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# Carbon Dioxide as Natural Refrigerant

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## Abstract

The use of halogen based chemical compounds as refrigerant has compromised the existence of life on the earth. This fundamental paper discusses the suitability of natural refrigerant $CO_2$ in refrigeration and air conditioning systems for high ambient climatic conditions encountered in India. The lower critical temperature of $CO_2$ converts the subcritical vapour compression cycle to transcritical mode whenever the ambient temperature crosses the critical temperature of 31$^o$C. The transcritical cycle gives lower cooling capacity and higher compressor power consumption which results in less energy efficiency of the system. The thermo-physical and transport properties of CO2 are much better than chemical refrigerants results in compact size of the system with competitive energy efficiency at lower ambient temperature. The matching of operation the transcritical air conditioning system with heating and cooling applications gives very high energy efficiency.

**Keywords:** Chemical refrigerants, subcritical cycle, transcritical cycle, thermo-physical properties, $CO_2$

## 1. Introduction

Environmental concern has become a significant motivating factor in recent times in design and development of any domestic or industrial products. Consumers have become increasingly aware of the environment and the need to try and preserve the world in which all live. It is challenge for developing energy efficient products for day to day use in any applications so that ecological foot print of the product will be very less. The refrigeration and air conditioning systems are not the exceptions to this trend! As per the estimation, more than one-third of world's produced power goes into refrigeration and air conditioning sector. At present in India alone, 7 to 8 million installed small capacity air conditioning systems are working and consuming whooping 14 to 15 thousand mWh of electrical energy per day [4]. Surprisingly, this statistics does not cover electrical usage for air conditioning of commercial buildings.

Since a decade, one specific area of concern has been developed about the effects of refrigerants have on ozone layer depletion and more recently on global warming. The Kyoto Protocol has caused environmental focus to grow beyond ozone depletion to also include global warming and equivalent emission of carbon dioxide into the atmosphere. The idea of monitoring global warming has brought about a new concept of considering not only the ozone depleting nature but also the global warming potential of products throughout their lifecycle. This had lead many researchers to concentrate on the development of new and improved refrigerants to minimize the harmful effect they have on the environment, while others looked at existing substances like hydrofluorocarbons and naturally occurring gases to try and create a more efficient refrigeration system.

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This article focuses on the feasibility of carbon dioxide as primary refrigerant vis-à-vis other working fluids used in refrigeration and air conditioning systems in Indian subtropical climatic conditions.

## 2. History of $CO_2$

Carbon dioxide is very old 'working fluid' in refrigeration system and needs to understand its history and why it was discontinued after the Second World War. Carbon dioxide has been known to mankind since first century AD. The Romans were aware of the effects of lethal gas coming out of volcano on blood circulations. They had also knowledge of suffocation due to displacement ventilation and called carbon dioxide – 'Spiritus Letalis', which killed without leaving any traces! In 1756, Joseph Black proved that carbon dioxide, which he called 'fixed air' present in the atmosphere and combines with other elements to form compounds. In mid 1700, Joseph Priestley dissolved carbon dioxide in water and created refreshing drink with a little tart flavor.

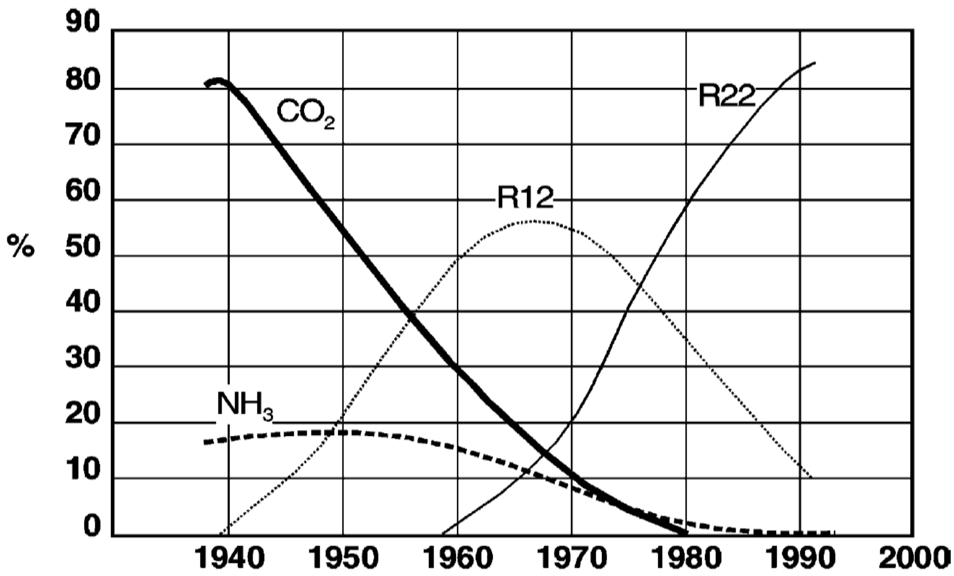


**Figure 1:** Use of primary refrigerants over last century

The first use of carbon dioxide was traced back to year 1748 for development of artificial refrigeration system by scientist William Cullen at Glasgow University but unfortunately it was never put for any use. In 1805, Oliver Evans proposed the concept of mechanical refrigeration system with coils and compressor. Later on in just 45 years, Alexander Twining proposed carbon dioxide as refrigerant for vapour compression based refrigeration systems. In 1886, Franz Windhausen had got the patent for design of carbon dioxide compressor, which was later on bought by J & E. Hall Company. They had further improved the design and commercially manufactured and sold the compressors till 1950 basically for marine applications replacing old air machines of that time. In America, Thaddeus Lowe developed his first ice machine in 1869. In 1881, Carl Linde developed carbon dioxide machine in Europe. In 1897, Sabroe also manufactured carbon dioxide compressor and developed first home carbon dioxide refrigerator.

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In late 1800, carbon dioxide based machines were used for display cabinets, cold storages, food markets, kitchens for refrigeration and theaters, hospitals, passenger ships, and trains for comfort cooling applications in Europe and America since other fluids – ammonia, sulphur dioxide were considered toxic and flammable and legally restricted their use in these application areas. However, introduction of man-made synthetic chemical refrigerants in 1930s had slowly put an end to use of natural refrigerants – ammonia, sulphur dioxide, carbon dioxide in refrigeration system. Actually, ammonia and sulphur dioxide were barred from use because of toxicity and flammability issues in human occupied areas. The reason why carbon dioxide discontinued from comfort air conditioning system is unknown. But, discontinuation of carbon dioxide might have occurred because of high working pressure, loss of cooling capacity at high ambient temperature. Aggressive marketing of synthetic refrigerants, possibility of use of low cost and light heat exchangers for chemical refrigerants and inability to develop competitive components and system for carbon dioxide. Figure (1) shows the use of carbon dioxide has considerably reduced after 1940-50.

## 3. Applications of $CO_2$ in other Areas

Carbon dioxide has been used in refrigeration and cooling in solid and liquid form because it sublimates to gas at very low temperature of -78.5$^o$C giving total loss of refrigerant. It is widely used in brewing of soft drinks, beers, other alcoholic drinks. Recently, it is being used in softening water to avoid corrosion problems in long water distribution lines and also in producing potable drinking water. The use of carbon dioxide as fire extinguisher is known from century. It also finds application in petroleum industry to bubble out crude oil, sand blasting and hardening of metal castings.

## 4. Safety Issues with $CO_2$

As shown in Figure 2, Carbon dioxide has 3 to 4 times more vapour pressure as compared to other refrigerants so there is always question about the safety of carbon dioxide and thickness of materials required to hold this gas in heat exchangers, receivers and in tubes/hoses. Explosion/rupture strength of pressure vessels depends on following factors

- Malfunctioning of safety equipments.
- Overcharging
- Overheating
- Incorrect operation practices
- Structural weaknesses in components like corrosion
- Mechanical impact

In case of rupture on explosion, the severity of casualty and an extent of potential damage is depends on explosion energy (stored energy in vessel) and Boiling Liquid Expanding Vapour Explosion (BLEVE) parameters. The explosion energy depends on refrigerant charge quantity in individual components, vapour fraction, and local pressure and temperature.

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Carbon dioxide has very high volumetric heat capacity, so the charge quantity in the system reduces considerably even though the vapour pressures are very high on low and high side of the systems as compared to other refrigerants.

**Table 1:** Comparison of mass of refrigerants with air

| Refrigerant | Molecular Mass, Kg/kmol | Density [kg/m$^3$] @ 20$^0$C, 1 atm |
|---|---|---|
| R134a | 102 | 4.336 |
| R22 | 86.47 | 3.651 |
| R407C | 86.2 | 3.639 |
| R410A | 72.58 | 3.062 |
| R290 | 44.1 | 1.865 |
| R744 | 44.01 | 1.839 |
| Air | 28.97 | 1.204 |
| R717 | 17.03 | 0.716 |

Authors have compared the charge quantity in HCFC22 and carbon dioxide in split air conditioning system for same cooling capacity. It was worked out to be 320 kg/m$^3$ for R22 and 255 kg/m$^3$ for carbon dioxide. At higher temperatures, R22 has more explosion energy in kJ as compared to carbon dioxide. Normally, the charge quantity in indoor unit is only 5 to 8% of total quantity so in case of explosion less damage will occur in indoor unit.

All the refrigerants listed in the Table 1 are heavier than air except ammonia (R717). In case of leakage of refrigerant, the refrigerant heavier than air will settle at the lowest point in the room if air is present in the room. Hence, handling these refrigerants care must be taken that enough cross ventilation is provided in the room otherwise possibility of causality cannot be ruled out. The density of carbon dioxide is second last in the least of most used refrigerants in industrial big capacity refrigeration plants and domestic refrigeration and air conditioning systems. As the percentage of carbon dioxide increases in the room, the air will get displaced out. Carbon dioxide is not only considered asphyxiate but it is known as narcotic agent and cerebral vasodilator. The vasodilator is substance which relaxes the blood vessel walls and reduced blood pressure. Carbon dioxide has also another effect on the red cells. If the percentage of carbon dioxide is more in the room air, then red cells get saturated with carbon dioxide and they lose their ability to exchange carbon dioxide for fresh oxygen. The percentage of carbon dioxide in air is 0.036%. If concentration goes up by 3% on volume basis then it cause hyperventilation, 5% will cause narcosis and 10% will cause a coma. The Immediate Danger to Life and Health (IDLH) concentration level is 4% by volume. The industry is well technologically advanced in handling the refrigerants much heavier and toxic than carbon dioxide so it is not a serious issue to use carbon dioxide as refrigerant.

### 5. $CO_2$: Promising Refrigerant

Carbon dioxide is colorless, odorless, naturally occurring gas with melting point -56.6$^o$C at 101.325 kPa pressure. It appears white solid substance like snow with surface temperature -78.5$^o$C and can be converted into bricks to make dry ice. It is present in the atmosphere at a

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concentration of 350 ppm from millions of years. Carbon dioxide has played key role for sustainability of plants and human kind on this planet.

**Table 2:** Comparison of properties of primary refrigerants

| Property | HCFC22 | R134a | R410A | R407C | HC290 | R717 | R744 |
|---|---|---|---|---|---|---|---|
| | CFC22 | HFC134a | HFC410a | HFC407c | HC290 | $NH_3$ | $CO_2$ |
| ODP/GWP | 0.05/1700 | 0/1300 | 0/1900 | 0/1600 | 0/3 | 0/0 | 0/1 |
| Molecular mass (kg/kmol) | 86.5 | 102 | 72.6 | 86.2 | 44.1 | 17 | 44 |
| Critical temperature ($^oC$) | 96 | 101.1 | 70.2 | 86.1 | 96.7 | 133 | 31.1 |
| Critical pressure (bar) | 49.7 | 40.7 | 47.9 | 46.4 | 42.5 | 114.2 | 73.8 |
| Volumetric heat capacity ($kJ/m^3$) | 4356 | 2868 | 6763 | 4029 | 3907 | 4382 | 22545 |
| Specific heat of vapour @ boiling temperature $7.2^0C$ (kJ/kg-K) | 0.7749 | 0.9271 | 1.194 | 0.8582 | 1.849 | 2.775 | 2.162 |
| Ratio of vapour density to liquid density @ boiling temperature $7.2^oC$ (kJ/kg-K) | 47.4 | 68.84 | 29.79 | 50.23 | 40.66 | 141.7 | 7.155 |
| Surface tension (N/m) | 0.01067 | 0.01053 | 0.008226 | 0.009562 | 0.009061 | 0.02378 | 0.003125 |
| First commercial use as refrigerant | 1936 | 1990 | 1998 | 1998 | NA | 1859 | 1869 |

The green leafy plants are producing carbohydrates (plant food) through photosynthesis process by using carbon dioxide. Carbon dioxide is a green house gas and has stabilized the temperature of the planet above $0^oC$ otherwise we would have been in ice age.

The ratio of vapour density to liquid density is lowest for carbon dioxide as compared with other refrigerants in figure 3.

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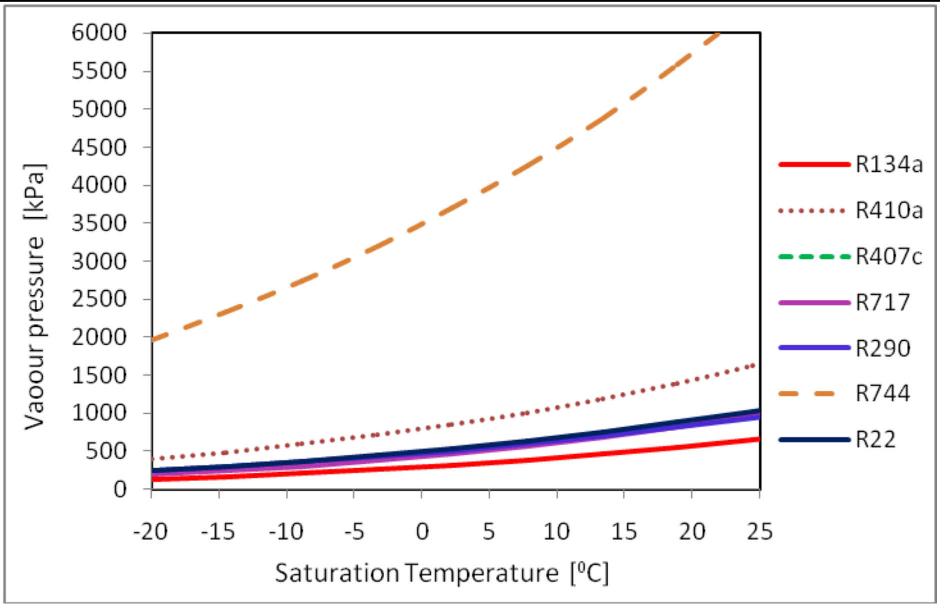


**Figure 2:** Vapour pressure of different refrigerant at saturation temperature

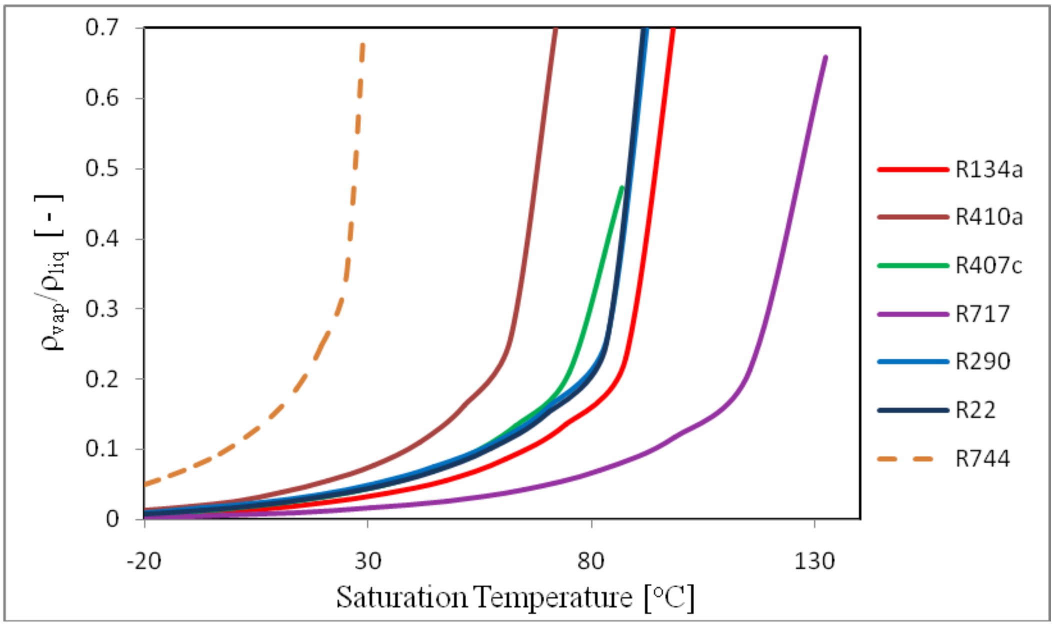


**Figure 3:** Ratio of vapour density to liquid density for saturation temperature

The refrigerant properties are very important for an energy efficient design of refrigeration system. The properties of carbon dioxide are compared with other chemical and natural refrigerants in Table (2). It is slightly acidic and soluble in water, ethanol and acetone. Carbon dioxide has very good thermo-physical and transport properties as compared to other refrigerants. It is environmental friendly refrigerant since its ODP is zero and GWP is one. It is nonflammable; chemically inactive and compatible with polyester oil.

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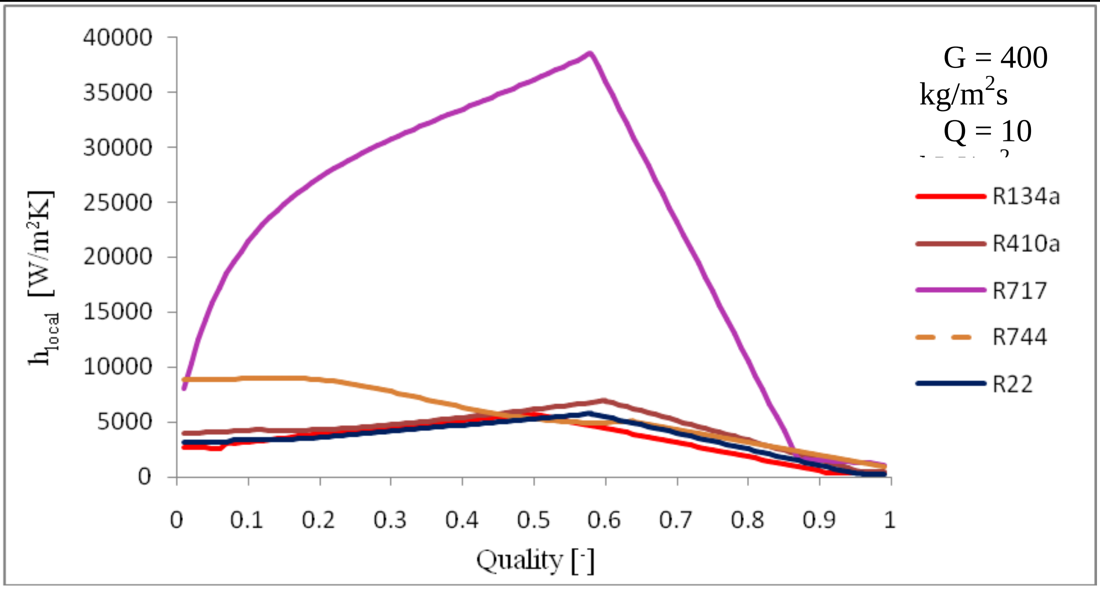


**Figure 4:** Local heat transfer coefficient for different refrigerant

The low value of the ratio gives high momentum for vapour phase, better shear force between liquid and vapour flow and results in homogenous flow in small channels.

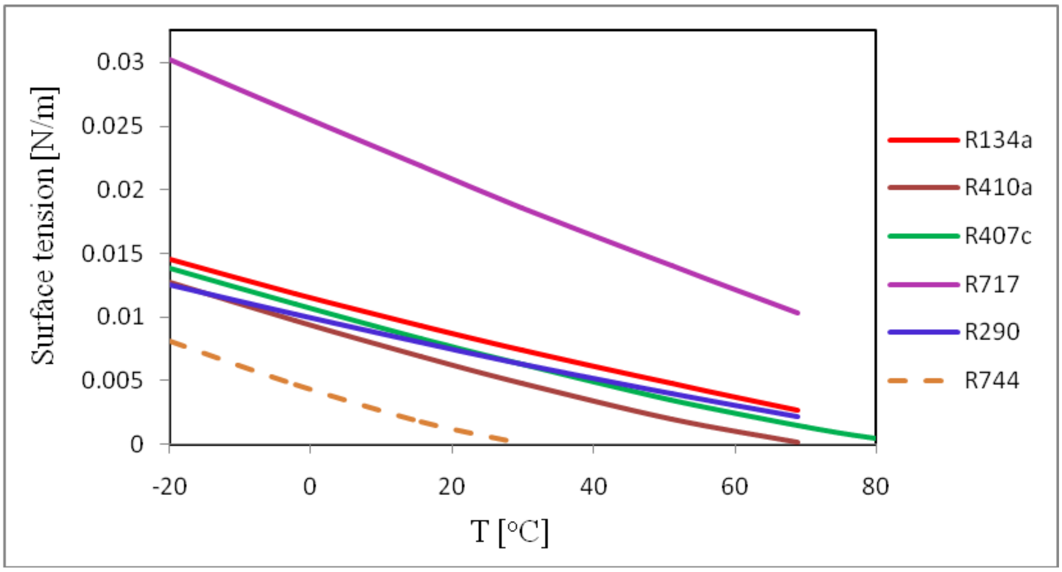


**Figure 5:** Surface tension of different refrigerant at saturation temperature

That is a basic reason, carbon dioxide has heat transfer coefficient 60 to 70% more than other refrigerants except ammonia. Figure (3) shows the comparison of heat transfer coefficients of different refrigerants. The high vapour density also increases the heat absorbing capacity per unit volume flow rate of the refrigerant.

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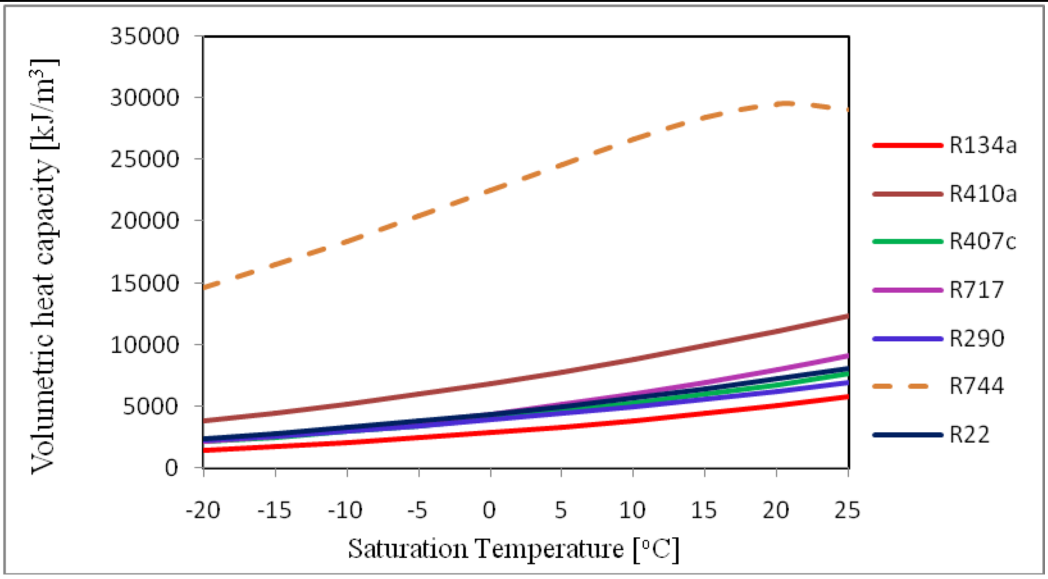


**Figure 6:** Volumetric heat capacity of different refrigerant

The volumetric heat capacity of carbon dioxide is 3 to 4 times more than other refrigerants shown in Figure 6. Hence, it reduces considerably the charge quantity of refrigerant and the size of compressor, heat exchangers and tubing, etc. as compared to other refrigerants.

## 6. Transcritical $CO_2$ Vapour Compression Cycle

The critical temperature of refrigerant fixes whether the heat rejection will takes place below or above the critical point of the refrigerant. In conventional refrigerants like R22, R410A, R717 etc., the critical temperature is 2 to 3 times above the ambient temperature as shown in property comparison Table (1).

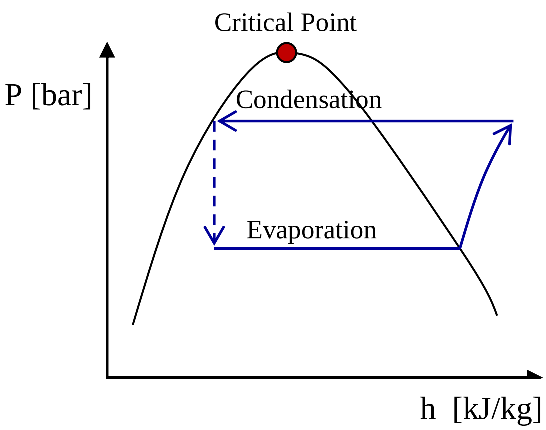


**Figure 7:** P-h chart for subcritical vapour compression cycle

The surface tension has effect on wetting characteristic of fluid. The lower surface tension improves wetting of tube surface and improves heat transfer. Further less surface tension reduces the amount of heat required to convert liquid bubble to vapour bubble and further improves heat transfer coefficient. But increased rate of conversion of liquid into vapour bubble due to instability of liquid on tube surface will increase the percentage of vapour

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bubble on the downstream side of the evaporator tube. This negatively affects the heat transfer coefficient. As shown in Figure (5) Carbon dioxide has very small value of surface tension among all the listed refrigerants. Refer Figure (7) for subcritical vapour compression cycle, where heat absorption and heat rejection are taking place well below critical point across saturated liquid-vapour mixture zone [1].

In normal subcritical vapour compression cycle, the heat absorption and rejections are refrigerant phase change processes. However in the case of ambient temperature above 31$^oC$, heat rejection process is not a phase change process with carbon dioxide. The saturation pressure of the condenser depends on ambient conditions assumed for the design of refrigeration system. In subcritical cycle, enthalpy of saturated liquid at condenser exit depends on the temperature alone. Carbon dioxide has critical temperature 30.9$^oC$, which is around ambient dry bulb temperature observed in Indian subcontinent. The heat absorption is subcritical process takes place at low pressure and temperature in a evaporator and heat rejection is supercritical process takes place above the critical point of the refrigerant at a supercritical pressure.

The heat rejection in supercritical region occurs by cooling of supercritical vapour at a constant pressure and no saturation phase exists. The pressure is independent of temperature in supercritical region. As shown in Figure (8), the process 4-1 is constant pressure and temperature heat absorption process, 1-2 is ideally an isentropic compression process, 2-3 is constant pressure and variable temperature heat rejection process and 3-4 is constant enthalpy expansion process. Normally, the temperature of supercritical gas at exit of gascooler (point 3) is above ambient temperature by 2 to 4$^oC$, called approach temperature. The approach temperature depends on the effectiveness of the gascooler. The enthalpy of supercritical carbon dioxide at point 3 depends on both the pressure and temperature. The phase of carbon dioxide at inlet to expansion valve is near-liquid near-vapour supercritical fluid, which converts into subcritical liquid-vapour saturated mixture while crossing saturated liquid line in process 3-4. In transcritical vapour compression cycle, the specific refrigeration capacity of the evaporator increases as the gascooler pressure increases up to certain maximum pressure for the constant gascooler outlet temperature, at the cost of increased power consumption; result in increase in COP of the system However, beyond maximum pressure rise in refrigeration capacity is not high which will compensate increased power consumption and result will be fall in COP.

This trend is observed because the constant temperature lines become vertical as gascooler pressure increases as shown in Figure 8. This optimum pressure gives better COP and depends on gascooler exit temperature of carbon dioxide. Hence in the design of carbon dioxide refrigeration system, gascooler pressure has much control on the energy performance. This gascooler pressure is controlled by solenoid valve, which controls outflow of refrigerant to expansion valve. The specific heat at constant pressure increases on gascooling and reaches its high value near critical point then it descends very sharply. The temperature at this peak value of specific heat is called pseudo-critical temperature, which is little higher than the critical temperature. The pseudo-critical temperature depends on the gascooler pressure as shown in Figure (9).

As gascooler pressure increases, the pseudo-critical temperature also increases. In the design of gascooler, it is necessary to consider the variations in the thermo-physical properties to determine the optimum size of heat exchanger. Consideration of constant values of thermo-

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physical properties in thermal design would result in either undersized or oversized gascooler. Carbon dioxide has shown very high values of Prandtle number among all listed refrigerants in Figure 10 and 11 for both saturated liquid and vapour phases.

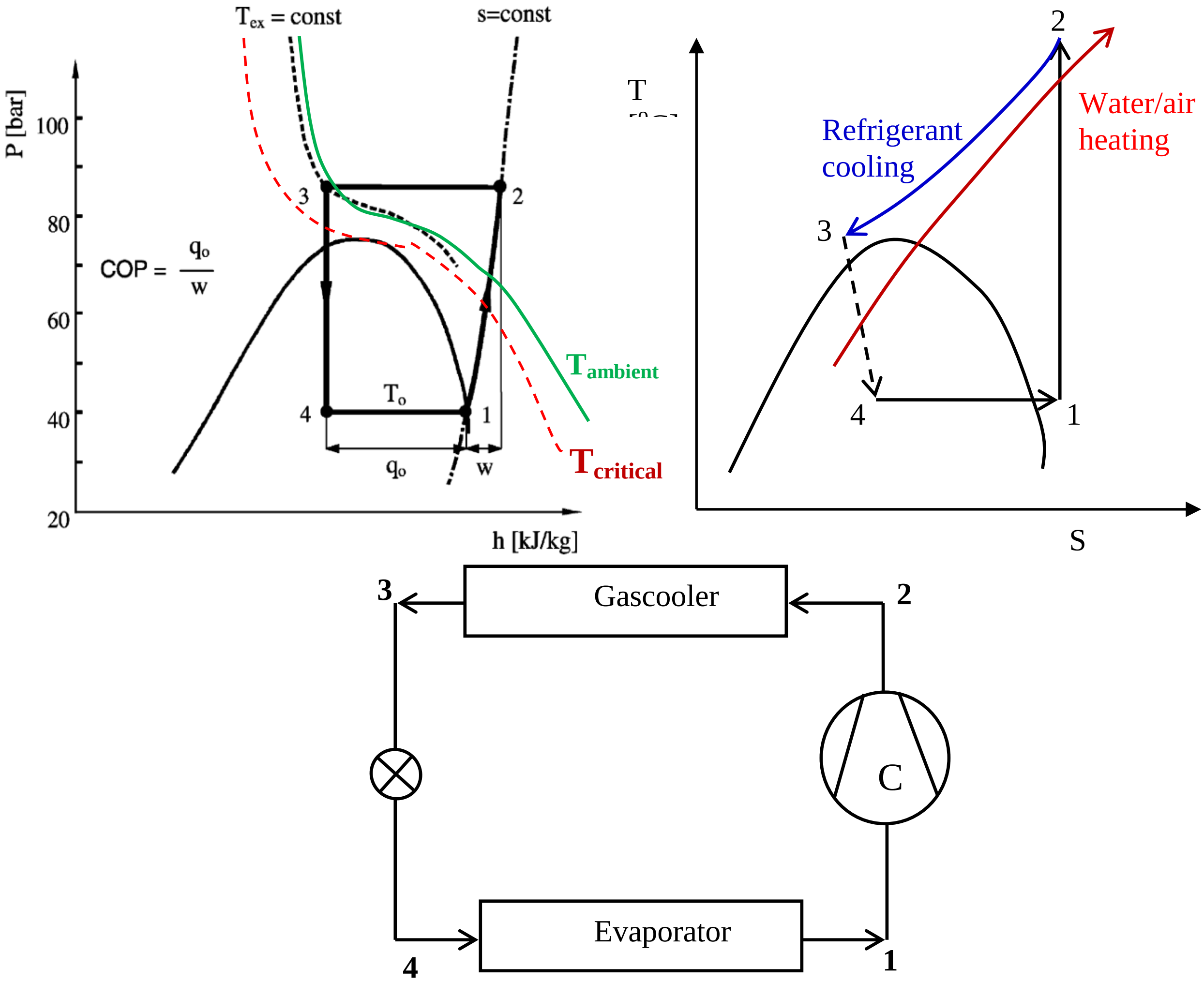


**Figure 8:** Transcritical vapour compression system ($T_{ambient} > T_{critical}$)

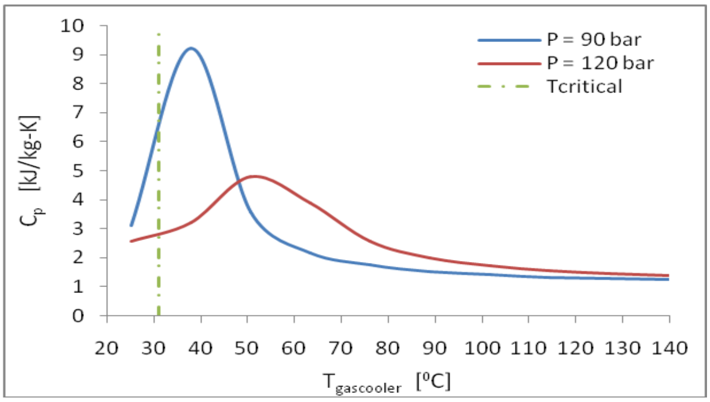


**Figure 9:** Variation in specific heat of supercritical $CO_2$

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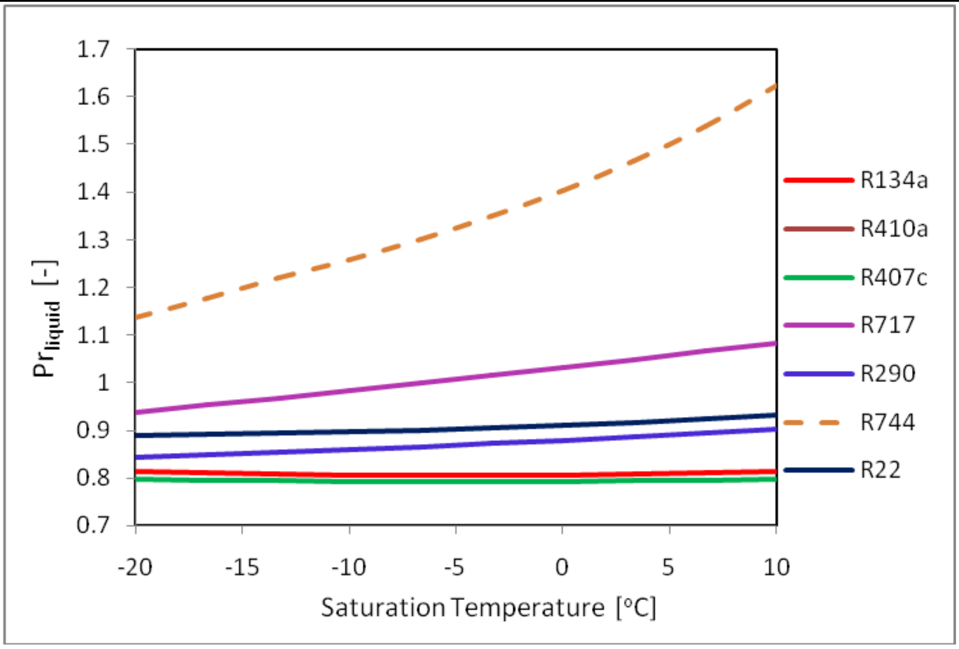


**Figure 10:** Prandtle number for saturated liquid refrigerants at saturation temperature 7.2$^{0}$C

Prandtle number of fluid decides the ability of fluid to absorb or reject heat since its value depends on fluid properties: surface tension, specific heat at constant pressure and thermal conductivity. The fluid with higher Prandtle number will reject or absorb more heat as compared to fluid with lesser value to bring about the same change in temperature. In convection heat transfer principle, heat transfer coefficient is depends on the Nusselt number. The Nusselt number is in turn depends on Reynolds and Prandtle number. More is the value of the Prandtle number; more will be the heat transfer rate.

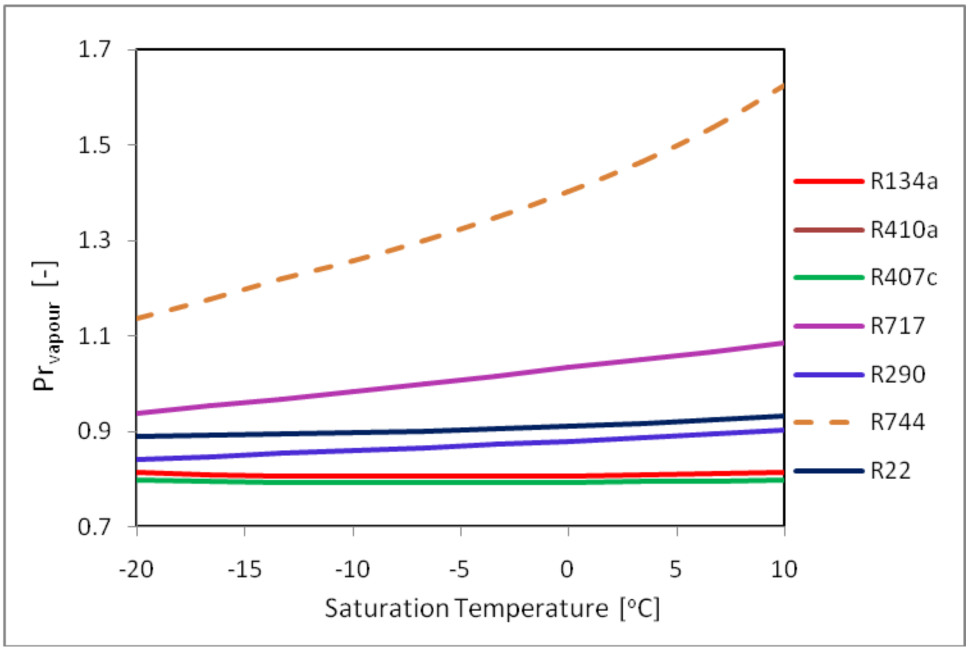


**Figure 11:** Prandtle number for saturated vapour refrigerants at saturation temperature 7.2$^{o}$C

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## 7. Conclusions

Carbon dioxide is naturally available, safe, environmental friendly refrigerant with best thermo-physical and transport properties after ammonia. The design of refrigeration system with carbon dioxide is depends on the low side temperature requirement of application and design ambient temperature. The thermo-physical properties of carbon dioxide are better than current refrigerants. The disadvantage of carbon dioxide is low critical point which makes cycle transcritical in high ambient climates. This results in loss of performance of the system. However, the steep temperature glide available in gascooler can be used for heating applications. This strategy gives cooling and heating applications and results in very competitive combined COP. So it is necessary to match the design of carbon dioxide refrigeration with applications to produce cold and hot utilities simultaneous and derive better financial mileage over existing subcritical refrigeration systems.

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