International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 06 Issue: 06 | June 2019 www.irjet.net p-ISSN: 2395-0072

CO_2 as a Refrigerant in Supermarket Refrigeration Systems: A Review

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Abstract – *In the present study, the focus is particularly on the natural refrigerants. The natural refrigerant carbon dioxide (R744) has become an interesting alternative to conventional and new chemical refrigerants in supermarkets refrigeration or food retail applications. Carbon dioxide (R744) presents itself as the suitable refrigerants in the supermarkets refrigeration because of it offers many advantages such as nontoxic, inflammable, easily available, well known properties, low critical point, and relative inertness, stability, compatible with standard materials and lubricants, components compactness, favorable thermodynamics and transports properties and low cost. The purpose of this paper is to compare various refrigerants on the basis of their environmental impacts and thermal properties. This paper also covers an ideal fluids properties (i.e. thermal, physical and chemical), safety aspects, advantages and disadvantages of CO_2 as a refrigerant. Finally, a few suggestions are discussed regarding possible future works and improvements that can be made future of CO_2 refrigeration technology.*

Key Words: **Refrigeration, Carbon Dioxide (R744), Environment, ODP, GWP, Safety, F-gas regulation, Supermarket.**

1. Introduction

Before the invention of CFCs refrigerants, ammonia, carbon dioxide, air, sulphur dioxide and other refrigerants such as ether, methyl chlorides etc were commonly used in the mechanical refrigeration system [Riffat et al. 1997, Cavallini and Zilio 2007]. After the invention of CFCs refrigerants ammonia remained a popular refrigerant due to cheapness and good thermo-physical properties. Its toxic, flammable and irritating nature did not affect its popularity to use as a refrigerant. Since 1930s, the use of synthetic refrigerants [Inlow and Groll 2011] dominated in the refrigeration industry because of their good performance and safety characteristics. They are great refrigerants because they compress easily to a liquid and carry away lots of heat when they evaporate. In fact, they are well suited to a variety of applications because these refrigerants don't react with anything. These refrigerants were found to be harmful to the environment or atmosphere i.e. ozone layer depletion and global warming [Messineo 2011, Llopis et al. 2015]. When the chemical bonds of CFCs are broken, the chlorine atoms drift free in atmosphere, and they become a catalyst that breaks unstable ozone molecules (O_3) into oxygen molecules (O_2). The chlorine isn't consumed in the reaction; therefore it continues ruining ozone for years. This is a big problem because stratospheric ozone works as shield that protects all living things on the planet from the Sun's ultraviolet (UV) radiation. Therefore, several regulations have been applied on their usage and banned on the production of CFCs [Montreal Protocol, 1987].

The Montreal Protocol is an international treaty designed to protect the ozone layer by phasing out the production of CFC refrigerants that are responsible for ozone layer depletion. It was agreed on September 16, 1987 and entered into force on January 1, 1989. Since the Montreal Protocol came into effect, the atmospheric concentrations of the most important chlorofluorocarbons and related chlorinated hydrocarbons have either decreased or stopped. So, these refrigeration systems were replaced by the ozone friendly refrigerants. The most systems now use new types of refrigerants based on hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). HFC refrigerants offer most of the same advantages as CFCs without damaging the earth's ozone layer but they have high GWP that affect the environment because the presence of fluorine atoms (due to the leakage of the refrigerant from the systems). Due to this direct impact on environment, the second Montreal Protocol (which is also known as Kyoto Protocol, 1997) is an international treaty that was adopted on December 11, 1997 and entered into force from February 16, 2005. The main goal of the Kyoto Protocol is to control the emissions of the main greenhouse gases (GHGs). Many GMGs, including water vapour, ozone, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are naturally present in the atmosphere. Other GMGs are synthetic chemicals (CFCs and HCFCs) that are emitted only as a result of human activity. Hence, they have global warming potential (GWP).

According to an international agreement [Montreal Protocol, 1987], the use of CFC refrigerants such as R-11(CCl_3F), R-12 (CCl_2F_2), R-113 ($C_2Cl_3F_3$) and R-114 ($C_2Cl_2F_4$) etc are considered to have high ODP have been phased out by 2000 AD and [Kyoto Protocol, 1997], the use of HCFC refrigerant such as R-22 ($CHClF_2$) also will have phased out by 2030 [Riffat et al. 1997, Inlow and Groll 2011], because of its high GWP. The CFC refrigerants such as R-11 and R-12 have the highest ODP i.e. 1, whereas HCFC refrigerants R-22 has quite low ODP i.e. 0.05 [Arora 2009]. Presently, the most usual refrigerants are HFCs such as R-404A, R-410A, R-507A, R-134a, R-152a, and R-125 [Kairouani et al. 2015] which are not considered to be responsible for the depletion of ozone layer. However, these refrigerants (HFCs) have direct impact on global warming because of the higher GWP than the CO_2 (thousands of times larger than CO_2 refrigerant). This being so, the use of synthetic refrigerants such as CFCs, HCFCs and HCFs are restricted.

Calm [2008] examined the outlook for current options which exist in international agreements, including the Montreal and Kyoto Protocols to avert stratospheric ozone depletion and global climate change, respectively. He also examined other environmental concerns and further international and local control measures and also identified the pending policy and regulatory changes that may impacts on the next generation of refrigerants significantly. Similar study was carried out by Naicker [2014]. The HFC refrigerants expected to be a replacement for the phased out CFCs and HCFCs refrigerants but they turned out to be a temporary solution due to their global warming potential (GWP). These both protocols and regulations on synthetic refrigerants such as CFCs and HCFCs have come big challenges in the refrigeration and heat pump technology. Thus, a new situation was created that resulted in the replacement of old refrigerants such as CO_2 [Lorentzen 1994], and introduction of new refrigeration system solutions [Lorentzen 1995, Pearson 2005] which require less refrigerant charge and less energy consumption. Nevertheless, the energy consumption of the system should be kept as low as possible and high performance. Right now the most likely replacement is another new class of fluorocarbon refrigerants called hydrofluoroolefins (HFOs) [Llopis et al. 2015, Gullo and Cortella 2016, Kandoliya and Mehta 2016, and Mota-Babiloni et al. 2017]. Their primary advantage is, their lower GWP than other refrigerants and they can be used with existing refrigeration system designs.

Nowadays, the CO_2 is going to become an alternative refrigerant in the refrigeration technology as well as its use in the heat pump technology [Ouadha et al. 2007]. The CO_2 is a natural refrigerant because it exists in the atmosphere or naturally. It is the most promising refrigerant to be replaced as a permanent refrigerant in the systems due to its safety and good thermo-physical properties [Bansal 2012]. The major problem of CO_2 refrigerant is low critical temperature and high working pressure. In addition, CO_2 is widely used as a volatile secondary refrigerant [Hesse 1996, Cecchinato et al. 2012 and Clark 2016] due to reduce the primary refrigerant charge and leakage as well as the health and safety issues such as flammability and toxicity.

2. Properties of CO_2 as a refrigerant

The CO_2 phase and P-h diagrams are shown in Figure 1 and 2 respectively. Properties of CO_2 (R744) refrigerant [ASHRAE Standard 62 (1889), Riffat et al. 1997, Kairouani et al. 2015, Megdouli et al. 2016, and Purohit et al. 2017] are:

1. Odourless, colourless, non-toxic and non-flammable.
2. Boiling point at atm pressure is -78°C and melting point from the solid is -56.6°C.
3. The ODP = 0 and GWP = 1.
4. Critical temperature and pressure are 31°C and 73.8 bar respectively.
5. Triple point is at -56.6 °C temperature and 5.2 bar pressure.
6. CO_2 has emerged as one of the most refrigerant which is eco-friendly and energy efficient to provide low temperature.
7. Used in the range of temperature from -25 °C to -50 °C for food retails, medical, cold storage, liquefaction of gases and supermarket refrigeration systems etc.
8. CO_2 has a vapour pressure higher than the atmospheric pressure i.e. a positive vapour pressure, which makes it an alternative solution to be used for a low temperature side of the refrigeration system.
9. Hence, CO_2 cycle always operates in subcritical conditions and it allows reducing pump power input and piping size and its better heat transfer properties.

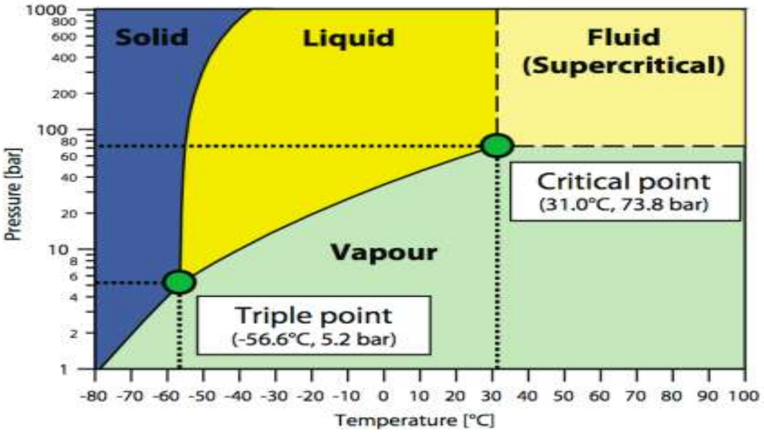

Figure 1: CO_2 Phase diagram [Danfoss 2009].

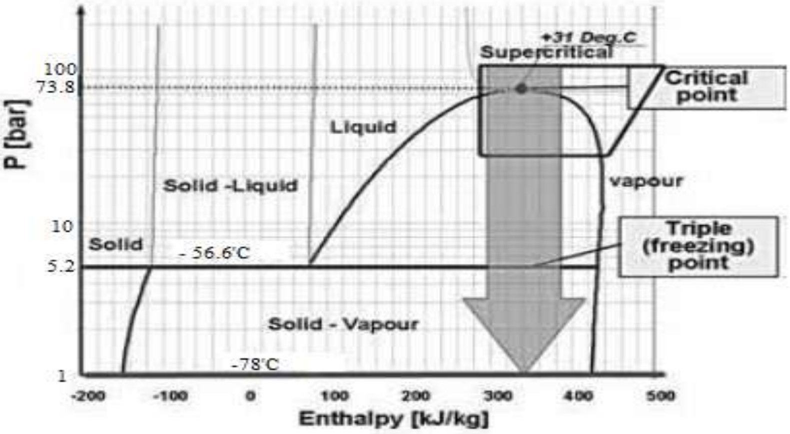

Figure 2: CO_2 P-h diagram [Bardia et al. 2009].

3. Desirable properties of an ideal refrigerant

The suitability of a refrigerant for a certain application is selected by its thermodynamic, physical, chemical and various practical factors [ASHRAE Handbook 2005, Arora 2009]. There is no one refrigerant which can be used for all applications. Generally, we can say that there are no ideal refrigerant. If one refrigerant has good advantages, it will have some disadvantages also. Hence, a refrigerant is chosen which has greater advantages and less disadvantages.

A refrigerant is said to be ideal [Arora 2009, Wang et al. 2010, and Tsamos et al. 2017] if it has all the following properties:

1. Boiling temperature – The boiling temperature of the refrigerant at atmospheric pressure should be low.
2. Freezing temperature – The freezing temperature of the refrigerant at atmospheric pressure should be low and well below the operating evaporator temperature.
3. Evaporator and condenser pressure – Both evaporating and condensing pressures should be positive i.e. above atmospheric and should be as near the atmospheric pressure as possible. It prevents leakage of air into the refrigerating system.
4. Critical temperature – The critical temperature of the refrigerant should be high i.e. above the normal condensing temperature.
5. Critical pressure – The critical pressure of the refrigerant should be high.
6. Latent heat of vaporisation – Latent heat of vaporisation of the refrigerant at evaporator temperature should be as high as possible i.e. specific heat of liquid should be low and specific heat of vapour should be high.
7. Specific volume – The specific volume of the refrigerant at evaporator temperature i.e. volume of suction vapour to the compressor should be as possible as low.
8. Liquefaction of refrigerant – The refrigerant should be easy to liquify at moderate temperature and pressure.
9. Coefficient of performance – The coefficient of performance of refrigeration system for a particular refrigerant should be high as far as possible i.e. power requirement should be low.
10. Flammability – Refrigerant should be non-flammable and nonexplosive.
11. Toxicity – Refrigerant should be non-toxic.
12. Miscibility – The refrigerant should mix well with oil which helps heat transfer easily.
13. Solubility of water- The refrigerant should be negligible soluble in water as the ice formed will chock the expansion valve.
14. Stability and inertness – A refrigerant should be most stable and inert with respect to all materials used in refrigeration system.
15. Corrosive property – A refrigerant should be non-corrosive for all metals.
16. Thermal conductivity – The thermal conductivity of the refrigerant should be very high for both liquid and vapour states.
17. Availability – A refrigerant should be easily and regularly available.
18. Viscosity – The viscosity of the fluid should be low for both liquid and vapour states.
19. Leakage tendency – The leakage tendency of refrigerant should be very low or negligible. Leakage should be easy to locate by odour or suitable indicator.
20. Ozone Depletion Potential – The refrigerant should be ozone friendly i.e. zero ODP.

21. Global Warming Potential – The refrigerant should be environmental friendly i.e. it should have low or negligible GWP.
22. Cost – The cost of refrigerant should low as it affects the high capacity refrigerating systems.

Therefore, in order to select a correct refrigerant, it is necessary that it should satisfy the above properties which make it ideal to be used for a particular application.

4. Comparison between CO_2 and other refrigerants properties

There are many properties that distinguish CO_2 from other conventional and natural refrigerants. These properties are operating pressure, density, latent heat of vaporisation, dynamic viscosity, thermal conductivity, surface tension, volumetric refrigeration capacity and, specific etc [ASHRAE Std 62 (1889), Arora 2009, Bansal 2012, and Emerson 2015]. It has low critical temperature with considerably higher operating pressure. At the pressures below 5.2 bars and a temperature of -56.6°C, CO_2 will turn into a solid. In the subcritical phase, CO_2 is similar to HFC refrigerants except that it has very high pressure. The pressures at which CO_2 operates are much higher than the working pressure of most common refrigeration components. The conventional refrigerant systems are designed for pressures of 28 to 45 bars, which mean that special attention must be taken in designing the system and selecting appropriate components for CO_2 system. Table 1 shows the chemical formulae and chemical names of the various common selected refrigerants including natural refrigerants.

Table 1: The chemical formulae and chemical name of the common selected refrigerants

Refrigerant		Chemical Formula	Chemical Name
CFCs	R-11	CCl_3F	Trichloromonofluoromethane
	R-12	CCl_2F_2	Dichlorodifluoromethane
HCFCs	R-22	$CHClF_2$	Monochlorodifluoromethane
	R-123	$C_2HCl_2F_3$	2,2-dichloro-1,1,1-trifluoroethane
HFCs	R-134a	$C_2H_2F_4$	1,1,1,2-tetrafluoroethane
	R-152a	$C_2H_4F_2$	1,1-difluoroethane
HFC Blends	R-404A	$C_2HF_5/C_2H_3F_3/C_2H_2F_4$	R-125 (44%)/R-143a (52%)/R-134a (4%)
	R-410A	CH_2F_2/C_2HF_5	R-32 (50%)/R-125 (50%)
HCs (Naturals)	R-290	C_3H_8	Propane
	R-600a	C_4H_{10}	Isobutane
HFOs	R-1234yf	$C_3H_2F_4$	2,3,3,3-tetrafluoropropene
	R-1234ze	$C_3H_2F_4$	1,3,3,3-tetrafluoropropene
Naturals	R-744	CO_2	Carbon Dioxide
	R-717	NH_3	Ammonia

Table 2: The molecular weight, critical temperature and pressure of the common selected refrigerants

Refrigerant		Molecular Weight (gm/mol)	Critical Temperature, T_C (°C)	Critical Pressure, P_C (in bar)
CFCs	R-11	137.38	197.98	43.08
	R-12	120.93	112.04	40.36
HCFCs	R-22	86.47	96.15	49.9
	R-123	152.93	183.68	36.62
HFCs	R-134a	102	101.06	40.59
	R-152a	66.05	113.26	45.17
HFC Blends	R-404A	97.6	72.14	37.35
	R-410A	72.58	70.17	47.70
HCs (Natural)	R-290	44.08	96.7	42.48
	R-600a	58.1	134.7	36.40
HFOs	R-1234yf	114.04	94.85	33.8
	R-1234ze	114.04	109.52	36.3
Naturals	R-744	44.01	31	73.8
	R-717	17.03	133	114.2

Table 2 shows the molecular weight, critical temperature and pressure of the most selected refrigerants. The critical temperature and pressure of the CO_2 are 31°C and 78.3 bar (7.83 MPa) respectively. The critical temperature of CO_2 is lower than other common refrigerants. The most distinguishing property of CO_2 is its high operating pressure. CO_2 has a much higher operating pressure than other refrigerants. Due to this high pressure, the heat rejection will take place in the super-critical region. The fluid can neither liquid nor vapour above the critical point. In the sub-critical region the pressure and temperature are expressed by same line and is called as saturation temperature pressure curve. In the super-critical region or above the critical point the temperature and pressure can be regulated. The molecular weight of the carbon dioxide is 44.01 gm/mol.

Figure 3 shows the saturation pressure for CO_2 and some common refrigerants that have been or are using in supermarket refrigeration for a wide range of temperatures. It shows that the saturation temperature and pressure curve of CO_2 is much steeper than other refrigerants. Thus, this feature makes it a favorable refrigerant especially at low temperatures with a small temperature difference. This results in higher flow velocities and two phase distribution inside a heat exchanger. The lower velocities often lead to phase separation and oil management problems in the system. At room temperature (25°C), CO_2 has a saturation pressure of 6.42 MPa. At 25°C, CO_2 has a pressure which is about 5 to 10 times higher than that the common selected conventional refrigerants.

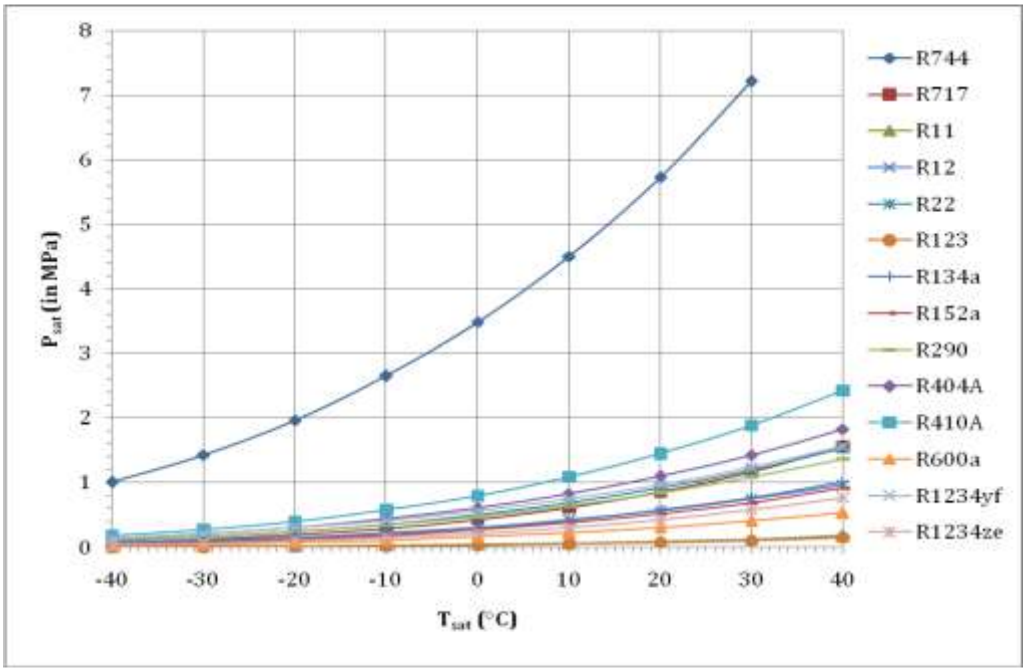

Figure 3: Saturation pressure v/s temperature for common selected refrigerants

The ozone depletion potential (ODP), global warming potential (GWP), flammability and toxicity of the common selected refrigerants are shown in Table 3. The CO_2 has zero ODP, negligible GWP, non-flammable and non-toxic refrigerant. These properties make it an almost ideal refrigerant. Thereby, it is used for those applications where large quantities of refrigerant are needed. There are some more important properties of refrigerants such as ASHRAE Standard safety group, boiling and freezing point, atmospheric lifetime and occupational exposure limit (OEL, ppm). The above properties are shown in Table 4 for some common refrigerants. The triple point of CO_2 is at 5.2 bar pressure and 56.6°C temperature. It means the cycle will always be above the 5.2 bar pressure limit, otherwise solid CO_2 will be formed.

Table 3: ODP, GWP, Flammability and Toxicity of the common selected refrigerants

Refrigerant		ODP	GWP (for net 100 years)	Flammability	Toxicity
CFCs	R-11	1	4750	N	N
	R-12	1	10900	N	N
HCFCs	R-22	0.05	1810	N	N
	R-123	0.02	77	N	N
HFCs	R-134a	0	1430	N	N
	R-152a	0	140	Y	N

HFC Blends	R-404A	0	3922	N	N
	R-410A	0	2088	N	N
HCs (Natural)	R-290	0	3	Y	N
	R-600a	0	3	Y	N
HFOs	R-1234yf	0	4	Y	N
	R-1234ze	0	6	Y	N
Naturals	R-744	0	1	N	N
	R-717	0	0	Y	Y

Table 4: ASHRAE Standard safety group, Boiling point, Freezing point, Atmospheric lifetime and OEL of the some common refrigerants

Refrigerant		ASHRAE Std. Safety Group	Boiling Point (°C)	Freezing Point (°C)	Atmospheric Lifetime (in years)	OEL (ppm)
CFCs	R-11	A1	+23.70	-111	45	1000
	R-12	A1	-29.75	-157.5	100	1000
HCFCs	R-22	A1	-40.81	-160	12	1000
	R-123	B1	+27.82	-107.2	1.3	50
HFCs	R-134a	A1	-26.07	-101	14	1000
	R-152a	A2	-24.02	-117	1.4	1000
HFC Blends	R-404A	A1	-46.22	-178	40.36	1000
	R-410A	A1	-51.44	-155	16.65	1000
HCs (Natural)	R-290	A3	-42.08	-190	9 – 15	1000
	R-600a	A3	-11.67	-145	9 – 15	1000
HFOs	R-1234yf	A2	-29.4	-150	0.030116	500
	R-1234ze	A2	-19	-156	0.05	800
Naturals	R-744	A1	-78.4	-56.6	29300 – 36100	5000
	R-717	B2	-33.33	-77.8	0.019165	25

The variation of liquid and vapour densities for CO_2 and some common selected refrigerants for a wide range of temperatures are shown in Figures 4 and 5, respectively. The liquid density of carbon dioxide (CO_2) decreases to increase temperature. For the refrigeration cycle, the high working pressure of CO_2 results in high vapour density. The vapour density of CO_2 increases to increase temperature. The liquid to vapour density ratio of carbon dioxide is increasing with increasing temperature.

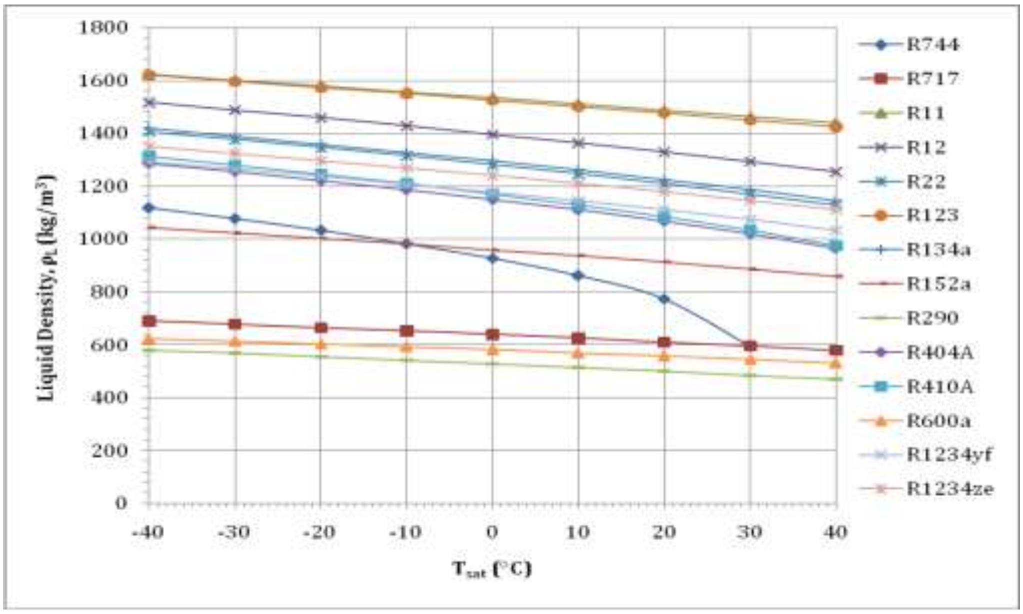

Figure 4: Saturated liquid density of the common selected refrigerants.

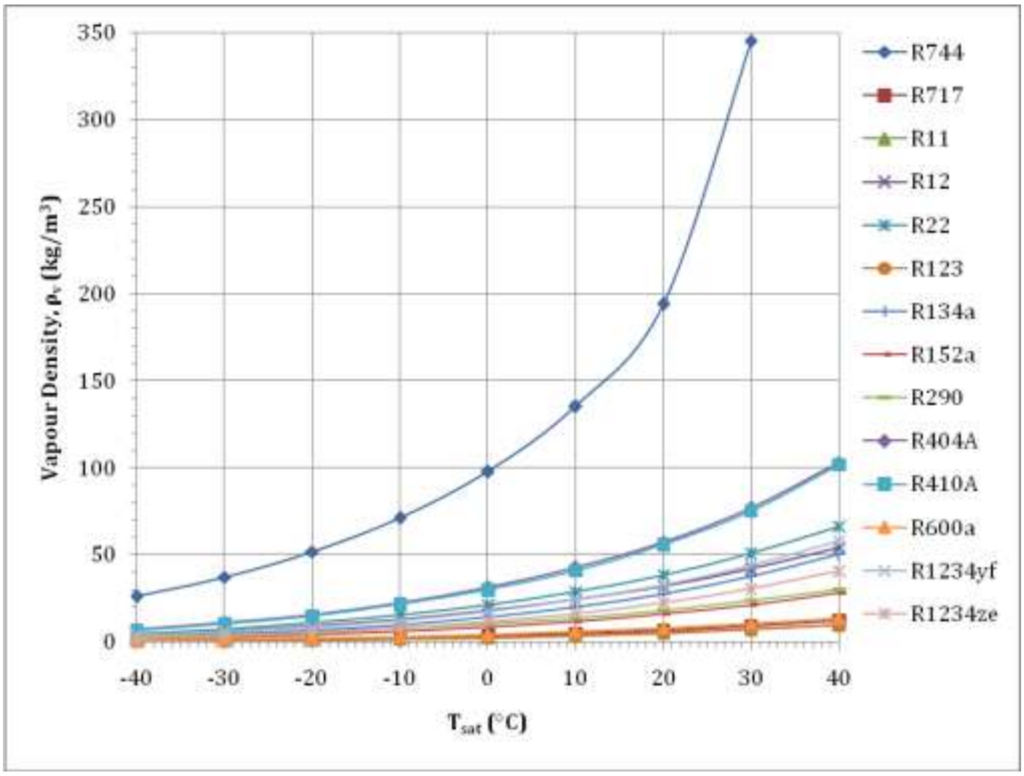

Figure 5: Saturated vapour density of the common selected refrigerants.

Table 5 shows the values of liquid and vapour densities for most of the common selected refrigerants at 25°C including CO$_2$. At 25°C the liquid and vapour densities are 710.50 kg/m^3 and 242.73 kg/m^3 respectively. At temperatures above 31°C, the density of liquid and vapour are identical, and liquid CO$_2$ cannot be distinguished from vapour. Because vapour CO$_2$ cannot condense into liquid, in this state the properties of temperature and pressure are no longer related. This is called "supercritical". In the supercritical phase, CO$_2$ system operates the best in high pressure range (110-172 bars). The transcritical CO$_2$ system can operate in the supercritical range. It is more efficient when operated in the subcritical range. That is why transcritical CO$_2$ systems are more widely accepted in this region where ambient temperatures are frequently below 31°C. The refrigerants with high vapour density require small compressors, pressure drop will be small, and tubes of smaller diameter can be used.

Table 5: Latent heat of vaporisation, Saturated density and Dynamic viscosity for the common selected refrigerants

Refrigerant		Latent Heat of Vaporisation, h_{fg} (kJ/kg) @ NBP	Density, ρ (kg/m^3) @ 25°C		Viscosity, μ (μPa.s) @ 25°C	
			Liquid	Vapour	Liquid	Vapour
CFCs	R-11	181.22	1476.26	6.11	424.04	11.028
	R-12	166.17	1311.02	36.83	191.05	11.785
HCFCs	R-22	233.75	1190.62	44.26	165.8	12.685
	R-123	170.19	1463.88	5.88	417.6	10.735
HFCs	R-134a	216.97	1206.67	32.37	197.9	11.805
	R-152a	329.91	899.45	18.46	163.2	10.06
HFC Blends	R-404A	201.10	1044.05	66.40	128.147	12.153
	R-410A	272.97	1058.60	64.87	122.04	13.46
HCs (Natural)	R-290	426.11	492.36	20.61	96.81	8.27
	R-600a	366.18	550.65	9.12	150.30	7.50
HFOs	R-1234yf	180.1	1091.90	37.92	155.4	12.3
	R-1234ze	195.4	1163.09	26.32	199.4	12.2
Naturals	R-744	571.5	710.5	242.73	57	20.16
	R-717	1369.5	602.8	7.80	131.7	9.835

Table 5 shows the values of latent heat of vaporisation for most of the common selected refrigerants at normal boiling point of related refrigerant. It is denoted by h_{fg} i.e. $h_{fg} = (h_g - h_f)$ in kJ/kg, where h_g and h_f are saturated vapour and liquid enthalpies respectively. The latent heat of vaporisation at evaporator temperature is also known as refrigeration effect. High value of latent heat of vaporisation results in high coefficient of performance (COP) because coefficient of performance (COP) is directly proportional to refrigeration effect (RE). The coefficient of performance [Arora 2009] is given by:

$$\text{COP} = \frac{\text{Refrigeration Effect}}{\text{Workdone}}$$

We know that a refrigerant should have a high latent heat of vaporisation at the evaporator temperature. The high latent heat results in high refrigeration effect per kg of refrigerant circulated (reduces the mass of refrigerant) which reduces the mass of refrigerant to be circulated per tonne of refrigeration (TR) i.e. lower mass flow rate. Figure 6 shows the latent heat of vaporisation of carbon dioxide (CO_2) and other selected common refrigerants at wide range of temperature (-40°C to 40°C). CO_2 has large value of latent heat of vaporisation, except NH_3 which has high value. The values of latent heat of vaporisation at 25°C and normal boiling point are 119.64 and 571.5 kJ/kg respectively.

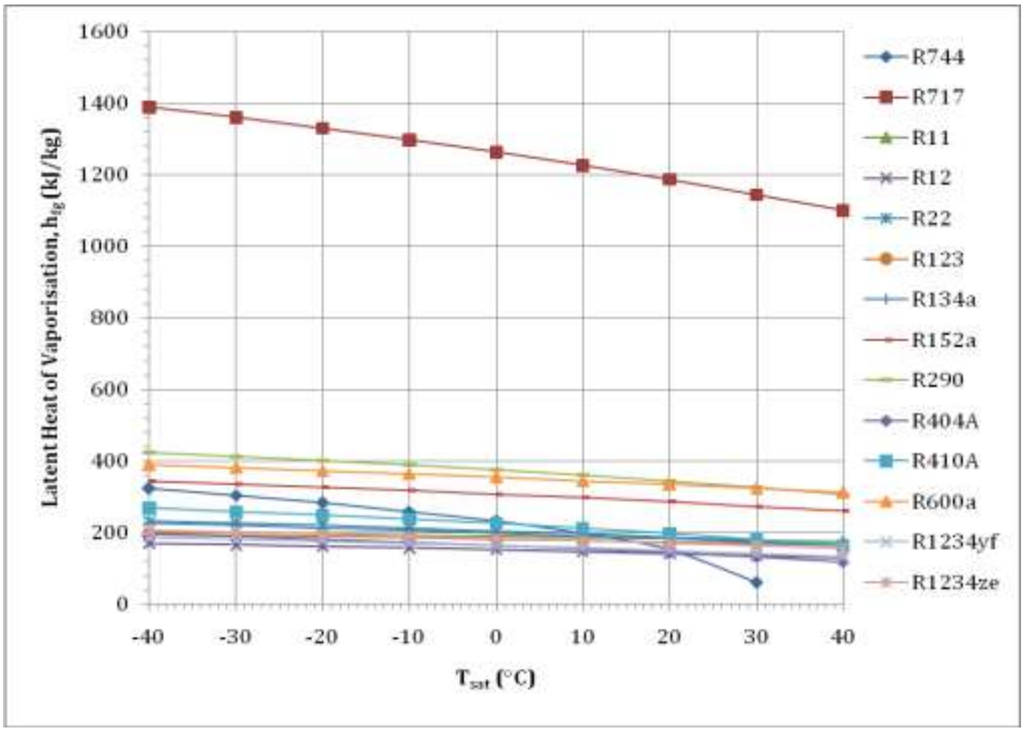

Figure 6: Latent heat of vaporisation for common selected refrigerants.

For an efficient system, both the volumetric refrigeration capacity (VRC) and coefficient of performance (COP) should be as high as possible. Due to its high operating pressure, the compressor of a carbon dioxide refrigeration system is very small even for a comparatively large refrigerating capacity. The high COP minimizes the running cost and the high VRC minimizes the investment cost. Carbon dioxide has a very high volumetric refrigeration capacity, as much as 5 or 6 time of other common refrigerants at low temperature due to its relatively lower specific volume. This means that the same volume of CO_2 can absorb much more heat than other refrigerants; therefore, much less CO_2 is required to provide the same cooling effect. The pressure drop is much lower as well as the corresponding temperature drop, which permits the design of smaller component and more compact systems. The volumetric refrigeration capacity [Bansal 2012] is defined as the ratio of the volumetric capacity in kJ to the swept volume in cubic meter.
Mathematically,

$$\text{Volumetric Refrigeration Capacity (VRC)} = \frac{\text{Volumetric Capacity}}{\text{Swept Volume}} \left(\frac{\text{kJ}}{\text{m}^3}\right)$$

The high value for the volumetric refrigerating effect means a smaller refrigerant vapour volume flow rate is needed for a given cooling capacity.

The liquid and vapour dynamic viscosity of the carbon dioxide and other common selected refrigerants for a wide range of temperature, are shown in Figures 7 and 8, respectively. The table 5 shows the values of liquid and vapour dynamic viscosities for common selected refrigerants at 25°C. The refrigerant in the liquid and vapour states should have low viscosity. The low viscosity is desirable because the pressure losses in passing through liquid and suction lines are smaller than other refrigerants. The heat transfer through condenser and evaporator is improved at low viscosities.

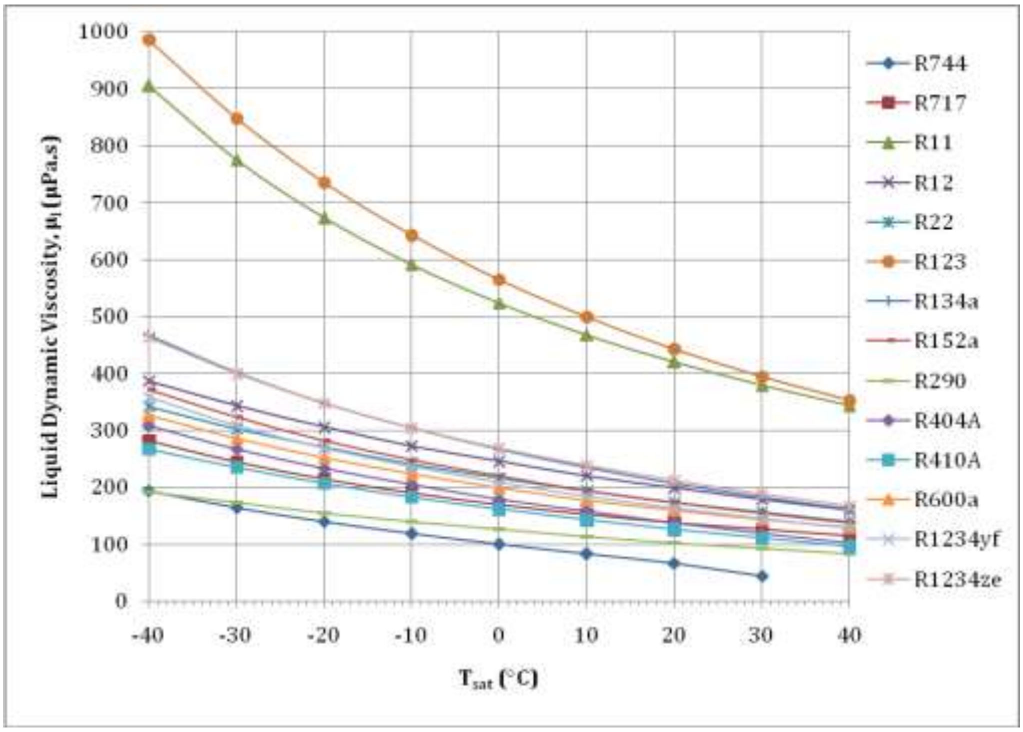

Figure 7: Saturated liquid dynamic viscosity for the common selected refrigerants.

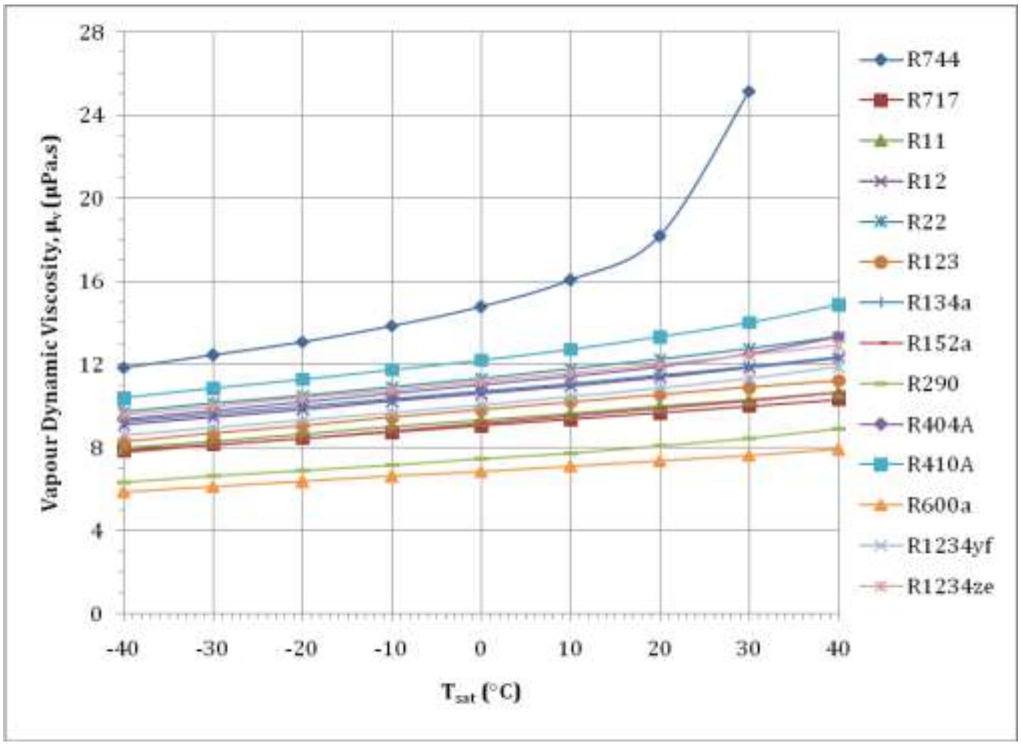

Figure 8: Saturated vapour dynamic viscosity for the common selected refrigerants.

The thermal conductivity and surface tension for the common selected refrigerants are given in Table 6.

Table 6: Saturated thermal conductivity and Surface tension for the common selected refrigerants

Refrigerant		Thermal conductivity, k (W/mK) @ 25°C		Surface Tension, σ (N/m) @ 25°C
		Liquid	Vapour	
CFCs	R-11	0.08983	0.00889	0.01777
	R-12	0.06715	0.010295	0.008545
HCFCs	R-22	0.08365	0.011395	0.00808
	R-123	0.0764	0.00918	0.01518
HFCs	R-134a	0.08115	0.01382	0.00808
	R-152a	0.09795	0.014785	0.009735
HFC Blends	R-404A	0.06703	0.01602	0.00455
	R-410A	0.09931	0.01572	0.005298
HCs (Natural)	R-290	0.09412	0.01896	0.006984
	R-600a	0.089004	0.01682	0.010102
HFOs	R-1234yf	0.067	0.016	0.00608
	R-1234ze	0.0781	0.0136	0.01280
Naturals	R-744	0.0808	0.04551	0.00055
	R-717	0.48555	0.02616	0.02481

Figures 9 and 10 shows the liquid and vapour thermal conductivities of CO_2 and some other selected common refrigerants at wide range of temperature (-40°C to 40°C). It should have high for both liquid and vapour. The thermal conductivity is required to find the heat transfer coefficients. Large thermal conductivities mean large amount of heat transfer rate.

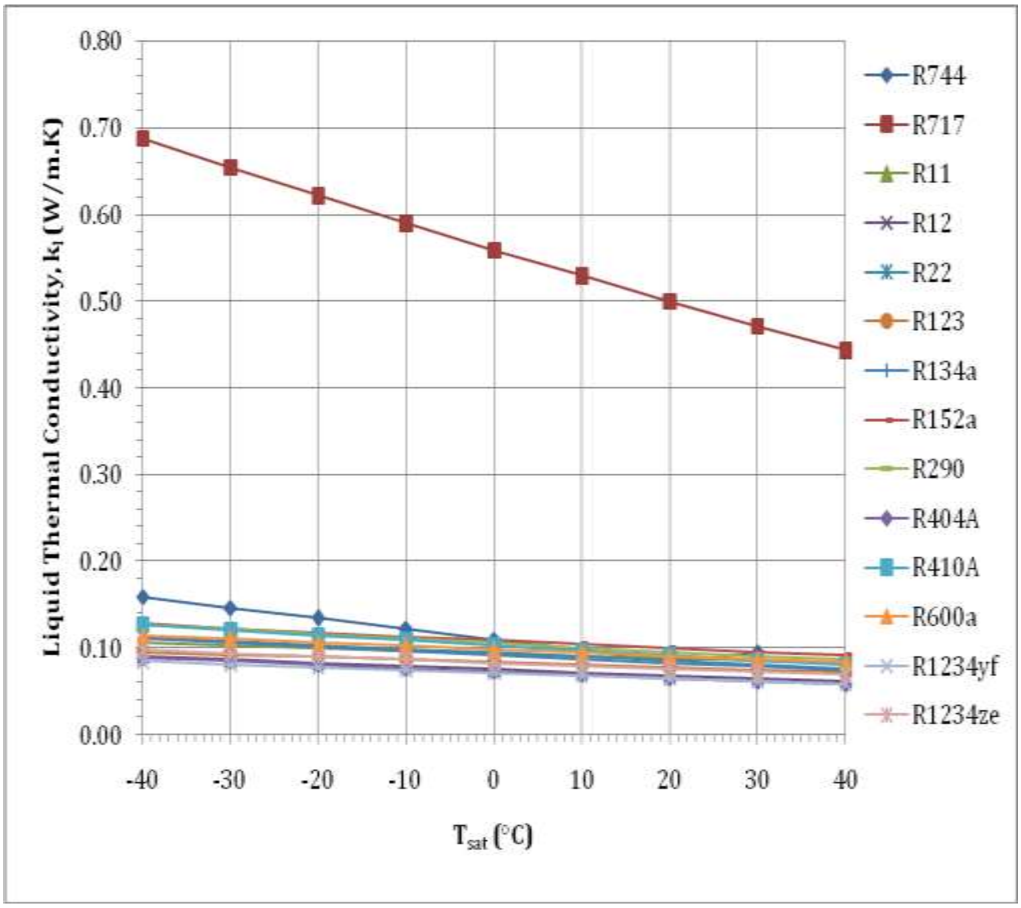

Figure 9: Saturated liquid thermal conductivity for the common selected refrigerants.

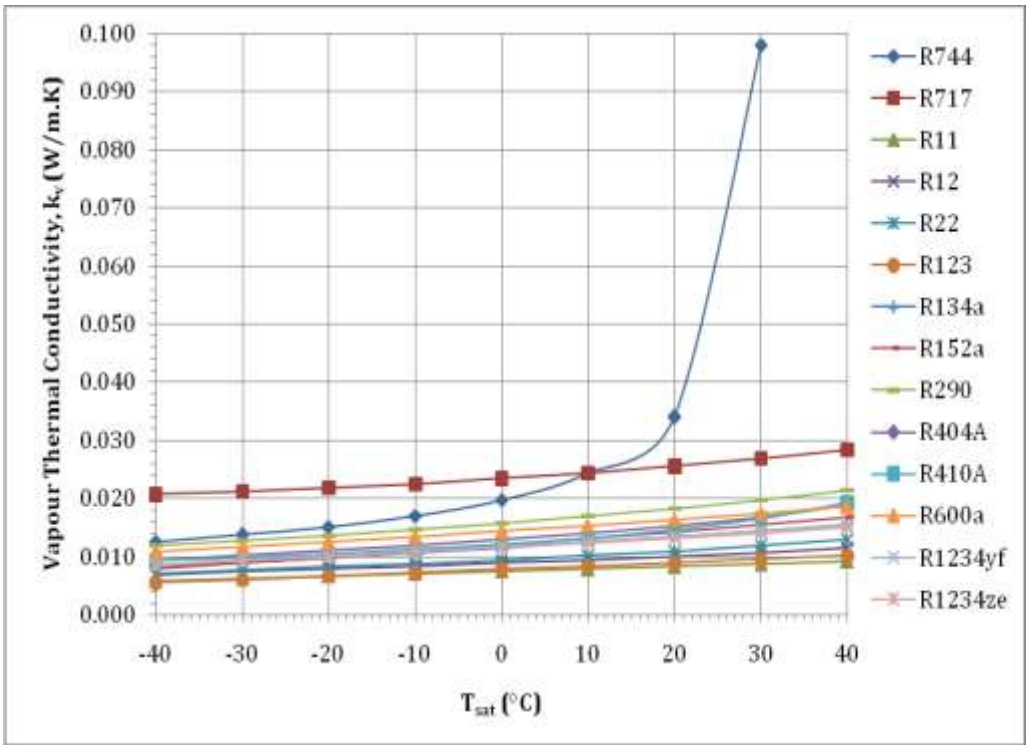

Figure 10: Saturated vapour thermal conductivity for the common selected refrigerants.

Surface tension in refrigerant fluids influences nucleate boiling and two-phase flow characteristics. A low surface tension reduces the overheating required for nucleation and growth of bubbles of steam, which will improve the heat transfer. Figure 11 shows the surface tension properties of common selected refrigerants. The surface tension of CO_2 is low compared to other common selected refrigerants. It has a coefficient of heat transfer higher than conventional refrigerants except for ammonia [Padalkar and Kadam, 2010].

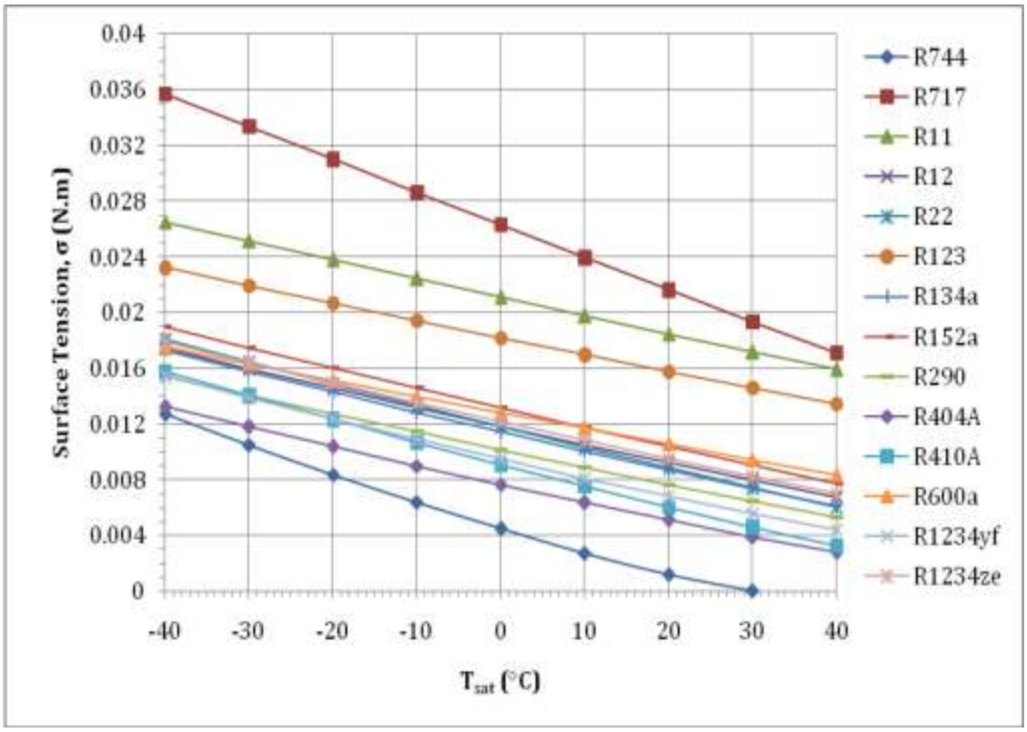

Figure 11: Surface tension for the common selected refrigerants.

Some other properties of the refrigerant CO_2 as compared to the common selected refrigerants which are used or using as following in Tables 7 and 8.

Table 7: Specific heat and Specific volume for the common selected refrigerants

Refrigerant		**Specific heat, C_p (kJ/kgK) @25°C**		**Specific volume (m^3/kg) @ -15°C**
		Liquid	**Vapour**	
CFCs	R-11	0.8802	0.6094	0.770
	R-12	0.9885	0.7005	0.0918
HCFCs	R-22	1.2565	0.8725	0.078
	R-123	1.0195	0.695	0.902
HFCs	R-134a	1.425	1.0315	0.121
	R-152a	1.800	1.2535	0.05417
HFC Blends	R-404A	1.543	1.228	0.01527
	R-410A	1.715	1.460	0.01511
HCs (Natural)	R-290	2.7386	2.0740	0.04847
	R-600a	2.4518	1.8202	0.1097
HFOs	R-1234yf	1.411	1.056	
	R-1234ze	1.383	0.9822	
Naturals	R-744	6.467	8.212	0.0167
	R-717	4.7845	3.1355	0.510

Table 8: State of refrigerant, Cylinder colour code/Refrigerant colour, Odour and Polytropic index for the common selected refrigerants

Refrigerant		**State of Refrigerant**	**Cylinder colour code /Refrigerant Colour**	**Odour**	**Polytropic Index, n**
CFCs	R-11	Liquid under pressure	Orange/Colourless	Faint ethereal and sweetish	1.13
	R-12	Liquid under pressure	White/Colourless	Odourless	1.126
HCFCs	R-22	Liquefied gas	Light green/Colourless	Faint ethereal and sweetish	1.166
	R-123	Liquid under pressure	Light Blue gray /Colourless	Faint ethereal and sweetish	1.134
HFCs	R-134a	Liquefied gas	Light Blue (sky) /Colourless	Slight ethereal	1.102
	R-152a	Liquefied gas	Blue/Colourless	Slight ethereal	1.26
HFC Blends	R-404A	Liquefied gas	Orange/Colourless	Odourless	1.1
	R-410A	Liquefied gas	Light pink/Colourless	Ethereal	1.32
HCs (Natural)	R-290	Compressed gas	-/Colourless	Odourless	1.27
	R-600a	Liquefied gas	-/Colourless	Odourless	1.086
HFOs	R-1234yf	Compressed liquefied gas	Red/Colourless	Slight ethereal	1.20
	R-1234ze	Liquefied gas	-/Colourless	Slight ethereal	1.22
Naturals	R-744	Liquefied gas	Green gray/Colourless	Odourless	1.3
	R-717	Liquefied gas	Silver/Colourless	Strong pungent	1.31

5. Major applications of the CO_2 refrigerant

Refrigeration, air-conditioning and heat pump systems use working fluids as a means of transferring heat between heat sources and heat sinks [Riffat et al. 1997, Rezayan and Behbahaninia 2011]. These fluids must have properties which are suitable for operating these systems. In the case of refrigeration and air-conditioning systems, the working fluids must generally absorb heat at low temperatures (below 0°C) without freezing, and reject heat at higher temperatures and pressures while in the case of heat pump systems, the rejected heat of refrigeration or air conditioning systems at higher temperature and pressure is used for heating.

The CO_2 as a refrigerant is used in many different applications. The following list gives an overview of possible applications with the refrigerant CO_2 [Kaiser and Froschle 2010, Wang et al. 2010, and Maina and Huan 2015] in subcritical and transcritical areas.

1. Commercial refrigeration such as pharmaceutical, large space cooling.
2. Industrial refrigeration such as ice-creams, dairies.
3. Mobile air conditioning such as cars, buses and railways.
4. Residential air conditioning such as buildings, space cooling.
5. Transportation refrigeration such as trucks and heavy container.
6. Supermarket refrigeration such as food retails, small to large markets.
7. Convenience stores such as data centres, petrol stations and kiosks.
8. Commercial heat pumps such as water heating in hotels and buildings, space heating.
9. Industrial heat pumps for large heating purposes, heat recovery systems.
10. Heat pump dryers such as washing machines.

Different applications have many different requirements for the components in the system. A wide range of performance requirements and different dimensions are required. In particular, the compressors must fulfil specific usage conditions. These days, CO_2 as a refrigerant is expected to find economic and efficient application [Llopis et al. 2015] in the under-mentioned areas:

1. Medium and large cold storage systems, as an alternative to R22 and R717.
2. Supermarket cold and freezer display cabinets, as an alternative to R404a.
3. Low temperature blast, spiral, belt and tunnel freezers, as an alternative to R717.

Many large users in the food industry, like Nestle and Unilever [Shecco Europe 2014, Shecco North America 2015 and Shecco China 2015] are already using CO_2 in low temperature applications due to both an economic and environmental reasons. Some very large applications are currently being planned and built to use CO_2 as a refrigerant in Europe and the USA. CO_2 is accepted as an economically feasible working fluid for low temperature applications like chilled and frozen and the number of new installations of CO_2 low temperature applications are likely to grow rapidly in the near future.

In the supermarket sector, the use of CO_2 in freezer cabinets and cold rooms is new applications today. This technology has evolved very rapidly in the last some years into an economically competitive working fluid accepted by both supermarkets and installers. In general, two temperature levels are required in supermarkets for chilled and frozen products (for two stage evaporator system). Product temperatures of chilled and frozen stages around +3°C and –18°C [Sawalha 2008] respectively are commonly maintained. In these applications, with a large difference between evaporating and condensing temperatures, the cascade or other two stage systems become favorable and are adaptable for the two temperature level requirements of the supermarkets. The following sections describe CO_2-based working fluid systems [Matthiesen et al. 2010] that fulfil the refrigeration requirements of supermarkets.

1. Cascade system
2. Transcritical system with only CO_2 refrigerant
3. Transcritical booster system
4. Indirect secondary working fluid system

5. Safety issues with CO_2 as a refrigerant

Safety [Padalkar and Kadam 2010] is a major concern in any refrigeration application and it is a main reason, why the synthetic refrigerants dominated in the refrigeration industry for the last several decades? In the specific applications of commercial refrigeration, safety is more carefully considered because of the large number of people that might be affected in case of refrigerant leakage. It is one of the main problems to apply CO_2 secondary cycle in the commercial refrigeration. CO_2 leakage may occur due to failure of one of the components in the cycle due to the relatively high working pressure of CO_2 in the secondary circuit of the system (12 bars at –35°C).

For the CO_2 systems, a common issue [Sawalha and Palm 2002, Bardia et al. 2009] is the high pressure level. If the plant is stopped for system maintenance, component failure, a power cut or any other reason, the refrigerant inside the plant will start to gain heat from the atmosphere and with the result, the pressure inside the plant will increase. Components in the indirect system and the low temperature level of the cascade and transcritical systems will not stand high pressure as they are usually designed for a maximum pressure of 40 bars. CO_2 refrigerant has one main drawback that it is odourless and colourless gas which indicates it is not self alarming at the time of leaking [Emerson 2015]. This result the system must be equipped with any sensors that trigger an alarm when the CO_2 leak concentration level exceeds 5000 ppm. For the specific safety, acoustic and flashing light alarm devices or proper gas concentration measuring devices must be provided in the high pressure component's system where there are possibilities of CO_2 leakage. We know that the CO_2 is heavier than air; therefore, it will collect close to the floor when it leaks; thus, the sensors and ventilators in the space where CO_2 might leak and should be located close to the floor.

In the supermarket refrigeration systems [Finckh and Sienel 2010], CO_2 is used relatively in larger scale than other refrigeration applications that requires long distribution lines to supply the refrigerant and an accumulation tank for solutions where a pump is used. This results in a large system volume and consequently large refrigerant charge. If the concentration level of the leakage refrigerant is high, a large number of people in the shopping area will be exposed to it. Therefore, the concern over safety is a major factor over the choice of the type of system and refrigerant to be used.

Due to the presence of an accumulation tank in CO_2 system solutions which increases the charge and volume of the system, the expected explosive energy may be higher than conventional systems. However, explosive energy is more of a concern with systems where the occupants are close to the system's components; such as mobile air conditioning and residential air conditioning while in supermarket systems the high pressure components are in the machine room. So, the distribution lines are usually kept at a distance from the consumers.

From safety point of view, CO_2 is classified in group A1, according to ASHRAE Handbook [2005], which is the group of refrigerants that are least hazardous and without an identified toxicity at concentrations below 400 ppm. Naturally, CO_2 exists in the atmosphere at concentrations is around 350 ppm. It has been observed that CO_2 concentration between 300 to 600 ppm is adequate and normally people do not notice the difference. According to ASHRAE Standard 62 [1989], a CO_2 concentration of 1000 ppm is the recommended limit to satisfy comfort for the occupants. Thus, in a CO_2 controlled ventilation system fresh air should be supplied so that the CO_2 concentration level will not exceed this value. This is the case of an application when a small CO_2 generation rate is expected due to different human activities.

However, in the case of high leakage rate that might occur in supermarket space or in the machine room, the consequences of serious health hazards, such as suffocation, must be taken into account. The following table is a list of selected concentration levels of CO_2 and expected effects on the human health. Apparently, safety requirements such as proper ventilations and alarm systems must be in the machine room.

Table 9: Different Concentrations of CO_2 and the expected health consequences [Sawalha and Palm, 2002]

PPM of CO_2	Effects on health
350	Normal value on the atmosphere
1,000	Recommended not to be exceeded for human comfort
5,000	Long-term exposure limit (LTEL): 8 hours per day or 40 hours per week
15,000	Short-term exposure limit (STEL): 10 minutes
30,000	Discomfort, Breathing difficulties, Headache, Dizziness etc.
40,000	Immediately dangerous to life or health (IDLH)
1,00,000	Few minutes of exposure produces unconsciousness or Loss of consciousness
3,00,000	Quick death or Quickly results in an unconsciousness

7. Advantages of CO_2 refrigerant

CO_2 has one of the most promising natural refrigerants which are eco-friendly, energy efficient to provide low temperature in the refrigeration applications as well as heating applications due to its favorable thermodynamic properties [Padalkar and Kadam 2010]. Thus, there are some advantages of CO_2 refrigerant [Arora 2009, Wang et al. 2010, Bansal 2012, and Mota-Babiloni et al. 2017] as given below:

1. High refrigeration capacity due to high volumetric cooling capacity to reduce compressor and pipe size.
2. Low pressure drop in pipe work and heat exchanger.
3. High heat transfer in evaporators and condensers due to the high pressure and density.
4. Greater pressure drop across an expansion valve than the other refrigerants.
5. Lower compression ratio leading to higher compressor isentropic efficiency.

6. Non-corrosive with most materials.
7. Good miscibility with compressor lubricants for oil return.
8. Low toxicity and non flammable.
9. Zero ozone depletion potential (ODP).
10. Negligible global warming potential (GWP).
11. Low cost and easy availability than other refrigerants.
12. High discharge temperature due to the high index of compression.
13. No impending legislation phasing out of R-744 (long term refrigerant).
14. Reduced carbon emissions (refrigerant is confined to a machine room where there are fewer braze joints and a significant reduction in potential for leaks in the system).
15. Additionally, various benefits such as better temperature control, reduced installation cost and space savings are found.

8. Problems of CO_2 refrigerant

There are many problems when CO_2 is used as a refrigerant [Riffat et al. 1997, Sawalha and Palm 2002, and Arora 2009] in the refrigeration system, e.g.:

1. High pressure is more hazardous and increase in leak potential requires specially designed components.
2. Special compressors are needed because of the higher refrigeration capacity.
3. Carbon dioxide (R-744) systems are more complex (either cascade or transcritical system), which requires higher costs in components and installation of the system.
4. Pipe working requires steel or stainless steel for which specially licensed welders are needed.
5. The greater complexity also increases the probability of poor performance and reliability.
6. For the transcritical systems two stage compressions is required for frozen food applications because of the high discharge temperature of carbon dioxide (R-744) refrigerant.
7. Carbon dioxide (R-744) is not controlled by any regulation; hence its use is not monitored carefully.
8. Very sensitive to water contamination and can cause unusual problems when there are leaks in a cascade heat exchanger.

The refrigerant will solidify and plant will stop, if the operating conditions are below approximately 5.2 bars and 56.6°C [Padalkar and Kadam 2010] within the refrigeration system.

9. Future opportunities of CO_2 as a refrigerant

There are many opportunities of carbon dioxide (CO_2) as a refrigerant in near future work to be needed. These future opportunities of carbon dioxide (CO_2) as a refrigerant are given following:

1. As there are tremendous market opportunities in India in the supermarkets sector, the opportunities for using natural refrigerants is also huge. So, more research and work regarding to the CO_2 as a refrigerant will need to be done.
2. Future CO_2 refrigeration technology needs to work closely with refrigerant and system manufacturers, industry organizations and government agencies to improve compressor performance, efficiency and reliability, while reducing environmental impact.
3. Increased uptake of natural refrigerants, India will require capacity building of informal and formal servicing sectors which will increase the scope of the servicing industry to grow in terms of equipment support, recovery, reclamation and reuse of refrigerants at the end of system life.
4. Contain refrigerants in tight or closed systems and containers, minimizing atmospheric releases.
5. Carbon dioxide has the potential to improve the performance, environmental impacts and economics of refrigeration systems. In order to gain a better understanding of the operating characteristics and feasibility of CO_2 in refrigeration systems, further theoretical and experimental research is needed.
6. Need to be worked towards short and long term social, economic, and environmental benefits of natural refrigerants (in particular CO_2 refrigerant) and sustainable refrigeration technologies.
7. Market competition needs to be introduced in the area of safety systems, supply of natural refrigerants and new technologies, and R&D for new efficient refrigeration systems.

10. Conclusions

In this section, there are many conclusions that can be drawn from this study. In this report, the overview, characterization and applications of CO_2 as a refrigerant have been studied. The CO_2 is a natural refrigerant because it exists in the atmosphere or naturally. The literature surveys show that amongst the natural refrigerants, the use of CO_2 and seem to be the most promising one particularly in the supermarket refrigeration that can be used in future for a long time. The key advantages of CO_2 include the fact that is not explosive, non-toxic, easily available, environmental friendly and has excellent thermo-physical properties. Being natural, CO_2 does not present unforeseen threats to the environment, it has no ODP and its GWP value is 1. It is cheap and has good safety characteristics which make it is an almost ideal refrigerant for use in refrigeration systems with relatively large quantities.

Carbon dioxide (CO_2) has proven its potential as an appropriate working fluid in today and in future environmental challenges. Therefore, CO_2 technologies are acceptable solution for India. With increasing focus on climate gas emission reductions, strict regulations on the use of CFC and HCFC refrigerants may be expected, possibly followed by phase-out targets and dates as announced by European Union (EU). These trends will clearly drive the interest in the direction of natural refrigerants in the near future. India will need to jump to the natural refrigerants from HCFCs skipping the use of the intermediary HFCs altogether. We need to switch to natural refrigerant based systems (e.g. CO_2 based systems) owing of the environmental issues. Some of yesterday's solutions have had consequences for today's environment, it is imperative that the industry looks ahead to find future proof solutions to current challenges.

11. Nomenclatures and Greek symbols

ρ – Density (kg/m^3)
η – Efficiency
μ – Dynamic Viscosity (Pa/sec)
σ – Surface Tension (N/m)
°C – Degree Celsius
c_p – Specific Heat (J/kgK)
CFC – chlorofluorocarbon
CO_2 – Carbon Dioxide
COP – Coefficient of Performance
EU – European Union
F-gas – Fluorinated gas
GHG – Greenhouse Gas
GWP – Global Warming Potential (100 years integration)
h – Specific Enthalpy (kJ/kg)
h_{fg} – Latent heat of vaporisation or phase change (kJ/kg)
HC – hydrocarbon
HCFC – hydrochlorofluorocarbon
HFC – hydrofluorocarbon
HFO – hydrofluoroolefin
J/kgK – Joule per kilogram per Kelvin
k – Thermal Conductivity (W/mK)
kg/m^3 – kilogram per cubic meter
kg/sec – kilogram per second
kJ/kg – kilojoules per kilogram
kW – kilowatt
N/m – Newton per meter
N – System Operating Lifetime (years)
NBP – Normal Boiling Point (°C)
NH_3 – Ammonia
ODP – Ozone Depletion Potential
OEL – Occupational Exposure Limit (ml/m^3)
p – Pressure (bars or MPa)
Pa/sec – Pascal per second
R/D – Research and Development
R404A – A common refrigerant that is a mixture of other refrigerants

R744 – The name of CO_2 when it's used as a refrigerant
T – Temperature (°C)
$\dot{W}$ – Power input (kW)
W/mK – Watt per meter per Kelvin

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Biography (Uga Ram Prajapat)

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