CHAPTER 1

Introduction

1.1 Refrigerant

The medium or working agent in a refrigeration or air-conditioning system that absorbs heat from the low temperature load, carries and releases the same to the high temperature sink is termed as a refrigerant. In a vapor compression cycle, the refrigerant is the working fluid in a cyclic process that alternately vaporizes and condenses as it absorbs and gives off heat, repeatedly. Refrigerants are broadly categorized as artificial or natural fluids. Typical, artificial refrigerants include Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs), Hydrofluorocarbons (HFCs) and Hydrofluorolefins (HFOs). Propane, carbon dioxide, nitrous oxide and ammonia constitutes natural refrigerants. Selection of a refrigerant for the applications like large commercial setup, mobile application (passenger car or cold chain truck), small scale domestic system etc., is decided based on many factors. To be suitable for use as a refrigerant, a fluid should possess certain favourable chemical, physical and thermodynamic properties.

Density of a refrigerant influences pressure drop through the refrigerant circuit as well as the compressor capacity. The lower the vapor density, the larger will be the pressure drop in the evaporator and the condenser for a given mass flux. In other words, for a given compressor size and speed, a lower vapor density will result into lower capacity. So, high density refrigerants are preferable.

Refrigerant viscosity should be small in both liquid and vapor phases to have smaller frictional pressure drops. Higher value of refrigerant viscosity leads to increase in pressure drop in both evaporators and condensers. Thus, with increase in refrigeration viscosity suction pressure at the compressor inlet as well as the mass flow rate of refrigerant decreases and the discharge pressure increases, resulting in reduction in system capacity. Higher liquid viscosities also give rise to reduced heat transfer coefficients. Hence low viscosity refrigerants are desirable.

Lower value of heat capacity of refrigerant may lead to increase in consumption of compression power as well as the discharge temperature. On the other hand, in case refrigerant possess a high heat capacity, wet compression may occur, resulting in damage to the compressor. Therefore, a trade-off in the value of the heat capacity of refrigerant is necessary. A higher liquid thermal conductivity of refrigerant is beneficial because it gives rise to a higher heat transfer coefficient.

The energy losses across a compressor's valves are high when the molecules are heavy. Therefore, a low value of molecular weight is preferred for high efficiency. Large value of enthalpy of evaporation is desirable and the same is found higher for substances with lighter molecules. Fluids having a higher vapor pressure would also have higher value of volumetric refrigeration capacity and will thus require a smaller compressor displacement rate to deliver similar capacity.

For better performance, the critical temperature should be high so that the condenser temperature remains below the critical point. This ensures reasonable refrigerating effect which becomes very small if the state of liquid before expansion is near the critical point. The critical pressure should be low to have lower condensing pressure.

The refrigerants should preferably be non-flammable and non-explosive. For flammable refrigerants, special precautions need to be taken to avoid accidents. ASHRAE, (2014) has divided refrigerants into six safety groups (A1 to A3 and B1 to B3). Abbreviation A stands for flammability with number 1 indicating no flammability and number 3 as most flammable. Abbreviation B stands for toxicity and number 1 to 3 indicates the increasing extent of toxicity. Consequently, refrigerants belonging to Group A1 (e.g. R11, R12, R22, R134a, R744) are least hazardous, while refrigerants belonging to Group B3 (e.g. R290) are most hazardous. Toxicity level of refrigerants is also an important criterion for decision making on its applicability to an application. A refrigerant may be poisonous/intoxicating when inhaled in sufficient quantity. Toxicity becomes meaningful only when the degree of concentration and time of exposure required to produce harmful effects are also specified. Some fluids are toxic even in very small concentrations. While, some other are mildly toxic, i.e., they are dangerous only when the concentration is large, and duration of exposure is long. Chlorofluorocarbons (CFCs) and Hydrochlorofluorocarbons (HCFCs) are non-toxic when mixed with air in normal condition. However, when they meet an open flame or an electrical heating element, they decompose forming highly toxic elements (e.g. phosgene-$COCl_2$).

The solubility of lubricant oil in refrigerant in a refrigeration system is also an important parameter, which affects system performance. When refrigerant containing oil passes through the evaporator, the oil may precipitate from the refrigerant, which can partially block or choke up the refrigerant passage, leading to drop in performance. Deficit of oil may lead to oil starvation in compressor. In general practice the oils that are non-miscible with refrigerant are generally separated using an oil separator after compression and this oil is returned to the crank case of compressor. In few applications where installation of oil separator is not feasible, oil which is miscible is adopted.

Slight odor in a refrigerant is beneficial to detect leakage. A strong odor may make it difficult to service equipment, for example, special gas masks are needed for servicing an ammonia plant as ammonia has strong pungent odor. Sometimes the refrigerated materials may be ruined if the odor is too strong. The size of the molecule makes a difference in the tendency of a refrigerant to leak. The higher the molecular weight, the larger the gap must be for the refrigerant to escape. The refrigerant with higher molecular weight are preferred to suppress the leakage.

The Ozone depletion potential (ODP) of refrigerants should be as low as possible. Preference is for non-ozone depleting substances. Refrigerants having higher ODP have either been already phased-out (e.g. R 11, R 12) and is in the process being phased out (e.g. R22). Refrigerants should possess a low Global Warming Potential (GWP). GWP is an index that relates the potency of a greenhouse gas to the CO_2 emission over a 100-year period. Use of refrigerants with zero ODP but a high value of GWP (e.g. R134a) are also not favorable.

1.2 Carbon dioxide (CO_2) as natural refrigerant

In 1857, CO_2 as a refrigerant was first proposed by Alexander Twining in his British patent and very soon, the same developed into one of the most favourable refrigerants (Bodinus, 1999). In the late eighteenth and the early nineteenth century majority of refrigeration plants world over were based on CO_2 having cooling capacity range from 3 tons to 350. However, the usage of CO_2 as a refrigerant was a challenge, owing to the slow running compressors and reduction in cycle performance at high heat rejection temperatures. Further, at that time, it was difficult to restraint and use CO_2 at its high saturation pressure with the available sealing technology. Ammonia (NH_3), although being toxic, was the preferred choice for large capacity systems.

Despite of the apparent stable market of CO_2 and Ammonia (NH_3) as preferred refrigerants, the scientific community was continuously in the lookout for better refrigerant fluids, which would be safe in operation and could offer better performance even at high ambient temperature and could operate at low saturation pressure. Eventually, the first kind of synthetic refrigerant, CFCs were introduced by Thomas Midgley, Jr in 1928 (Midgley and Henne, 1930). The CFCs were non-toxic fluids having lower vapor pressure and excellent thermo-physical properties. Invention of CFCs allowed enormous penetration of refrigeration devices to domestic and commercial applications. While CO_2 and NH_3 were natural fluids, CFCs were patented and was aggressively marketed. This lead to quick decline of CO_2 system world over. Use of NH_3 however continued for industrial application. Factors such as efficiency loss at high temperature, problem of containment of high pressure CO_2, negligible improvement in the system design over the years were some of the other probable reasons for the very quick decline and demise of CO_2 refrigeration systems world over.

Owing to regulations laid by the Montreal Protocol to protect stratosphere on the usage of CFCs (Protocol, 1987), a short-term replacement introduced was HCFCs, which have much lower ODP as compared to CFCs. However, revisions were made to the Montreal Protocol, leading to restrict the usage of HCFCs and eventually, complete phase out of the same, by 2015 in developed countries. Following the awareness about the hazardous effects of CFCs and HCFCs on the environment, a second class of synthetic refrigerants, Hydrofluorocarbons (HFCs) were introduced in 1970s. HFCs possessed zero ODP and exhibited thermal and transport properties like those of CFCs and HCFCs. Therefore, HFCs were compatible to be used with machinery already designed for CFCs and HCFCs with only minor modifications. For instance, over the years R134a has grown as one of the most extensively used HFC for automobile air conditioning.

Meanwhile the world was getting conscious about greenhouse effect caused by industrial gases and some of the refrigerants. Finally, in 1997, the Kyoto Protocol (Protocol, 1997) was introduced that included HFCs in the class of fluids which were partly responsible for 'Global Warming' due to their high GWP. Subsequently, production of HCFC was reduced by 7.7m tonnes (equivalent to 26 giga tonnes of CO_2 emissions) owing to an immediate phase-out call for HCFCs decided in Montreal in 2007. Fluorinated-gases (F-gas) regulation, developed as a part of Montreal Protocol, also came under action leading to regulated use of fluorinated greenhouse gases such as HFCs, perfluorocarbons (PFCs) and sulphur hexafluoride (SF6). The new F-gas regulation was adopted in 2015, which stipulated ban of HFCs having GWP higher than 150 (EU 517/2014, 2014). In such situation, focus shifted to natural refrigerants such as air, water, ammonia, carbon dioxide (CO_2), noble gases, hydrocarbons etc. which can be utilized as refrigerants, as long-term solutions for Heating Ventilation and Air Conditioning (HVAC) applications. These substances are already present in biosphere and are harmless. The roadmap of return of era of natural refrigerants and projected long term refrigerants is presented in Fig. 1.1.

Fig. 1.1 Roadmap of return of era for natural refrigerants

Among these, CO_2 is one of the preferred choices owing to its high specific heat, non-toxicity, non-flammability, eco friendliness and low cost. From the engineering perspective, CO_2 used as a refrigerant in vapour compression cycle has number of advantages such as high volumetric cooling capacity, compatibility with normal lubricants and common machine construction materials and along with favourable thermo-physical properties. It was in 1993, when Norwegian Professor Gustav Lorentzen through his work on automotive air conditioning (AAC) system, revived the attention of scientific community towards CO_2 (Lorentzen and

Pettersen, 1993). Subsequently, CO_2 as refrigerant gained considerable growth. Today, the major applications of CO_2 systems are in supermarket refrigeration, mobile air conditioning, heat pumps, water heaters, driers, simultaneous heating and cooling in dairy/ food processing industries etc. CO_2 is commercially available in compressed liquid form, stored in cylinders. The ranges of CO_2 charge (mass), purity and the pressure in the commercial cylinder are available in the range 4.5 kg to 200 kg, 95 % to 99.5 % purity and 2 MPa to 5.75 MPa. The properties of CO_2 are distinct from other commonly encountered refrigerants. The most distinguishing feature of CO_2 is its low critical temperature (31.1°C) with relatively higher critical pressure (73.9 bar). Owing to its low critical temperature, a CO_2 system will operate at high pressure and trans-critical mode and at pressures higher than that of conventional refrigerants. In a trans-critical cycle, high side pressure and temperature can be independently controlled to get the optimum operating condition. High pressure allows very high volumetric cooling capacity, leading to a compact design. Application areas where heat is discharged at gliding temperature, such as in a heat pump, can easily adapt the trans-critical process of the CO_2 cycle which has a temperature glide during heat rejection.

Variation of a few important properties of CO_2 such as isobaric specific heat, density, thermal conductivity and viscosity for a wide range of temperature and pressure covering most application areas are shown in Fig. 1.2 to Fig. 1.5 (Lemmon et al., 2002). The rapidly changing nature of thermo-physical properties near critical temperature are evident from Fig. 1.2 to Fig. 1.5. Consequently, the heat transfer characteristics of CO_2 is much different from other refrigerants and design of system is more challenging. A Pseudo-critical temperature is defined as the temperature at which the corresponding specific isobaric heat capacity attains the maximum value. Pseudo-critical temperature is a strong function of pressure and temperature. Some thermo-physical properties of carbon dioxide at pseudo-critical temperature are listed in Table 1.1 (Lemmon et al., 2002). Referring to Fig. 1.2, the spike in the isobaric specific heat decreases with increase in the CO_2 pressure, further, the maxima shift towards higher temperature.

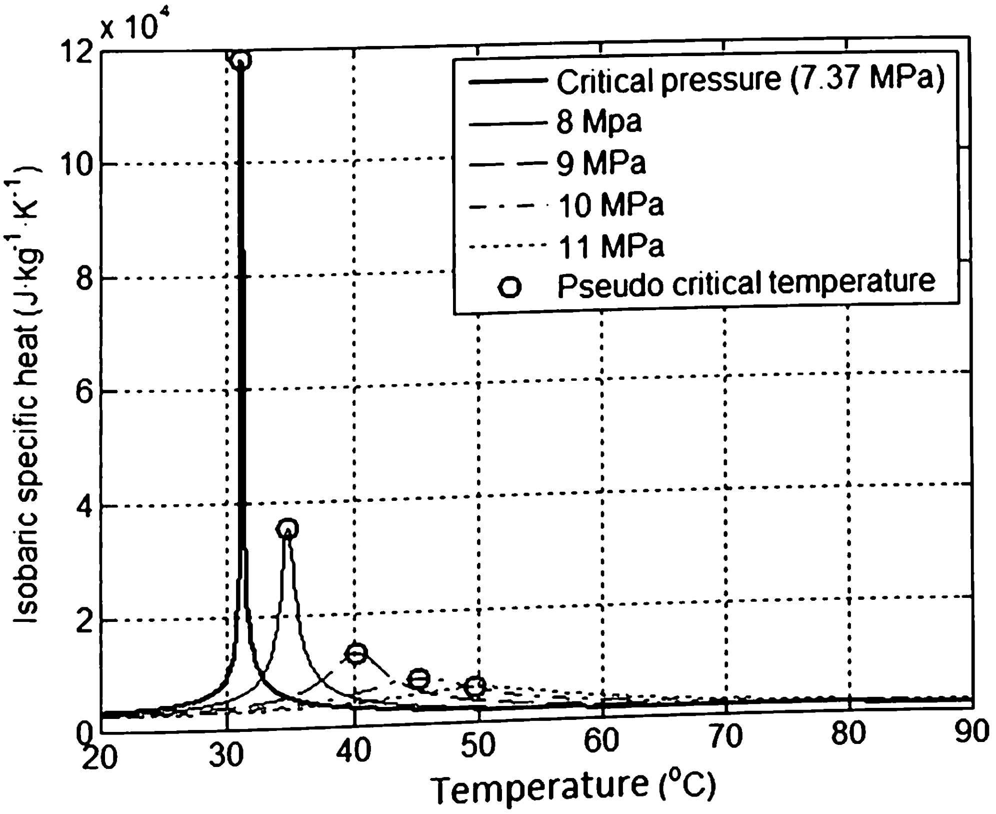

Fig. 1.2 Isobaric Specific heat versus temperature in supercritical range

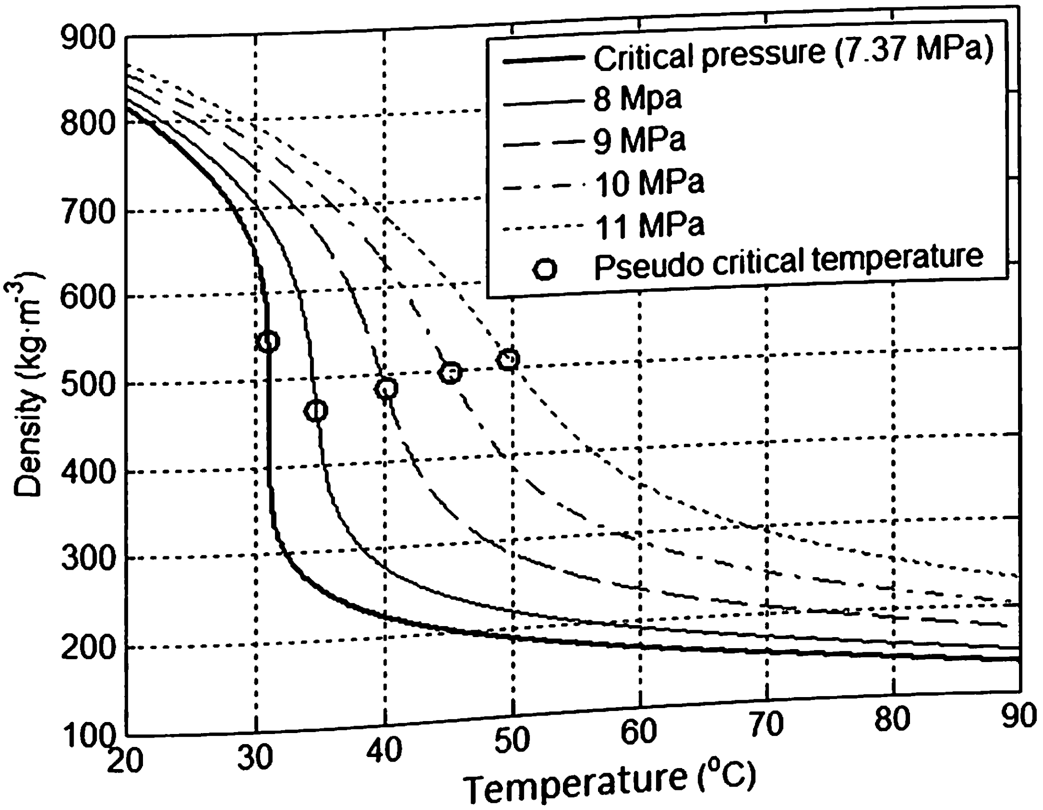

Fig. 1.3 Density versus temperature in supercritical range

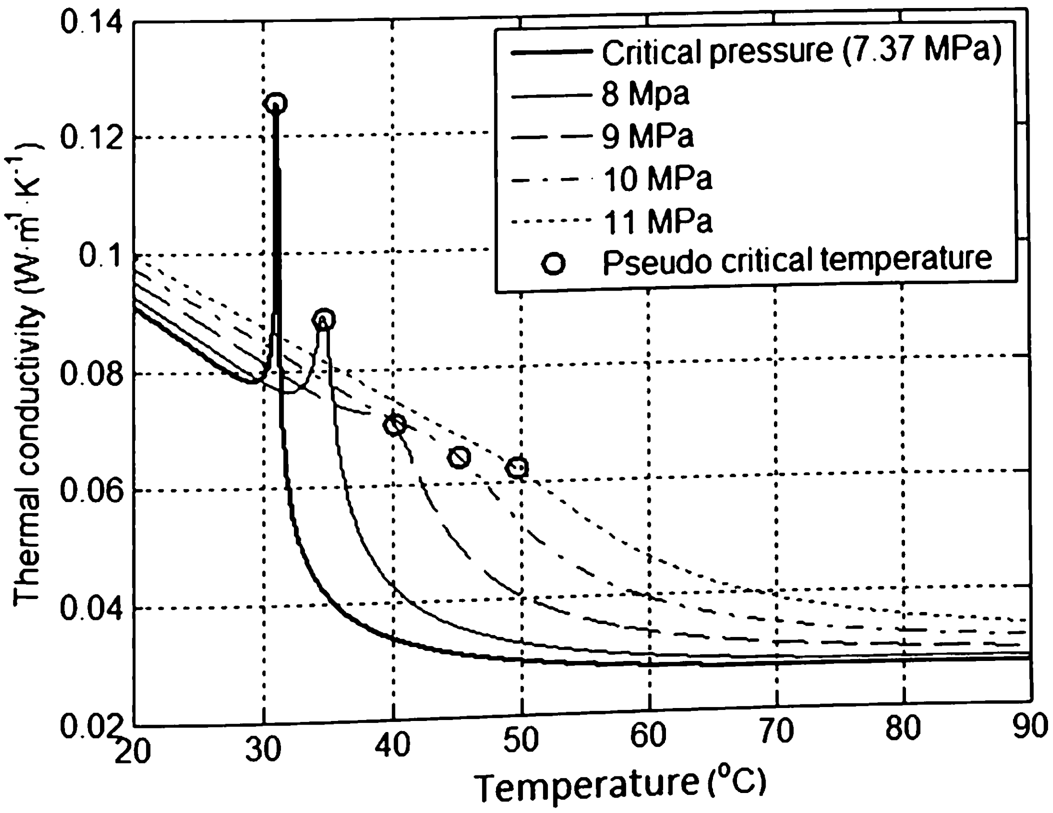

Fig. 1.4 Thermal conductivity versus temperature in supercritical range

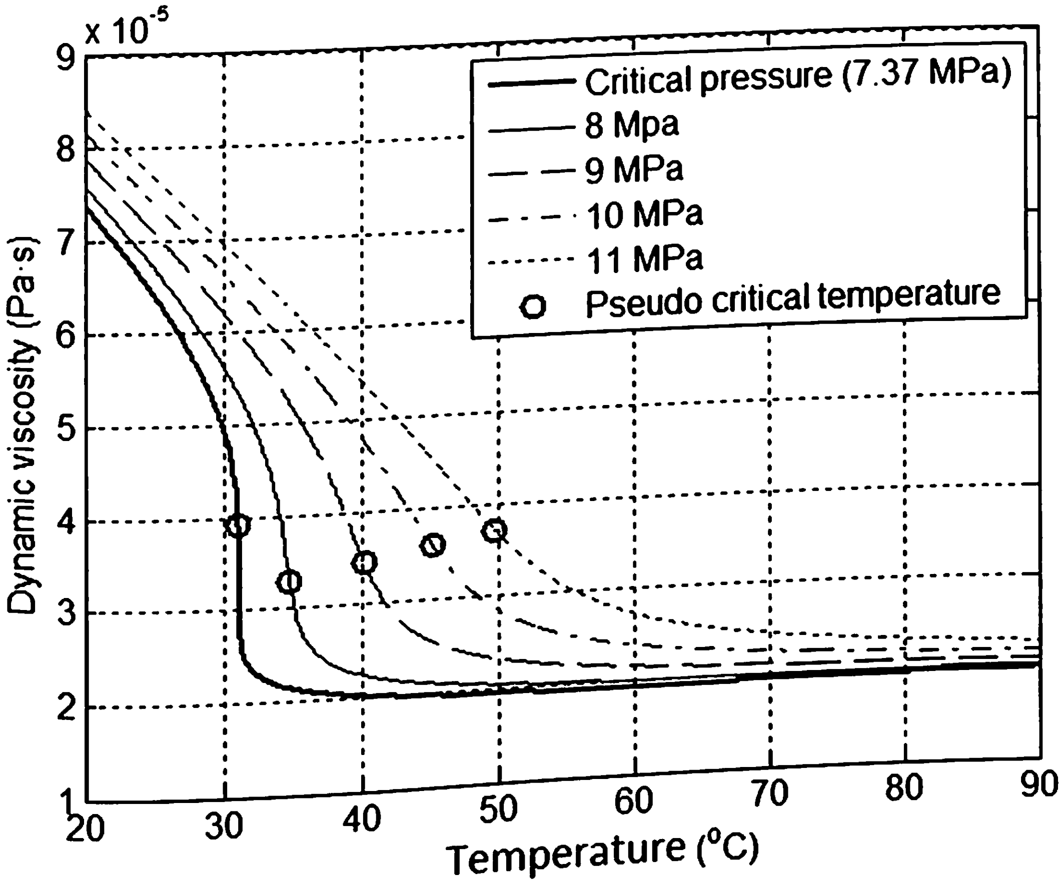

Fig. 1.5 Dynamic viscosity versus temperature in supercritical range

Table 1.1 CO_2 properties at pseudo-critical temperature

Property	7.39 MPa (Critical pressure)	8 MPa	9 MPa	10 MPa	11 MPa
T_{psc} (°C)	31.1	34.8	40.2	45.2	49.8
C_p (kJ·kg^{-1}·K^{-1})	118.1	35.2	12.8	8.08	6.07
ρ (kg·m^3)	544.3	456.2	486.7	498.1	509.7
K (W·m^{-1}·K^{-1})	0.1259	0.08874	0.07081	0.06485	0.0622
μ (mPa·s)	0.039	0.032	0.034	0.035	0.037

In general, CO_2 has some advantages and disadvantages as a refrigerant listed below:

✓ Being a naturally occurring substance, it is an environment friendly refrigerant. It is characterized by zero ODP and GWP of unity. It is a non-flammable and non-toxic refrigerant and requires no recycling.

✓ It has good compatibility with normal lubricants and commonly employed machine building material.

✓ CO_2 systems are quite compact due to high volumetric efficiency at high working pressure with pressure ratio much lower compared to conventional refrigerants. However, pressure and temperature need to be independently controlled in the supercritical region.

✓ High pressure and high density of CO_2 offers reduction in size of piping to almost ½ to 1/3 diameter to conventional refrigerants and the compressor size reduction of almost by a factor of 4. However, higher pressure operation requires extra attention owing to the safety aspects.

✓ Large temperature glides occur in the gas cooler during heat transfer and wider applicable temperature range is possible with such systems.

1.3 Comparison of CO_2 with other refrigerants

CO_2 is perceived to be a viable working fluid in a vapour compression refrigeration system. CO_2 has volumetric refrigeration capacity three times higher than that of popular synthetic refrigerant R134a, ensuring a reduction in components size as well as piping. It has lower surface tension, promoting substantially higher heat transfer coefficient than other conventional refrigerants, except Ammonia. It is relatively cheaper, environmentally benign (GWP: 1; ODP: 0), non-toxic and non-flammable. However, CO_2 possess a rather lower value of latent heat, which is a disadvantage, necessitating higher value of mass flow rate per unit cooling load. Table 1.2 lists important properties of CO_2 as refrigerant in comparison with other conventional refrigerants. CO_2, owing to its high operating pressure, easily meets the requirement of having minimum pressure at the inlet of compressor higher than 0.52 MPa (Kim et al., 2004). However, the high operating pressure as well as the low critical temperature of CO_2 (31.1°C), imparts a significant drop in efficiency of the refrigeration system when operated in warm climate (Gupta and Dasgupta, 2014; Sharma et al., 2014a).

Table 1.2 Comparison of CO_2 properties with other refrigerants (Lemmon et al., 2002)

Refrigerant			**ODP/ GWP**	**Flammable/ Toxic**	**p_{cr} (MPa)**	**T_{cr} (°C)**	**VC (0°C) ($kJ \cdot m^{-3}$)**
Synthetic	***CFCs***	***R11***	1/4000	No/No	4.43	198	392.4
		R12	1/2400	No/No	4.11	112	2113.3
	HCFCs	***R22***	0.05/1700	No/No	4.99	96.3	3425.4
		R141b	0.12/725	No/No	4.21	204.5	288.76
	HFCs	***R134a***	0/1430	No/No	4.05	101.1	2149.1
		R143a	0/4300	No/No	3.77	72.89	3582.9
	HFOs	***R1234yf***	0/4	Yes/No	3.38	94.85	2032.8
		R1234ze	0/6	Yes/No	3.63	109.52	1592.5
Natural		***R744***	0/1	No/Yes	7.39	31.1	11999.9
		R717	0/0	Yes/Yes	11.33	132.4	3770.9
		R744A	0.01/310	No/No	7.24	36.52	12614.5

Owing to high critical temperature of majority of conventional refrigerants, for example 101.1°C in case of R134a and 72.89°C in case of R143a (refer to Table 1.2), the conventional air-cooled condensers are operated based on floating condensing mode, with a set minimum condensing temperature. The high side pressure and the fan speed are thus modulated to meet the designed condenser approach temperature and the required sub-cooling. Such systems are also possible to be operated under simpler control system. Further, at a particular ambient condition, the efficiency of the system is observed to decrease monotonously with an increase in the operating pressure (in other words, increase in the approach temperature). However, in case of CO_2, which has a lower critical temperature when operated in warm climate in trans-critical mode, the design of air-cooled condenser and its real-time control is much more complex. For operation above the critical point, pressure and temperature of the refrigerant are no longer dependent on each other and instead, control of both, pressure and temperature, become necessary to achieve maximum possible COP (Kauf et al., 1999; Sarkar et al., 2004).

1.4 Motivation

Revival of CO_2 as a preferred working fluid for various HVAC applications took place post 1990s due to enhanced awareness about direct or primary environmental impact like ozone depletion and direct greenhouse effect caused by the synthetic refrigerants which, when released into atmosphere due to leakage at various stages of its production and handling. Further, secondary impact of carbon release due to substantial share of power consumption by HVAC sector was a concern. Certain synthetic refrigerants also have harmful water and soil contaminating potential. CO_2 is a biosphere gas having favourable thermo-physical properties and unit greenhouse effect and as a refrigerant in vapour compression cycle it has number of advantages such as lower compression ratio, higher vapor pressure and higher volumetric cooling capacity which leads to compact design. However, CO_2 as refrigerant, when operated in high ambient, has inherent challenges in operating such a high-pressure, drop in performance owing to the trans-critical operation and higher power consumption in the compressor. The operational performance parameters also become more sensitive to operating pressure at high ambient. It is imperative, therefore, to probe various possible means of enhancing COP to remove road blocks to large scale implementation of such system in high ambient.

1.5 Structure of the thesis

The work reported in this thesis has been organized into seven chapters. The content of each chapter is briefly described below:

Chapter 1 presents an introduction to the refrigerant, its nomenclature accompanied by revival of CO_2 and its typical thermo-physical properties. Comparison of properties of CO_2 with other conventional refrigerants is also presented. Lastly, the motivation of the work and the organization of thesis is elucidated.

Chapter 2 deals with a comprehensive review of literature. The review conducted includes the major cycle components of CO_2 refrigeration system followed by discussion on the studies reported for various modification strategies. The recent information on the commercial aspect of CO_2 refrigeration system followed by literature on supermarket application and research gap areas are discussed.

Chapter 3 presents the objectives of the thesis work.

Chapter 4 and 5 deals with the laboratory evaluation as well as theoretical investigation of a CO_2 refrigeration system equipped with internal heat exchanger.

Chapter 4 deals with experimentation on a designed and fabricated CO_2 trans-critical refrigeration system equipped with internal heat exchanger. Performance evaluation of the CO_2 trans-critical refrigeration system is conducted based on energetic and exergetic perspectives for operation in warm climate up to ambient temperature of 45°C.

Chapter 5 presents performance optimization of the CO_2 trans-critical refrigeration system tested experimentally in Chapter 4. Two different models are developed viz a physics-based model and an Artificial Neural Network model built from experimental input-output data. Evaporation temperature, ambient temperature, gas cooler pressure and air velocity over the gas cooler are chosen as input parameters to predict the energy efficiency using the models. The trained and validated neural network is employed to explore optimization of two controllable parameters (gas cooler pressure and gas cooler face velocity) for various ambient and evaporation conditions.

Chapter 6 deals with the application of CO_2 in supermarket refrigeration. First part of chapter presents the comparison of performance of five CO_2 booster refrigeration systems. The major focus is to quantify benefits in energy and economic perspectives for various modifications applied to the standard booster configuration. In addition, performance of standard booster configuration equipped with parallel compressor is compared to that of indirect/cascade configurations. Thereafter, integrated CO_2 based supermarket refrigeration system are investigated. The performance of an integrated all-CO_2 multi-jet ejector system is compared to that of a proposed all-natural integrated NH_3/CO_2 cascaded booster system for operation in cities with extreme weather conditions like Jodhpur in India and Kuwait in Middle East.

Chapter 7 reports the overall conclusion and the scope of future work.