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Alternative To Hcfc/Cfc Refigerants – R 134a, Its Production And Properties

[1] Mr.B.Sai Venkata Krishna, [2] Dr.A.Raj Kumar
[1]Assistant professor , *[2]Associate Professor*
[1]Department of Mechanical Engineering , Megha Institute of Engineering and Technology for Women.
[2]Department of Mechanical Engineering , Guru Nanak Institutions Technical Campus

Abstract*:* This paper will make an attempt to give necessary information regarding to alternative refrigerants being used in operating refrigerating facilities in the area of moderately low temperatures. There have been considered in detail alternative one component refrigerants and service blends of HCFC,CFC groups for refrigerating systems and air conditioning systems , refrigerating transport , their compatibility with refrigerating oils, metals , plastics and elastomers. The operating pressures of these refrigerants are made to be convenient and appropriate for the design, construction and economic operation also. Now a day's most alternative refrigerant R-134a is widely applied as a substitute to some of the refrigerants. The manufacturing process of this refrigerant is explained in detail in this paper and their property, applications, is discussed.

Key Words: R 134a refrigerant, production, properties, applications.

1. INTRODUCTION:

Refrigeration is the process of removing heat from an enclosed space, or from a substance, and moving it to a place where it is unobjectionable. The primary purpose of refrigeration is lowering the temperature of the enclosed space or substance and then maintaining that lower temperature.

Methods of refrigeration can be classified as non-cyclic and cyclic, as said by Ari[1],

Non-cyclic refrigeration: In these methods, refrigeration can be accomplished by melting ice or by subliming ice dry. These methods are used for small-scale refrigeration such as in laboratories and workshops, or in portable coolers.

***Cyclic refrigeration*:** This consists of a refrigeration cycle, where heat is removed from a low-temperature space or source and rejected to a high-temperature sink with the help of external work, and its inverse, the thermodynamic power cycle. In the power cycle, heat is supplied from a high-temperature source to the engine, part of the heat being used to produce work and the rest being rejected to a low-temperature sinks. This satisfies the second law of thermodynamics.The most common types of refrigeration systems use the reverse-Rankine vapor compression refrigeration cycle although absorption heat pumps are used in a minority of applications.

A **refrigerant** is a compound used in a heat cycle that undergoes a phase change from a gas to a liquid and back which effects the cooling and heating on the coils side. Since it was discovered in the 1980s that the most widely used refrigerants were major causes of ozone depletion, a worldwide phase out of ozone-depleting refrigerants has been undertaken. These are being replaced with "ozone-friendly" refrigerants, according to Araki [2].

Refrigerants by class:

Refrigerants may be divided into three classes according to substances their manner of absorption or extraction of heat from the to be refrigerated:

Class 1: This class includes refrigerants that cool by phase change (typically boiling), using the refrigerant's latent heat.

Class 2: These refrigerants cool by temperature change or 'sensible heat', the quantity of heat being the specific heat capacity vs the temperature change. They are air, calcium chloride brine, sodium chloride brine, alcohol, and similar nonfreezing solutions. The purpose of Class 2 refrigerants is to receive a reduction of temperature from Class 1 refrigerants and convey this lower temperature to the area to be air-conditioned.

Class 3: This group consists of solutions that contain absorbed vapors of liquefiable agents or refrigerating media. These solutions function by nature of their ability to carry liquefiable vapors, which produce a cooling effect by the absorption of their heat of solution.

Azeotropes**:**A mixture of two or more substances whose liquid and gaseous forms have the same composition (at a certain pressure); the substances cannot be separated by normal distillation, those are azeotropes, as said by A.Kundu [3].

Zeotropes: A zeotrope is a liquid mixture that obeys Raoult's law. It shows no maximum or minimum when vapor pressure is plotted against the composition at a constant temperature.

2. NEED FOR ALTERNATIVE REFRIGERANT:

Measures performed by the government of many countries on fulfillment of resolutions of the Vienna Convention (1985), Montreal protocol (1987) and following amendments to them allowed to considerably reduce production and consumption of chlorofluorocarbons (CFC). Thus, if in 1986 total production of Freon's in the world constituted 1.123 million tons, in 1994 production and consumption of CFC more than 50 % decreased. However, in the countries of European Union there is still used up to 110 thousand tons of CFC in the operating refrigeration equipment.

There exist so many refrigerants that sometimes it is difficult for a customer to choose the required refrigerant for separate operating conditions according to S.K.Kalla[4].For substitution of R12, main world producers of chemical products recommend R134a, including transitional ones containing in their composition R22, - R401A, R401B, R401C, R409A, and also natural refrigerants R600a, R290, propane - butane blends and R717.

R134a is widely used all over the world as a basic substitute for R12 for the refrigeration equipment operating in the average temperature range. R134a is used in automobile air-conditioners, domestic refrigerators, commercial average temperature equipment, industrial facilities, air-conditioning systems of buildings and production areas, as well on the refrigeration transport. Energy data of R134a are lower than those of R12; for operation with R134a there are required expensive synthetic oils characteristic for their high hygroscopicity; the refrigerant has high GWP parameter.

In the USA and the countries of Western Europe it constitutes 10-15 thousand tons per year. Production capacities after R134a output in the industrially developed countries was estimated as 170 thousand tons in 1997 with the world demand equal to 85 thousand tons. Service blends R401A, R401B, R401C, R409A of HCFC group are recommended to use for retrofit in the operating high-, average-, low-temperature refrigeration systems. They are not mixed with mineral oils (except R409A) and intended for operation with synthetic oils.

In domestic refrigeration appliances and commercial refrigeration equipment of the countries of Western Europe, the so-called "natural" refrigerants R290, R600a and the blends on their base are more widely used. At present time, consumption of hydrocarbons constitutes about 0.07 kg per 1 kwt of cold-productivity and there is observed the tendency to its further decrease. These are ecologically pure refrigerants resolvable with mineral oils and as to their energy data they are comparable with R12. At the same time there should be inserted some alterations into the compressor structure. Refrigerants are fire risky and explosive; therefore, safety rules should be strictly observed.

For retrofit of R502 in the operating refrigeration systems it is recommended to use refrigeration blends R402B, R402A, R404A, R507 and R408A. Thermodynamic properties of R402A and R402B are similar to properties of R502. Refrigerants are resolvable with synthetic oils. Selection of the type of refrigeration blend is dictated by concrete using and characteristic conditions of the refrigeration equipment being used.

R404A refrigerant is supposed to be used for retrofit of the operating average- and low-temperature equipment operating on R502 and R22, as well as for charging of the new refrigeration equipment. It is compatible with synthetic oils, is related to HFC group. It is perspective for using in the sphere of low temperatures on the vessel refrigeration transport.

R507 refrigerant has been developed for retrofit of the low-temperature refrigeration systems operating on R502, as to its characteristics it is close to R502, resolvable in synthetic oils, is related to HFC group.

Using of R22 refrigerant, which has properly shown itself in the air-conditioning systems, commercial and transport refrigeration facilities, as well as in air-cooling systems and heat pumps, does not comply with long-term perspectives of development of the refrigeration equipment in connection with the resolution of the Montreal protocol. Moreover, as to its energy data R22 is inferior to R12 in average-temperature refrigeration facilities, and therefore does not meet the world tendencies of increasing of energy effectiveness of the equipment and statements of the Convention (Kyoto, 1997) on restriction of emission of hotbed gases.

At present time production of R22 is n the state of considerable excess of offer over demand. In particular, capacities on R22 production in the Western Europe are estimated as 150 thousand per year, and consumption - 100 thousand per year. In future there will be traced the tendency to reduction of its production. For substitution of R22 there are recommended such refrigerants as R404A, R407C, R410A, R407A, R290 and R717.

R410A refrigerant serves for substitution of R22 in the new high pressure air-conditioning systems; at that there are required structural alterations in the compressor and heat-exchangers. It is compatible in synthetic oils. In future R410A can serve as an alternative refrigerant for substitution of R22, because it has high specific volumetric cold-productivity and low critical temperature.

R407C refrigerant according to its energy effectiveness is close to R22 and is considered as optimal alternative to R22. At present it is widely used in the air-conditioning systems. There's not necessity to insert considerable changes into the refrigeration system.

During operation of zoetrope blends there appeared a number of problems. It is "temperature glide", changing of the blend composition in case of leakage of one of the components, immiscibility of a number of refrigerants with mineral oils, vapor-liquid separation of zoetrope blends in each of the system elements: compressor, heat-exchangers, condenser and evaporator; different resolvability of the blend components in the refrigeration oil.

At present time, 70 % of refrigeration facilities for vegetable- and fruit-storehouses operate on R717, 60% - in the meat industry, 50 % - in the confectionery production; 80 % - in the production of beer and beverages.

3. PRODUCTION OF R 134a:

R134a is also known as Tetrafluoroethane (CF_3CH_2F) from the family of HFC refrigerant. With the discovery of the damaging effect of CFCs and HCFCs refrigerants to the ozone layer, the HFC family of refrigerant has been widely used as their replacement.

It is now being used as a replacement for R-12 CFC refrigerant in the area of centrifugal, rotary screw, scroll and reciprocating compressors. It is safe for normal handling as it is non-toxic, non-flammable and non-corrosive. Currently it is also being widely used in the air conditioning system in newer automotive vehicles. The manufacturing industries use it in plastic foam blowing. Pharmaceuticals industries use it as a propellant. It exists in gas form when expose to the environment as the boiling temperature is -14.9°F or -26.1°C. This refrigerant is not 100% compatible with the lubricants and mineral-based refrigerant currently used in R-12. Design changes to the condenser and evaporator need to be done to use this refrigerant. The use of smaller hoses and

30% increase in control pressure regulations also have to be done to the system.Basic production block diagram is shown in Fig.1

4. PROCESS DESCRIPTION:

The BFD and two PFDs show a process to produce R-134a1. Liquid hydrogen fluoride (HF) enters the system at 25°C and 2 atm in Stream 1. It is pumped up to 3 atm by P-201 before being mixed with a recycle stream (Stream 16) consisting of HF, R-133a (CF3CH2Cl), R-134a (CF3CH2F), and trichloroethylene (TCE). The mixed stream (Stream 3) then enters H-201 where it is heated to 400°C before being fed to the R-134a reactor R-201. This isothermal plug-flow reactor converts 99.3% of the R-133a to R134a. The heat of reaction is removed from the process by means of a Dowtherm A cooling loop.As shown in Fig 2.

The product stream of R-201 (Stream 5) is then mixed with a feed of TCE (Stream 8). The mixed stream (Stream 9) is then fed through E-203 where it is cooled to 290°C. R-202 next converts HF and TCE to R-133a and hydrochloric acid (HCl). R-202 is quite similar in operation to R-201, including the use of a Dowtherm loop to remove the heat of reaction.

Stream 10 leaves R-202 and is then sent to E-205 where it is cooled to 30°C to reduce the costs associated with C-201. C-201 compresses the stream adiabatically to 9.8 atm, with a temperature increase to 595°C. The stream is then cooled to 30°C by E-206.

The cooled stream (Stream 13) is then fed to T-201, the first of three distillation towers. T-201 operates at 9 atm, with the distillate temperature being 0.1°C and the bottoms temperature being 88.5°C. The reboiler uses low-pressure steam, with the bottom stream being recycled and mixed with the HF feed.

The condenser uses a refrigerant mixture produced on site and processed in a refrigeration loop (not shown). In the loop, the refrigerant mixture removes heat from the process in the condensers of the towers. It is then compressed, cooled, and throttled back to the initial pressure.

The distillate (Stream 14) from T-201 consists mainly of R-134a, HCl, R-125, R-143a, and R-23. This stream is next compressed in C-202 to 20 atm before being fed into T-202. Here, R134a and trace amounts of HCFC-1133 are removed from the rest of the refrigerants and the HCl.

The 99.99% pure R-134a bottom stream (Stream 20) is then fed to a zeolite column (A-201 A/B) where the toxic HCFC-1133 is adsorbed. A-201 A/B is two zeolite columns in parallel. This allows for continuous operation, with one operating while the other is being regenerated. E-207 then cools the R-134a to 40°C before P-205 pumps the stream to 28 atm (Stream 23) for storage.

The distillate from T-202 (Stream 19) is then sent to T-203 where HCl and R-23 are removed from the refrigerant mixture. The refrigerant mixture obtained as the bottoms from T-203 (Stream 25) is cooled in E-208 to 15°C and pumped to 25 atm in P-206. It is then stored.as shown in Fig 3.

The distillate of T-203 (Stream 24) contains mainly HCl and R-23. The HCl is absorbed into water in T-204. The result is a stream of HCl in water that is 99.99% pure HCl at a concentration of 35.12 weight percent (Stream 30) which is stored. The unwanted R-23 stream (Stream 29) is sent to the waste incineration facility.

Necessary Information and Simulation Hints

R-134a is produced by the following series of reactions:

3HF+TCE (HC_2Cl_3) ----→ R-133a ($H_2C_2ClF_3$) + 2HCl

R-133a ($H_2C_2ClF_3$) + HF ----→ R-134a ($H_2C_2F_4$) + HCl.

These reactions are based on limited data found in US Patent 5,243,105. It was determined that the activation energies for the two main reactions were as follows:

167 kJ/mol for TCE to R-133a

237 kJ/mol for R-133a to R-134a

Using data from the patent the rate constants were determined from the following equations:

-rA = k CA CB

t =*AA rdX C* 0

These were found to be:

k = 10.94 l/(mol s) for R-133a to R-134a

k = 11.82 l/(mol s) for TCE to R-133a

And the pre exponential factors were found to be:

A = 6.5´1018 l/(mol s) for TCE to R-133a

A = 5.5´1020 l/(mol s) for R-133a to R-134a

These values account for the two primary reactions for the process. However, the patent demonstrated that side reactions also occur in the R-134a reactor. This has been accounted for by adding a component separator and a small feed stream to the simulation immediately following this reactor, specified to correlate with the patent.

A major difficulty in simulating the process outlined in the patent is the lack of available data for R-133a. The simulation is based on R-133a as a user-added component, with all properties based on the normal boiling point2 and the UNIFAC group contribution method. All simulations were run using ideal vapor pressure for *K* values and latent heat for enthalpy except for the HCl absorber (T-204). In T-204, PPAQ (partial pressure aqueous) was used for the *K* values which automatically accesses the library heats of solution for enthalpies.

The nomenclature for refrigerants is as follows. For saturated hydrocarbon refrigerants, the nomenclature is R *xyz*a . The a denotes a specific stereoisomer. The *x* is the number of carbons minus one (which means *x* = 0 for old, single-carbon refrigerants). The *y* is the number of hydrogens plus one, and the *z* is the number of fluorine's. The remaining number of atoms needed to saturate the molecule is chlorines.

Therefore, R-134a has two carbons, 2 hydrogen's, 4 fluorine's, and no chlorines. R-133a has two carbons, 1 hydrogen, 1 fluorine, and 1 chlorine. R-125 has two carbons, 1 hydrogen, and 5 fluorine's.

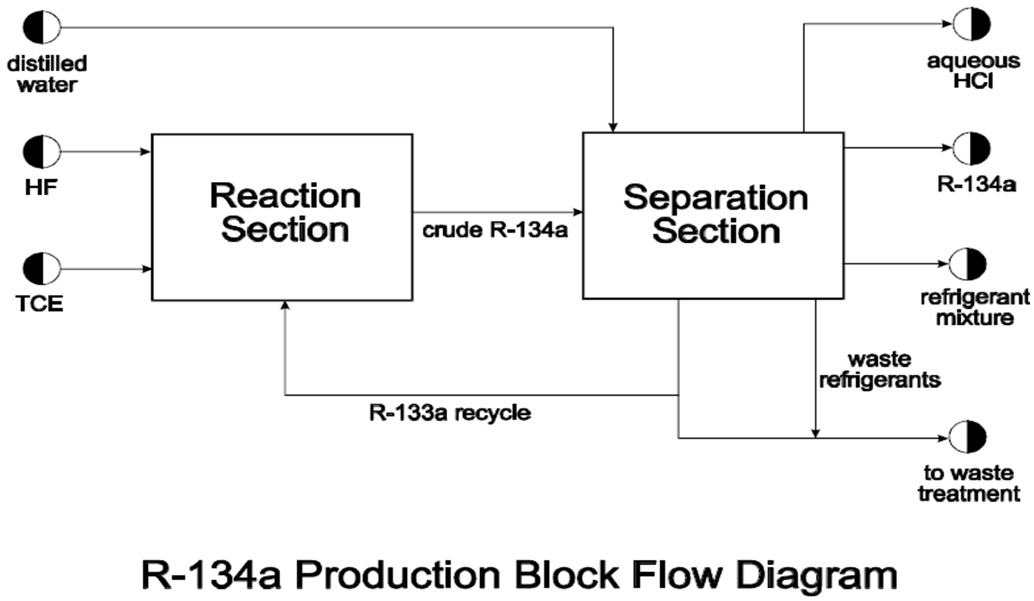


Fig.1: Block Diagram Showing Production of R 134a

5. EQUIPMENT DESCRIPTION:

P-201 A/B HF Pumps
H-201 Fired Heater
P-202 A/B TCE Pumps
E-201 TCE Vaporizer
R-201 R-134a Reactor
P-203 A/B R-134a Reactor Dowtherm Pump
E-202 R-134a Reactor Dowtherm Cooler
E-203 R-133a Reactor pre-cooler
R-202 R-133a Reactor
P-204 A/B R-133a Reactor Dowtherm Pump
E-204 R-133a Reactor Dowtherm Cooler
E-205 Reactor Effluent Cooler
C-201 Compressor
E-206 Reactor Effluent Cooler
T-201 TCE Recycle Tower
E-209 TCE Tower Condenser
V-201 TCE Tower Reflux Vessel
P-207 A/B TCE Tower Reflux Pumps
E-210 TCE Tower Reboiler
C-202 Compressor
T-202 R-134a Tower
E-211 R-134a Tower Condenser
V-202 R-134a Tower Reflux Vessel
P-208 A/B R-134a Tower Reflux Pumps
E-212 R-134a Tower Reboiler
A-201 HCFC 1122 Absorber
T-203 Mixed Refrigerants Tower
E-213 Mixed Refrigerants Tower Condenser
V-203 Mixed Refrigerants Tower Reflux Vessel
P-209 A/B Mixed Refrigerants Tower Reflux Pumps
E-214 Mixed Refrigerants Tower Reboiler
E-207 R-134a Cooler
P-205 A/B R-134a Pumps
E-208 Refrigerant Mixture Cooler
P-206 A/B Refrigerant Mixture Pumps
T-204 HCl Absorber

6. PROPERTIES OF R-134a:

1. Molecular weight of this refrigerant is 102.03 gm/mole.
2. In its solid phase its melting point at 1.013bar is -101^{0}C.
3. At its liquid phase liquid density at 1.013bar and 25^{0}C is 1206kg/m^3.
4. Boiling point at 1.013bar is -26.6^0 C.
5. Latent heat of vaporization at 1.013bar at boiling point is 215.9 KJ/kg.
6. Vapor pressure at 20^0 C is 5.7bar.
7. Its critical temperature is 100.9^{0}C.
8. And its critical pressure is 40.6bar.
9. Critical density is 512 kg/m^3.
10. At its gaseous state, gas density (1.013bar of boiling point) is 5.28kg/m^3.
11. Compressibility factor (Z)(1.013bar and 15^{0}C) is 1.
12. Specific gravity (air=1)(1.013bar and 15^{0}C) is 3.25
13. Specific volume (1.013bar and 15^{0}C) is 0.235m3/kg.
14. Heat capacity at constant pressure (Cp)(1.013bar and 25^{0}C) is 0.087 kJ/(mol)
15. Solubility in water (1bar and 25^{0}C) is 0.21 vol/vol.

Fig.2: Block Diagram Showing Production of R 134a(Reaction Section)

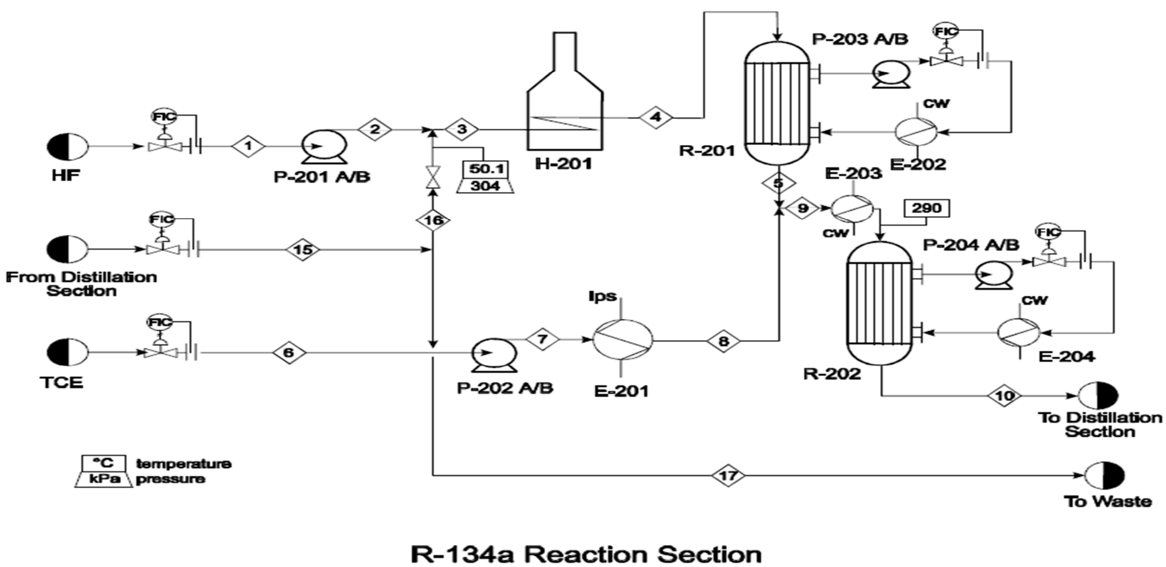
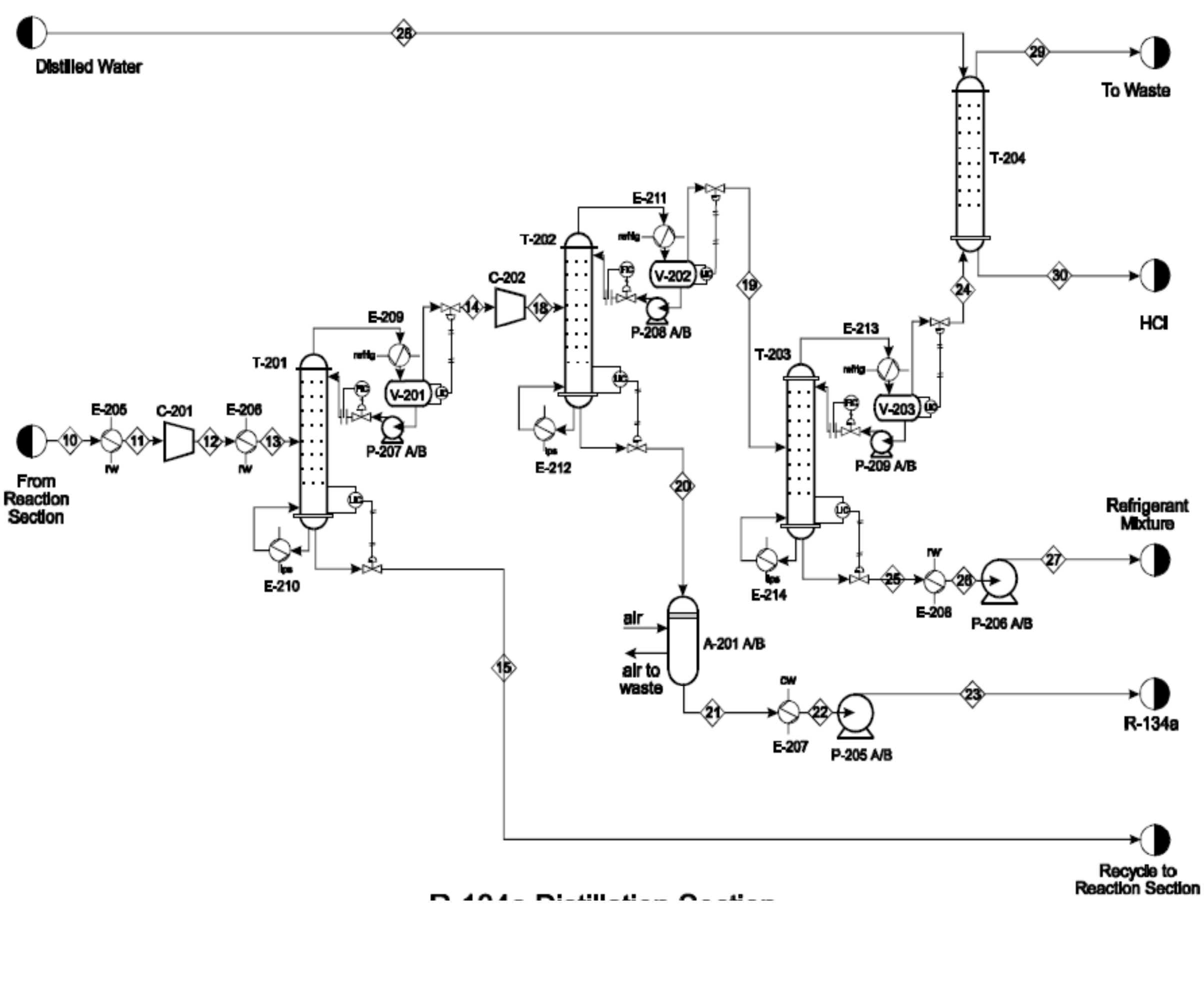


Fig.3: Block Diagram Showing Production of R 134a(Distillation Section)



7. APPLICATIONS of R-134a:

1, 1, 1, 2-Tetrafluoroethane is an inert gas used primarily as a "high-temperature" refrigerant for domestic refrigeration and automobile air conditioners. Other uses include plastic foam blowing, as a cleaning solvent and as a propellant for the delivery of pharmaceuticals (e.g. bronchodilators), gas dusters, and in air driers, for removing the moisture from compressed air. Moisture present in compressed air has a harmful effect on pneumatic systems. Tetrafluoroethane has also been used to cool computers in some over clocking attempts. It is also commonly used as a propellant for air soft air guns.

Recently, tetrafluoroethane has been subject to use restrictions due to its theorized contribution to climate change. In the EU, it is banned as from 2011 in all new cars. SAE (International, an auto engineers association)[5] has proposed tetrafluoroethane (HFC-134a) to be best replaced by a new fluorochemical refrigerant HFO-1234yf (CF3CF=CH2) in automobile air-conditioning systems. California may prohibit the sale of canned tetrafluoroethane to individuals to avoid non-professional recharge of air conditioners.

8.CONCLUSION:

Further reductions in contributions to climate change can be anticipated during the CFC phase-out in developing countries and the HCFC phase-out in developed countries. Remaining uses of HFCs are primarily in what are generally considered the applications with higher societal value where the unique properties of fluorocarbons are needed to meet specific use requirements. In applications where emissions reductions are feasible, emissions have and continue to be reduced. These reductions have occurred in large part because of cooperation among stakeholder groups and the flexibility of regulations that allowed, and even encouraged, innovation.

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