrofluoro carbon (HFC) chemical. These re modified second generation refrigerants which protect Another new class of fluorocarbon refrigerators called hydrofluoro olefin (HFO) with reduced GWP capacity has been improved. Their main advantage, apart from their low GWP, is that they can be used with existing refrigeration system designs. This is good for the industry and their customers, but it is still a fluorine gas.

Table-3: Third generation refrigerants and their applications

Third generation refrigerants and their applications								
Sr. no	Name	R-number	Chemical formula	NBP (°C)	Applications	ODP	GWP	Price/kg
1	Difluoromet hane	R-32	CH ₂ F ₂	51.65	<ul style="list-style-type: none"> • Low temp. refrigeration • Replacement of 410a 	0	580	₹ 45
2	tetrafluoroet hane	R-134a	CF ₃ CH ₂ f	-26.07	<ul style="list-style-type: none"> • Automotive air conditioning • Medium temperature refrigeration • Replacement of R12 	0	1300	₹ 420
3	Pseudo azeotropic mixed Refrigerant	R-404a	R125+R143A+R134A	-46.6	<ul style="list-style-type: none"> • Low and medium temperature replacement 	0	3800	₹ 400
4	Nonazeotropic mixed refrigerant	R-407c	R32+R125+R134a	-43.8	<ul style="list-style-type: none"> • Commercial air conditioning • Replacement of R-22 	0	1600	₹ 350
5	Near azeotropic refrigerator	R-410a	R32+R125	-51.6	<ul style="list-style-type: none"> • Air conditioning 	0	1900	₹ 365

Nowadays there is continuous development and innovation in every sector of industry and majorly in refrigeration sector. With this continuous development we are continuously harming our environment and unfortunately pushing ourselves in major problem. In such conditions third generation refrigerants can be great alternatives. Government is also trying to encourage developers for low impact refrigeration and use of third generation refrigerants. The third generation of refrigerators incorporates chemical groups, such as hydro-fluoro-carbons (HFCs) that do not damage the ozone layer as it was a natural hazard at the time. However, as the effects of refrigeration leaks on global warming and climate change have been evident, next-generation refrigerators are needed.

5. NEW GENERATION REFRIGERANTS

This new generation refrigerants are nothing but the more environment concern. This group of refrigerants is transitional refrigerants which can be called as HFC/HCFC partly chlorinated refrigerants for having long term refrigerants. Some second generation refrigerants are on their way to get shut for the use in industries due to environment concern so, in such situation this new generation refrigerants looks like great option for future they have very low ODP and GWP. They are classified as low global warming potential and HFC/HCFC blend.

Next generation refrigerants and their applications								
Sr. no	Name	R-number	Chemical formula	NBP (°C)	Applications	ODP	GWP	Price/kg
1	Tetrafluoropropene	R-1234yf	C ₃ H ₂ F ₄	-30	<ul style="list-style-type: none"> In automotive industries As a replacement of R-134a 	0	Less than 1	₹ 850
2	Tetrafluoroprop-1-ene	R-1234ze	C ₃ F ₄ H ₂	-18.97	<ul style="list-style-type: none"> Replacement of R-134a Medium temperature applications 	0	7	₹ 360
3	hydrofluoroolefin	R-449A	R32+R125+R134A+R1234YF	-46	<ul style="list-style-type: none"> Low and medium temperature refrigeration Replacement of R404a 	0	1397	₹ 3500
4	Opteon	R-513	-	-29.58	<ul style="list-style-type: none"> Replacement for R-134a Centrifugal chillers Direct expansion chillers Ice rink system 	0	573	₹ 10000

Table-4: Low global warming potential refrigerants

Table-5: HFC/HCFC blend refrigerants

Next generation refrigerants and their applications								
Sr. no	Name	R-number	Chemical formula	NBP (°C)	Applications	ODP	GWP	Price/kg
1	HCF Blend refrigerants	R-407F	R125+R32+R134A	-39.7	<ul style="list-style-type: none"> Replacement for R-22 Medium temperature refrigeration 	0	1628	₹ 380
2	HCF Blend refrigerants	R-401B	R22+R152a+R124	-55.4	<ul style="list-style-type: none"> Replacement for R-12 Transport refrigeration Dehumidifiers 	0.036	1288	₹ 500
3	HCF Blend refrigerants	R-422D	R125+R134a+R22	-44.7	<ul style="list-style-type: none"> R-22 in low- and medium-temperature commercial refrigeration systems 	0	2729	₹ 800
4	HCF Blend refrigerants	R-409A	R22+R124+R142B	-27.4	<ul style="list-style-type: none"> Walk in coolers Beverage dispensers 	0.046	1909	₹ 6500

For this new generation refrigerants we are again coming back to the first generation refrigerants and trying to use the optimum in order to save our environment. Low global warming refrigerants are proved to be great alternatives for second and third generation refrigerants which have high GWP. These modern refrigerants are advantageous not only in the sense of finance but also for safe environment. The refrigeration system of future will be based on further research on refrigerants, regulation changes and optimum use of natural refrigerants. There will be no ideal refrigerant but it must be less harmful in every aspect. Further we will see the desirable properties of refrigerants.

6. DESIRABLE PROPERTIES OF REFRIGERANTS

Every refrigerant should have some properties for its proper appropriate functioning of design system of particular application. These desirable properties are as follows:

- Low boiling point
- Low freezing point
- Positive evaporative and condenser pressure
- Critical temperature must be higher than the condenser temperature
- High latent heat of refrigeration
- Less toxicity, flammability and corrosiveness
- Chemical stability
- High thermal conductivity
- Low viscosity
- Low odor and leak tendency

7. CONCLUSIONS

In this study we reviewed the construction of refrigerators in four phases

- First-generation refrigerators
- Second-generation refrigerators
- Third-generation refrigerators
- New generation refrigerators

By their comparison in various factors such as applications, global warming power, ozone depletion power and price. The development of a new generation refrigerator comes with benefits and key points like these

1. Next-generation refrigerators have zero ODP and lower GWP.
2. R1234ze and R1234yf are items worth replacing R134a.
3. HFC / HCFC Blends R-407F and R-422D are non-ODP spaces instead of R-22 and R-409A instead of R12.

With the increasing threat of ozone layer depletion and global warming our all development activities whether in refrigeration field or any field should have base of natural things which will not harm our environment. Our government is also coming forward to encourage this by banning some hazardous refrigerants, keeping limits of pollutants in the exhaust of chimneys of industries, encouraging use of electric vehicles, etc. Everyone should take a step forward to save ourselves by saving our nature.

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