A DISSERTATION ON

THEORETICAL EXERGY ANALYSIS OF HFO-1234yf AND HFO-1234ze AS AN ALTERNATIVE REPLACEMENT OF HFC-134a IN SIMPLE VAPOUR COMPRESSION REFRIGERATION SYSTEM

Submitted in partial fulfillment of the requirement

For the award of the degree of

Master of Technology

In

Thermal Engineering

Submitted By

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DECLARATION

I hereby declare that the work, which is being presented in this dissertation, entitled **“Theoretical Exergy Analysis of HFO-1234yf and HFO-1234ze as an alternative replacement of HFC-134a in Simple Vapour Compression Refrigeration System”** towards the partial fulfillment of the requirements for the award of the degree of Master of Engineering with specialization in Thermal Engineering, from Delhi technological University Delhi, is an authentic record of my own work carried out under the supervision of **Naushad A. Ansari,** Asst. Professor, Department Mechanical Engineering, at Delhi technological university, Delhi.

The matter embodied in this dissertation report has not been submitted by me for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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CERTIFICATE

It is certified that Bipin Yadav, Roll No. 2K11/THE/05, student of M.Tech. Mechanical Engineering, Delhi Technological University, has submitted the dissertation titled "Exergy Analysis of HFO-1234yf and HFO-1234ze as an alternative replacement of HFC-134a in Simple Vapour Compression Refrigeration System" under my guidance towards the partial fulfillment of the requirements for the award of the degree of Master of Technology.

He has developed a mathematical computational model for performing the energy and exergy analysis of the simple VCR system using EES software. His work is found to be satisfactory and his discipline impeccable during the course of the project. His enthusiasm, attitude, towards the project is appreciated.

I wish him success in all his endeavors.

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LIST OF SYMBOLS/ABBREVIATIONS

GWP	Global Warming Potential
ODP	Ozone Depletion Potential
COP	Coefficient of Performance
EDR	Exergy destruction ratio
$\dot{Q}$	Rate of heat transfer (kW)
$\dot{W}$	Work rate (kW)
$\dot{ED}$	Exergy destruction rate (kW)
$\dot{X}$	Exergy rate (kW)
$\dot{X}^{Q}$	Rate of thermal exergy flow rate (kW)
$\dot{m}_r$	Mass flow rate of refrigerant (kg/s)
T	Temperature (K)
s	Specific entropy (kJ/kg-K)
h	Specific enthalpy (kJ/kg)
V	Velocity of fluid (m/s)

Greek symbols

η	Efficiency
ε	Effectiveness
x	Specific exergy
δ	Efficiency defect

Subscripts

E	Evaporator
comp	Compressor
c	Condenser
lvhe	Liquid vapour heat exchanger
t	Throttle valve
j	jth component of the system
r	Region to be cooled or refrigerant
i	Inlet to the control region
e	Outlet to the control region
R	refrigerator
O	Ambient state

rev	Reversible
sub	Sub-cooling
su	Superheat
vcr	Vapour compression refrigeration system

ABSTRACT

An Exergy method for theoretical analysis of a traditional vapour-compression refrigeration system equipped with liquid vapour heat exchanger (lvhe) for HFO-1234yf (**2, 3, 3, 3-Tetrafluoropropene**) and HFO-1234ze **(trans-1, 3, 3, 3-tetrafluoroprop-1-ene)**, both ultra low GWP and zero ODP refrigerants and comparison of the results with HFC-134a refrigerant as possible alternative replacements in Automotive air-conditioning and stationary refrigeration is presented. A mathematical computational model has been developed for calculating Coefficient of performance (COP), exergetic efficiency, exergy destruction and efficiency defects for HFO-1234yf, HFO-1234ze and HFC-134a.During the investigation, condenser temperature is kept at 313K and 323K, evaporator temperature is kept in the range from 223K to 273K. Results obtained for selected condenser temperature are compared and discussed elaborately. It indicates that HFO-1234yf can be a good drop-in replacement of HFC-134a and HFO-1234ze can replace the HFC-134a after some modifications as the results are almost similar. Among the system components, condenser shows highest efficiency defect value and liquid vapour heat exchanger shows the lowest.

CHAPTER 1: INTRODUCTION

1.1. OVERVIEW

The first known instance of refrigeration was demonstrated by William Cullen at Glasgow University in 1748. Following that, in the early 19th century Michael Faraday compressed ammonia vapour into a liquid, and then followed the invention of the first refrigerator. During 1900’s, chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs) were extensively used in refrigeration and air conditioning vapour compression systems.[1] When their ozone-depleting potential became recognized, a general consensus that the next generation of refrigerants needs to have zero ozone depletion and low global warming potential was reached. This consensus is also supported by proposed legislation in various countries to enforce a shift to refrigerants with a reduced environmental impact and more energy efficient [2]. The Clean Air Act Amendments were passed by the U.S. Congress in 1990 following the Montreal Protocol in 1987. The main impetus was of course the ozone depleting potential of the chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs) commonly used in refrigeration leading to the phasing out of CFC-12.

Under the terms of the Montreal Protocol, the U.S. agreed to a phase-out schedule as follows:

January 1, 2010 – Equipment manufacturers can no longer manufacture equipment that contains R22. Chemical manufacturers may still produce R22 to service existing equipment, but not for use in new equipment.

January 1, 2020 – Manufacturers will no longer be able to produce R22 to service existing equipment.

So, hydro-fluorocarbons (HFCs) were developed as long term alternative to substitute CFCs and HCFCs, and while they were non-ozone depleting, they did have large global warming potential (GWP) [3]. This results in successful development and adoption of HFC134a in domestic refrigerators and mobile air conditioners, having similar vapour pressure and performance as that of CFC-12.

However, next serious global environmental problem is concerning the refrigerant. It is the global warming problem. In 1997, United Nations Framework Convention on Climate

Change (UNFCCC), held in Kyoto, proposed ‘Kyoto Protocol’ to control emission of greenhouse gases. HFCs were considered as greenhouse gases (GHGs) and currently they are target compounds for green house gas emission reduction under the Kyoto Protocol [4]. The HFC-134a was identified as having a high global warming potential (GWP) of 1,430 and hence needs to be replaced by more environmentally friendly refrigerant. In this way, the growing international concern over relatively high GWP refrigerants has motivated the study of low GWP alternatives for HFCs in vapour compression systems. According to a survey by IPCC, HFC’s atmospheric concentrations rise at a rate of 13% - 17% per year between 2001 and 2003.

To meet its global warming obligations and emissions reduction targets, a new legislation was passed by the EU requiring both automotive Original equipment manufacturers (OEMs) and suppliers to adopt an alternative refrigerant with a GWP of 150 or less by the year 2012. The European Union's F-gas Regulation (Regulation (EC) No 842/2006 and Directive 2006/40/EC) became law on 4 July 2006 and many of the requirements came into force on 4th July 2007. The F-Gas regulation specifies beginning on January 1, 2011 new models and on January 1, 2017 new vehicles fitted with air conditioning cannot be manufactured with fluorinated greenhouse gases having global warming potentials (GWP) greater than 150. Hence, will phase out the use of HFC-134a in automotive air conditioning systems for all new models beginning in 2011 [5].

In anticipation, extensive research is being carried out to develop new low global warming potential fluids to support the refrigeration and air-conditioning industry. The main candidates to replace HFC-134a in vapour compression systems are natural refrigerants like ammonia, carbon dioxide or hydrocarbons (HC) mixtures; low GWP HFCs, highlighting HFC-32 and HFC-152a; and HFO, specifically HFO-1234yf and HFO-1234ze, developed by Honeywell and DuPont [6],[7]. HFO-1234yf, which has a 100 year GWP of 4 as compared to that of CO_2 [8] could be used as a "near drop-in replacement" for HFC134a, which means that the automobile manufacturers would not required to make significant alterations in the assembly lines or in vehicle system designs to accommodate the product.

1.2. LITERATURE REVIEW

Brown [9] gives an overview of the feasibility of HFOs as replacement refrigerants. The researches on HFO are mostly focused on measuring or reckoning their thermodynamic properties. Several works can be found in the literature presenting theoretical studies to determine the feasibility of direct substitution (or with slight modifications) using HFO-1234yf in facilities working with HFC-134a [10], [11], [12], [13], [14]. Minor et al. [6] has been proposed HFO-1234yf as a replacement for HFC-134a in mobile air conditioning systems, and its similar thermo physical properties makes HFO-1234yf a good choice to replace HFC-134a in other applications of refrigeration and air conditioning. HFO-1234yf has low toxicity, similar to HFC-134a, and mild flammability, significantly less than HFC-152a [15]. Leck [16] evaluated the performance of HFO-1234yf theoretically and showed that it had 2-9% less capacity and 2-7% less COP than HFC-134a. Also HFO-1234yf had similar lubricant miscibility and polymer compatibility as that of HFC-134a.

Henne et al. [17] analyzed other environmental effects of HFO-1234yf, and conclude that this refrigerant if released into the atmosphere, it is almost completely transformed to the persistent trifluoroacetic acid (TFA), and the predicted consequences of some studies of using HFO-1234yf show that future emission would not cause significant increase in TFA rainwater concentrations. Leck [18] theoretically analysed the performance of R-1234yf and other alternative refrigerants in air conditioning and stationary heating, and concluded that R-1234yf was having 57% less capacity and 7% higher COP than R-410a. Minor et al. [19] performed optimization of beverage cooler using HFO-1234yf and found that performance is comparable to HFC-134a.

Yana Motta et al. [20] experimentally established that performance of HFO-1234yf was similar to R-134a in a representative vending machine. Additionally, HFO-1234ze when tested in the vending machine with a 75% larger displacement compressor had slightly more capacity and less efficiency. Reaser et al. [21] investigated and compared the thermophysical properties of HFO-1234yf to those of HFC-134a and R410a to determine the drop-in replacement potential of HFO-1234yf and concluded that properties were similar to that of HFC-134a and not similar to that of R410a. Zang et al. [22] developed the non-azeotropic mixtures composed of HFOs (HFO-1234yf, HFO-1234ze(e), HFO-1234ze(z) and HFO-1234zf) as a replacement of HFC-134a and CFC-114 in air-conditioning and high temperature heat pump systems. It investigated theoretical cycle performance and found that COP of mixture of HFO-1234zf/HC-290 (60%/40% in mass) was 1.5% higher than that of HFC-134a, thus a good substitute in air conditioning system.

Lee et al. [23] theoretically analysed the drop-in performance of HFO-1234yf in a simple bench tester and examined the possibility of replacing HFC-134a in MAC systems. Zilio et al. [24] experimented with R1234yf in a typical R134a European automotive air conditioning system with some modifications. Bryson et al., [25] tested a car air conditioning system using refrigerants R152a and R1234yf to replace R134a. Endoh et al. [26] modified a room air conditioner that had been using R410A to meet the properties of R1234yf, and also evaluated the cycle performance capacity. Okazaki et al. [27] studied the performance of a room air conditioner using R1234yf and R32/R1234yf mixtures, which was originally designed for R410A, with both the original and modified unit.

Leighton et al. [28] theoretically showed that HFO-1234yf had 9% lower COP and 6% less capacity than HFC-134a and also showed HFO-1234ze had 8% higher COP and 21% lower capacity than HFC-134a. Abdelaziz et al. [29] evaluated experimentally and compared the performance of HFC-134a to HFO-1234yf and HFO-1234ze, and concluded that HFO-1234yf had 2.7% higher energy consumption than HFC-134a, indicating that HFO-1234yf is a suitable drop-in replacement of HFC-134a in domestic refrigerators. While HFO-1234ze had 16% lower energy consumption than HFC-134a, hence to replace HFC-134a with HFO-1234ze lower capacity refrigerators were required, thus HFO-1234ze might not be suitable for drop-in replacement. Kontomaris et al. [30] suggested an azeotropic mixture composed mainly of HFO1234yf, called DR-11, for replacing HFC134a in centrifugal chillers.

Jung et al. [31] evaluated the performance of HFO-1234yf and HFO-1234yf/HFC-134a mixture in three compositions and drawn the results that COP, capacity and discharge temperature of HFO-1234yf and mixture of refrigerants are similar to those of HFC-134a, with decrement in flammability as the content of HFC-134a increases. HFO1234yf could be used as a ‘near drop-in replacement’ for HFC134a and this implies that automobile manufacturers would not have to make significant modifications in assembly lines or in vehicle system designs to accommodate the product. HFO1234yf has the lowest switching cost for automobile manufacturers among the currently proposed alternatives, although the initial cost of the product is much higher than that of HFC134a.

Esbri et al. [1] experimentally analysed HFO-1234yf as a drop-in replacement for HFC-134a in a vapour compression system and summarized as, the cooling capacity of HFO-1234yf is about 9% lower than that of HFC-134a, which diminishes with the use of internal heat exchanger. Volumetric efficiency was about 5% less than that obtained with HFC-134a.

Up to now, the climate friendly chemical was set to be used worldwide in the automotive industry and was previously perceived to be safe. This was determined by numerous laboratory and crash tests carried out by international vehicle manufacturers and independent institutions.

Firstly, literature survey emphasizes that HFO-1234yf and HFO-1234ze can be a promising alternative to HFC-134a. Secondly, it has been observed that in most of the studies referred above, the analysis of the systems is based on first law of thermodynamics i.e. estimating coefficient of performance. In this study a more comprehensive exergy approach is followed, based on both first and second laws of thermodynamics. It is a powerful tool in the design and performance evaluation of the systems, and allows an explicit presentation of thermodynamic processes by quantifying the effect of irreversibility occurring during the processes. Exergy balance applied to processes tells us how much of the exergy input to the system has been consumed (irreversibly lost) by the system. An exergy analysis of a domestic refrigerator using R134a indicated that the highest exergy destruction occurred in compressor followed by condenser, capillary tube, evaporator, and superheating coil [32], [33]. The performance in compressor and condenser was investigated by exergy analysis using several environmentally friendly refrigerants, and it was found that the refrigerants presented inferior exergy behaviour than environmentally hazardous ones; nevertheless, the highest amount of exergy destruction occurs in the compressor [34]. Arora et al. [35] used R502, R404A and R507A in a vapour compression refrigeration system and investigated its components performance by exergy analysis. They concluded that the worst component from the viewpoint of exergy destruction is condenser, followed by compressor, throttle valve, evaporator and liquid vapour heat exchanger. This analysis takes into account all the losses appearing in the refrigeration system, for calculating exergetic efficiency. The various parameters calculated are COP, exergetic efficiency, exergy destruction and efficiency defects. Effects of degree of sub-cooling, liquid vapour heat exchanger effectiveness and dead state temperature are also computed and discussed.

1.3. OUTLINE OF THE THESIS

The thesis is formulated as,

- In the second chapter, theory of refrigerant is discussed, which includes the detailing about refrigerant blends, its properties, uses, advantage and disadvantage over pure or single component refrigerant. The Ozone depletion potential (ODP) and Global warming potential (GWP) and the properties of refrigerants studied in this thesis.
- In the third chapter of thermodynamics, laws of thermodynamics have been discussed. Ist law of thermodynamics, its application, mathematical formulation and IInd law of thermodynamics, its application, mathematical formulation.
- In the fourth chapter, titled as Theoretical analysis, theory of Vapour compression refrigeration system along with its energy analysis and exergy analysis is discussed.
- In the fifth chapter, the results obtained after performing the energy and exergy analysis on the system and an elaborate discussion on the results obtained are presented.
- In the sixth chapter, the essence of whole thesis is presented in the form of conclusion, where the writer has concluded about the project and its future scope.

"Refrigerant is the fluid used for heat transfer in a refrigerating system that absorbs heat during evaporation from the region of low temperature and pressure, and releases heat during condensation at a region of higher temperature and pressure."

The first refrigerant used was ether, employed by Perkins is his hand operated vapour compression machine. In 1875 ammonia replaced ethyl chloride (C_2H_5Cl) as a refrigerant. Sulphur dioxide (SO_2) in 1874, methyl chloride (CH_3Cl) in 1878 and carbon dioxide (CO_2) in 1881, found application as refrigerants [36]

2.1. REFRIGERANT BLEND

Refrigerant blends are mixtures of refrigerants that have been formulated to provide a match to certain properties of the refrigerants originally used. These blends have been researched and developed since the issue of the ODS phase-out emerged and are being produced by many chemical companies. Blends can have 2-3 or even 4 components, and can have a major component of a HCFC, HFC or HC; in most cases they will consist of a combination of these chemicals. Azeotropes or azeotropic mixtures are blended refrigerants of two or more liquids. When mixed together, they behave like CFC-12 and HCFC-22 when phase changing from liquid to vapour. Only one boiling and/or one condensing point exists for each given system pressure. R-500 and R502 are both azeotropic blends. R-500 is made up of 73.8% CFC-12 and 26.2% HFC-152a by weight. R-502 is made up of 48.8% HCFC-22 and 51.2 % CFC-115 [37]

Near-azeotropic mixture is a blend of two or more refrigerants that can still separate into individual refrigerants. These blends act differently because two or three molecules instead of one are present in any one sample of liquid or vapour. Thus a difference arises in pressure/temperature relationships of the near-azeotropic blends versus refrigerants like CFC-12, HCFC-22, HFC-134a, and azeotropic blends. Near-azeotropic blends experience a *temperature glide.* Temperature glide occurs when the blend has many temperatures as it evaporates and condenses at a given pressure. This implies that as the near-azeotropic refrigerant blend changes phase from liquid to vapour and back, more of one component in the blend will transfer to the other phase faster than the rest. Zeotropic refrigerant blends also exhibit these properties, but to a greater extent. [37]

Figure 2.1 illustrates a pressure/temperature graph of an azeotropic refrigerant blend showing the refrigerant boiling at one temperature for a given pressure through the length of the heat exchanger (evaporator) as exhibit by pure compound like CFC-12 as they evaporate and condense. [37]

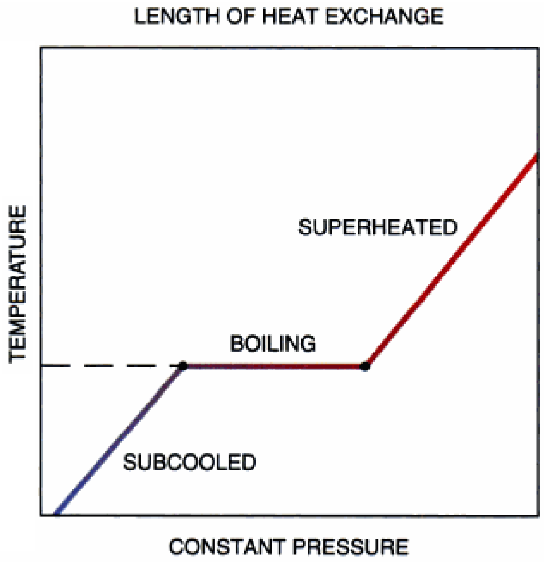


Figure 2.1 an azeotropic refrigerant blend showing only one temperature for a given pressure as it boils.

Figure 2.2 illustrates a pressure/temperature graph of a near-azeotropic refrigerant blend showing the refrigerants boiling at many temperatures (temperature glide) for a given pressure through the length of the heat exchanger (evaporator). [37]

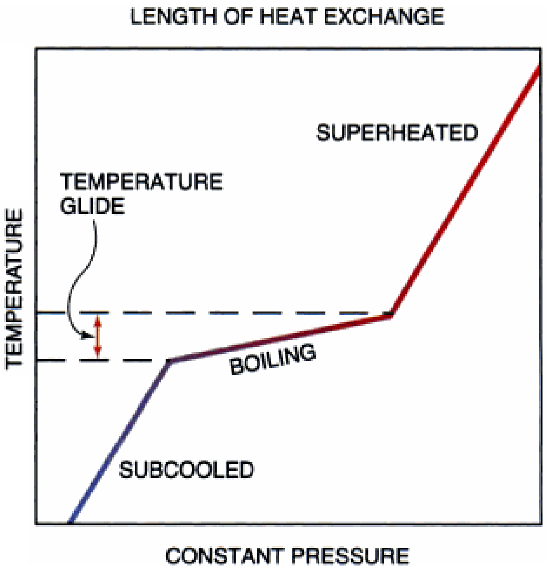
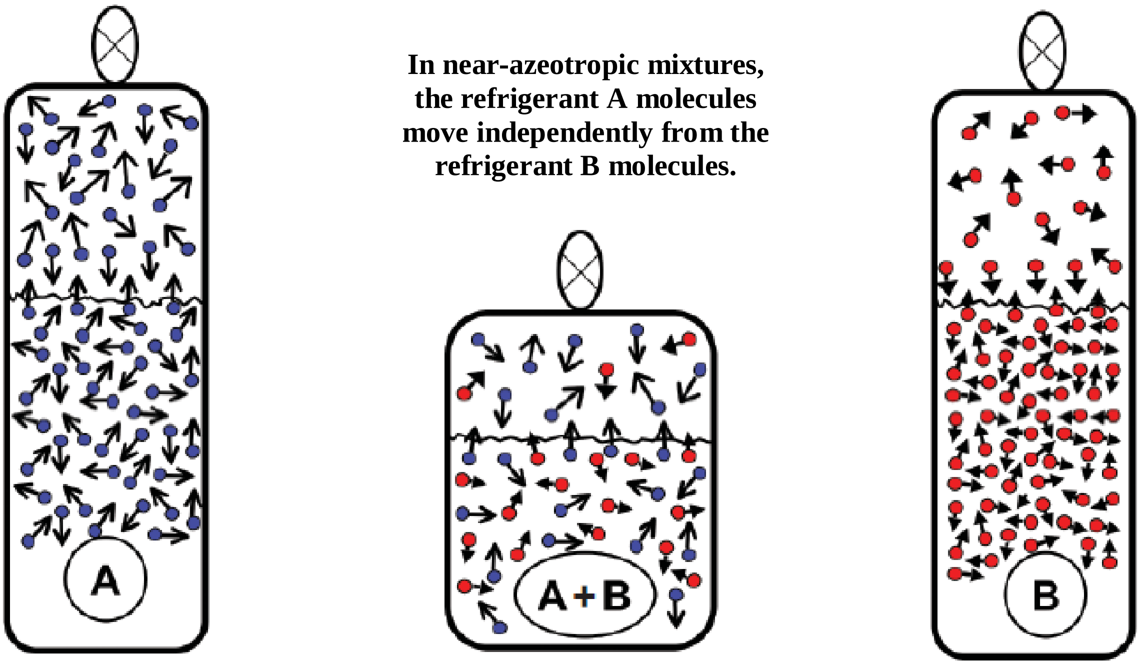


Figure 2.2 a near-azeotropic refrigerant blend showing temperature glide as it boils at a constant pressure.

Near-azeotropic refrigerant blends may also experience fractionation. Fractionation is the change in composition of a blend because one (or more) of the components is lost or removed faster than the other(s). This different rate is caused by the slightly varied vapour pressure of each refrigerant in the blend. Zeotropes also exhibit the same behaviour but to a large extent than near-azeotropic blends. Figure 2.3 [38] illustrates two basic behaviours of refrigerant molecules in a refrigerant blend. If a greater amount of A is mixed with B, then the blend will have a pressure closer to A. If a greater amount of B is in the mix, then the blend will have a pressure closer to B. If we mix equal amounts, the blend will fall in between the pressures of A and B.

When refrigerants A and B are mixed together and they don’t form an azeotrope, the individual refrigerant molecules behave as if the other type is not there. The refrigerant A molecules bounce harder than the refrigerant B molecules, contributing more pressure to the blend. The composition can be adjusted so that the combined pressure from the two types of molecules matches the desired pressure. [38]



In near-azeotropic mixtures, the refrigerant A molecules move independently from the refrigerant B molecules.

Pressure of refrigerant A is higher (more movement)

Combined pressure: refrigerant A more active than refrigerant B

Pressure of refrigerant B is lower (less movement)

Figure 2.3 shows the behaviour of individual refrigerant molecules in a refrigerant blend.

The refrigerant blends have their own trade names. The well known ASHRAE (American Society of Heating, Refrigerating and Air Conditioning Engineers) refrigerant number also applies to blends.

“R” numbers for the Blends

- The 400 series blends are the near-azeotropic (zeotropic) blends. R-410 is a near-azeotropic blend, where 10 indicate that it is the tenth one commercially produced. They all have temperature glide and can fractionate.
- The 500 series blends represent the azeotropic blends. R-502 is an azeotropic blend and 2 means that it is the second one produced in the market.
- Blends can also be represented by the percentage of each refrigerant that makes up the blend. The refrigerant with the lowest boiling point at atmospheric pressure will be named first. Example: a blend of 20% (R-12) and 80% (R-22) would be represented as R-22/12 (80/20). Because R-22 has the lowest boiling point.
- Blends can also have capital letters at their ends. The capital letters at the end of R-401A, R-401B, and R401C mean that the same three refrigerants make up these near-azeotropic blends, but their individual percentage differ.

The US Environment Protection Agency (EPA) through its Significant New Alternatives Policy (SNAP) provides lists of “Acceptable Substitutes for Class I (CFCs) Substances” in Air Conditioning, Commercial Refrigeration and Non-commercial refrigeration for new production and retrofitting, which could be used as a good reference. The blends that are currently widely used around the world are HFC based such as R-407C and R-410A to replace R-22. However, due to the increase of the prices of R-134a, the HCFC-based blends1 such as R-406A and R-415B have entered into the regional and world servicing market for the replacement of R-12, and even R-134a.

2.1.1. Pros and Cons of refrigerant blends [39]

2.1.1.1. Pros

- The refrigerant blends provide another way to assist the country in compliance with the CFCs phase-out provision under the Montreal Protocol while not harming the interests of the end users;
- The refrigerant blends (if main components are either R-22/R152a/HC) are cheaper than R- 134a and other alternatives; they are easy to get in the region;

- The HCFC based refrigerant blends as mentioned above aimed to replace R-12 can mostly be used with mineral oils and can provide acceptable performance in retrofitted equipment.

2.1.1.2. Cons

- HCFC based blends are an interim CFC replacement solution. Due to the non-azeotropic and possible flammable characteristics, the servicing procedure especially charging would be complicated and the technicians should be informed to follow proper handling procedures.
- The introduction of more refrigerants in the market might confuse the technicians, causing more cases of cross-contamination in running the refrigeration system. Even though the short-term impact on the performance of the equipment might not be noticed by the equipment owner, it is believed the cross-contamination of refrigerant/lubricant will reduce the equipment’s energy efficiency and its performance, and shorten the operational life of the equipment.
- More blends will also complicate the recovery/recycling programme due to the cross contamination, as equipment with the blends might not be properly labelled or the technicians may just ignore the label (recovery/recycling will not work as all these blends have temperature glide, the recycled blends cannot be used because of change in composition).
- Some blends are advertised to replace R134a, so it might cause backward retrofitting from R-134a to HCFC based blends.

2.1.2. Tips to handle blends issue [39]

- NOU needs to discuss and share experience and lessons for better management of the HCFC blends once they are entering into your national market.
- Request the dealer to label the blends correctly, provide manufacturer’s literature to technicians.
- Alert the customs officers on the limitation of the refrigerant identifier and advice them not to use the identifier to confirm the composition of the blend in question.
- Alert the customs officers on the limitation of the refrigerant identifier and advice them not to use the identifier to confirm the composition of the blend in question.
- Request the customs authority to provide a separate HS code for the blends under the 2903.40 (for HCFC/HFC/HC blends) 3824.71 (for CFC blends).

2.2. OZONE DEPLETION POTENTIAL (*ODP*) AND GLOBAL WARMING POTENTIAL (*GWP*)

2.2.1. Ozone depletion potential

Ozone Depletion Potential (*ODP*) of a chemical compound is the relative amount of degradation it can cause to the ozone layer. Ozone Depletion Potentials are indices that provide a simple way to compare the relative ability of various ODSs to destroy stratospheric ozone [40]. The ozone depletion potential (ODP) of a compound is a simple measure of its ability to destroy stratospheric ozone [41] It was defined as a measure of destructive effects of a substance compared to a reference substance. It is a relative measure: the ODP of CFC-11 is defined to be 1.0, and the ODP's of other compounds are calculated with respect to this reference point. Precisely, ODP of a given substance is defined as the ratio of global loss of ozone due to given substance over the global loss of ozone due to CFC-11 of the same mass [42]. More precisely, the ODP of a compound "x" is defined as the ratio of the total amount of ozone destroyed by a fixed amount of compound x to the amount of ozone destroyed by the same mass of CFC-11 [41]

$$ODP_X = \frac{global\ ozone\ loss\ due\ to\ unit\ mass\ emission\ of\ X}{global\ ozone\ loss\ due\ unit\ mass\ emission\ of\ CFC - 11}$$

Thus the ODP of CFC-11 is 1.0 by definition. The right-hand side of the equation is calculated by combining information from laboratory and field measurements with atmospheric chemistry and transport models. Since the ODP is a relative measure, it is fairly "robust", not overly sensitive to changes in the input data or to the details of the model calculations. That is, there are many uncertainties in calculating the numerator or the denominator of the expression, but most of these cancel out when the ratio is calculated.

The ODP of a compound will be affected by:

- The nature of the halogen (bromine-containing halocarbons usually have much higher ODPs than chlorocarbons, because atom for atom Br is a more effective ozone-destruction catalyst than Cl.)
- The number of chlorine or bromine atoms in a molecule.
- Molecular Mass (since ODP is defined by comparing equal masses rather than equal numbers of moles).

- Atmospheric lifetime (CH_3CCl_3 has a lower ODP than CFC-11, because much of the CH_3CCl_3 is destroyed in the troposphere).

2.2.2. Global warming potential

Global Warming Potential (*GWP*) is a measure of how much a given mass of a gas contributes to global warming. *GWP* is a relative scale which compares the greenhouse gas to Carbon Dioxide where *GWP* by definition is 1. A GWP is calculated over a specific time interval, commonly 20, 100 or 500 years. GWP is expressed as a factor of carbon dioxide (whose GWP is standardized to 1). For example, the 20 year GWP of methane is 72, which means that if the same mass of methane and carbon dioxide were introduced into the atmosphere, that methane will trap 72 times more heat than the carbon dioxide over the next 20 years [43]

The GWP depends on the following factors:

- The absorption of infrared radiation by a given species.
- The spectral location of its absorbing wavelengths.
- The atmospheric lifetime of the species.

2.2.2.1. Low GWP Refrigerants

There are many viable low GWP candidates to replace the current HFC refrigerants. These candidates can be generally classified into hydrofluoroolefins, hydrocarbons, and refrigerant mixtures.

- **Hydrofluoroolefins**

  HFOs are fluorinated propene isomers, which include R-1225 isomers, R-1234 isomers, and R-1243 isomers. R-1234yf appears to be the leading candidate for replacing R-134a in automotive applications [19]. R-1243 isomers have largely been ruled out due to their flammability and R-1225 isomers are no longer being developed because of toxicity concerns [44].

  R-1234yf is mildly flammable, classified as A2L by ASHRAE Standard 34 [45] due to its low burning velocity and high minimum ignition energy. R-1234yf shows low toxicity, performing as well or better than R-134a in toxicity tests [6]. Leck [16] performed an ASHRAE/ANSI Standard 97 evaluation of R-1234yf with copper, steel, aluminum, and POE refrigeration oils show no evidence of breakdown or reaction.

Additional testing with polymers and lubricants shows R-1234yf to have material compatibilities similar to R-134a.

R-1234ze is classified as A2L by ASHRAE Standard 34 [45]. It has two stereoisomers, R-1234ze(E) and R-1234ze(Z), which exhibit different properties. An ASHRAE/ANSI Standard 97 evaluation of R-1234ze showed it to be thermally stable and compatible with POE oils [20]

- **Hydrocarbons**

  Hydrocarbons are already prevalent in domestic refrigeration, with propane and isobutane being the most common [46]. Isobutane (R-600a) is found in the majority of Chinese refrigerators and all European and Japanese units [47]. The Environmental Protection Agency Significant New Alternatives Policy (2011) approved the use of R-600a in domestic refrigerators and R-290 (propane) in stand-alone retail refrigerators [48].

  The hydrocarbons that would likely serve as refrigerants have a GWP less than 5 [46]. These hydrocarbons show superior transport properties and experimental efficiency improvements of 2-10%.

- **Mixtures**

  If no single component refrigerant performs acceptably in domestic refrigerator/freezers, a combination of refrigerants can be used to achieve the desired properties. Some mixtures have been shown to improve efficiency in optimized systems, while others have shown a slight increase in energy consumption. The temperature glide exhibited by a zeotropic refrigerant mixture can be used to a thermodynamic advantage in the modified Lorenz-Meutzner cycle, which has shown a 16.5 to 17.3% energy savings [49].

  Koyama et al. [50] found that adding R-32 to R-1234ze improves the COP and capacity in a heat pump, and they state that this type of mixture is a strong candidate for replacing R-410a in domestic heat pumps. Fujitaka et al. [51] found that a mixture of R-1234yf/R-32 (50/50 wt%) has 95% of the cooling COP and 94% the heating COP compared to R-410a in a room air conditioner as a drop in. EPA 2011 approved the use of hydrocarbon mixture R-441a in domestic refrigerators.

Table 2.1: ODP and GWP of various CFC, HCFC, HFC refrigerants and mixtures [52], [53]

Refrigerant	**ODP**	**GWP**	**Comments**
CFC-12	1	10900	Phase out under Montreal Protocol
HCFC-22	0.055	1810	To be phased out because of chlorine atom
HFC-23	0	14800	High GWP
HFC-32	0	675	Low GWP and high performance, but flammable
HFC-125	0	3500	Low flammability, but high GWP and low performance
HFC-134a	0	1430	CFC alternative for mobile air conditioner
HFC-143a	0	4470	High GWP and high flammable
HFC-152a	0	124	Low GWP, but high flammable
R-410A	0	1730	CFC alternative for room air conditioner, high GWP
R-407C	0	1530	High GWP
R-404A	0	3260	CFC alternative for large refrigeration system, high GWP
Propane	0	3	Natural refrigerant, but flammable
Iso-butane	0	3	CFC alternative for domestic refrigerator, flammable
CO_2	0	1	Natural refrigerant, no flammable, low GWP, but high pressure
DME	0	1	Natural refrigerant, low GWP, but flammable
HFO-1234yf	0	4	Low GWP, but softly flammable not stable (with double bond)
HFO-1234ze(E)	0	6	Low GWP, but softly flammable not stable (with double bond)

2.3. REFRIGERANT ‘HFO-1234yf’

2, 3, 3, 3-Tetrafluoropropene, or **HFO-1234yf**, is a hydrofluoroolefin with the formula CH_2=$CFCF_3$. It has been proposed as a replacement for R-134a as a refrigerant in automobile air conditioners [6]. Due to increased pressure to address the issue of global warming, the European Commission has effectively banned the use of R-134a refrigerant in air conditioning in new car platforms in EU countries starting January 1, 2011 [4]. R-134a has a 100 year global warming potential value (GWP) of 1430 according to the Intergovernmental Panel on Climate Change 4th Assessment Report (AR4) [43].

2.3.1. Thermodynamic Properties

Boiling point, critical point, and liquid and vapour density are comparable to R-134a. Vapour pressure is slightly higher at temperatures below 25°C and slightly lower at temperatures above 60°C which can yield a lower compression ratio and better compressor efficiency [54].

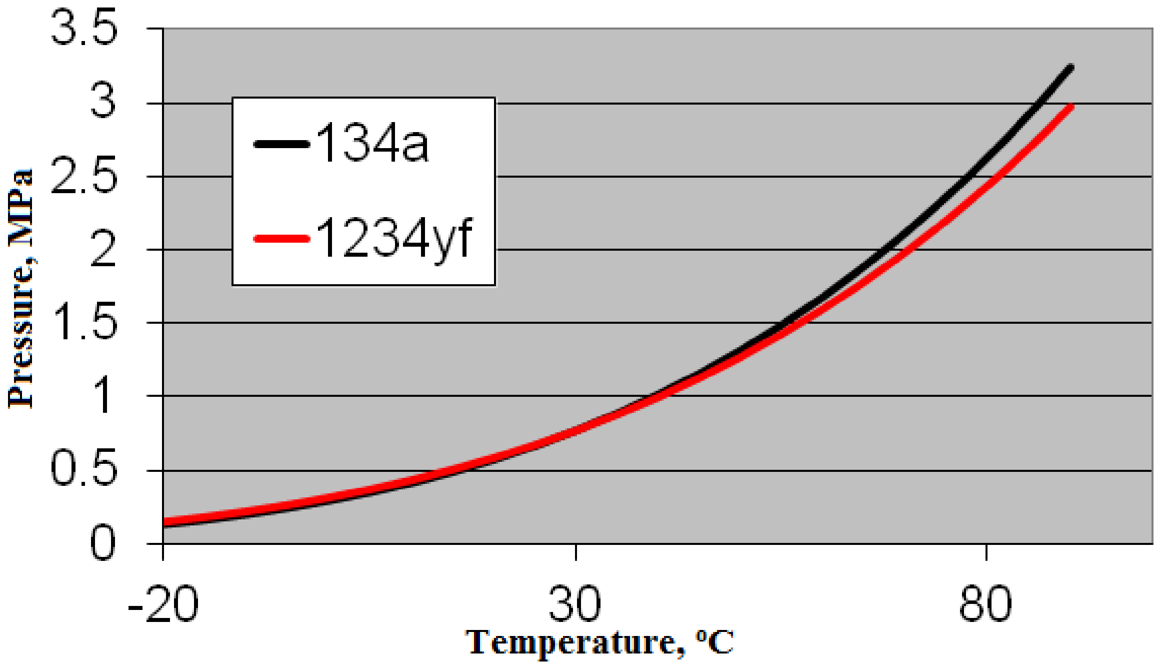


Figure 2.4 shows variation of Vapour Pressure with temperature of HFO-1234yf and HFC-134a [6]

2.3.2. Toxicity

Significant toxicity testing for HFO-1234yf has been completed following Organization for Economic Cooperation and Development (OECD) guidelines. HFO-1234yf is not mutagenic. Environmental tests on daphnia, fish and algae results are also similar to R-134a [6].

Table 2.2: HFO-1234yf Toxicity and Environmental Summary

Test	**HFO-1234yf**	**R-134a**
LC50	No deaths 400,000 ppm	No deaths 359,700 ppm
Cardiac Sensitization	NOEL > 120,000 ppm	NOEL 50,000 ppm LOEL 75,000 ppm
Ames	Slight activity	Not active
Chrom AB	Not active	Not active
13 Week Inhalation	NOEL 50,000 ppm	NOEL 50,000 ppm
Developmental (Rat)	NOAEL 50,000 ppm	NOAEL 50,000 ppm
Environmental Tox (acute daphnia, fish, algae)	NOEL > 100 mg/L	NOEL > 100 mg/L

2.3.3. Environmental Effect

HFO-1234yf has no ozone depletion potential. Atmospheric lifetime was determined to be 11 days versus R-134a at 14 years. Global warming potential based on a 100 year time horizon was determined to be 4 versus R-134a at 1430. Atmospheric breakdown products are also very similar to R-134a with no high GWP breakdown products formed.

2.3.4. Flammability

HFO-1234yf was determined to be flammable by exhibiting lower and upper flammability limits when tested using ASTM-E681-04. However, results indicate mild flammability when comparing the lower flammability limit versus other refrigerant. Flammability limits are only one factor in determining whether HFO-1234yf can be safely used in a given application. Another important consideration is the amount of energy that is required to ignite the refrigerant, represented by the minimum ignition energy and the damage potential if an ignition were to occur, represented by the burning velocity.

Table 2.3: HFO-1234yf Flammability Summary

Property	**Propane**	**R-152a**	**R-32**	**NH_3**	**HFO-1234yf**
Flame Limits (ASTM E681-04) at 21°C					
LFL (vol% in air)	2.2	3.9	14.4	15.0	6.2
UFL (vol% in air)	10.0	16.9	29.3	28.0	12.3
Delta UFL-LFL	7.8	13.0	14.9	13.0	5.8
Minimum Ignition Energy (mJ)	0.25	0.38	30-100	100-300	5000-10,000
Burning Velocity (cm/s)	46	23	6.7	7.2	1.5

2.3.5. Materials Compatibility

2.3.5.1 Thermal Stability

HFO-1234yf has been evaluated for thermal stability per ASHRAE Standard 1997-99 [55]. Tests were conducted with refrigerant and either polyalkylene glycol (PAG) or polyolester (POE) lubricant and water concentrations varying from less than 100 ppm to 10,000 ppm. Refrigerant and lubricant were placed in sealed glass tubes containing aluminium, copper and carbon steel coupons and held at 175°C or 200°C for two weeks. Results indicate HFO-1234yf is thermally stable with no significant corrosion to the metals observed.

2.3.5.2. Plastics and Elastomers Compatibility

HFO-1234yf and R-134a have been evaluated for compatibility with typical plastics and elastomers used inautomotive air conditioning systems. Some commonly used plastics and elastomers were immersed in sealed tubes containing HFO-1234yf and PAG lubricant and held at 100°C for two weeks. Plastics were then inspected for weight change after 24 hours and physical appearance. Elastomers were evaluated for linear swell, weight gain and hardness using a durometer.

Table 2.4: HFO-1234yf Plastics Compatibility

Refrigerant	**Plastics**	**Rating**	**24h Post Weight Chg %**	**Physical Change**
HFO-1234yf	Polyester	1	4.4	0
HFO-1234yf	Nylon	1	-1.5	1
HFO-1234yf	Epoxy	1	0.3	1
Refrigerant	**Plastics**	**Rating**	**24h Post Weight Chg %**	**Physical Change**

HFO-1234yf	Polyethylene Terephthalate	1	2.0	0
HFO-1234yf	Polyimide	0	0.2	0
R-134a	Polyester	1	5.6	0
R-134a	Nylon	1	-1.4	1
R-134a	Epoxy	1	0.3	1
R-134a	Polyethylene Terephthalate	1	2.8	0
R-134a	Polyimide	0	0.7	0

Rating = 0 if weight gain is less than 1% and there is no physical change.

Rating = 1 if weight gain is between 1 and 10% and physical change = 2.

Table 2.5: HFO-1234yf Elastomers Compatibility

Refrigerant	**Elastomers**	**Rating**	**24h Post Linear Swell %**	**24h Post %Weight Gain**	**24h Post Delta Hardness**
HFO-1234yf	Neoprene WRT	0	0.0	-0.3	1.0
HFO-1234yf	HNBR	0	1.6	5.5	-7.0
HFO-1234yf	NBR	0	-1.2	-0.7	4.0
HFO-1234yf	EPDM	0	-0.5	-0.6	4.0
HFO-1234yf	Silicone	1	-0.5	2.5	-14.5
HFO-1234yf	Butyl rubber	0	-1.6	-1.9	0.5
R-134a	Neoprene WRT	0	-0.6	-1.3	2
R-134a	HNBR	0	2.1	8.6	-5.5
R-134a	NBR	0	0.0	3.0	-3.5
R-134a	EPDM	0	-1.1	-0.4	-2
R-134a	Silicone	0	-1.4	1.4	-2.5
R-134a	Butyl rubber	0	-1.1	-1.6	-3.5

For elastomers,
Rating = 0 if for < 10% weight gain, < 10% linear swell and < 10% hardness change.
Rating = 1 for > 10% weight gain or > 10% linear swell or >10% hardness change.

2.4. REFRIGERANT 'HFO-1234ze'

HFO-1234ze is an unsaturated fluorocarbon. The full chemical name is trans-1, 3, 3, 3-tetrafluoroprop-1-ene. HFO-1234ze is currently being used in aerosol and other products in Europe and Japan. The primary applications today are in one-component foams, novelty aerosols, such as party strings and air horns, and an insect spray. It is also being used in dusters and defluxing products for electronics. Other potential uses are in Tire Inflators, Topical Anesthetics, Degreasers, other Technical Aerosols and Personal/Consumer Care products, such as hair sprays, antiperspirants, deodorants, and shaving creams [56].

2.4.1. Thermodynamic Properties

In most ways, HFO-1234ze behaves like HFC-134a, so it can be handled and used very much like HFC-134a. The key differences are that HFO- 1234ze has an extremely low GWP and its vapour pressure is lower than that of HFC-134a.

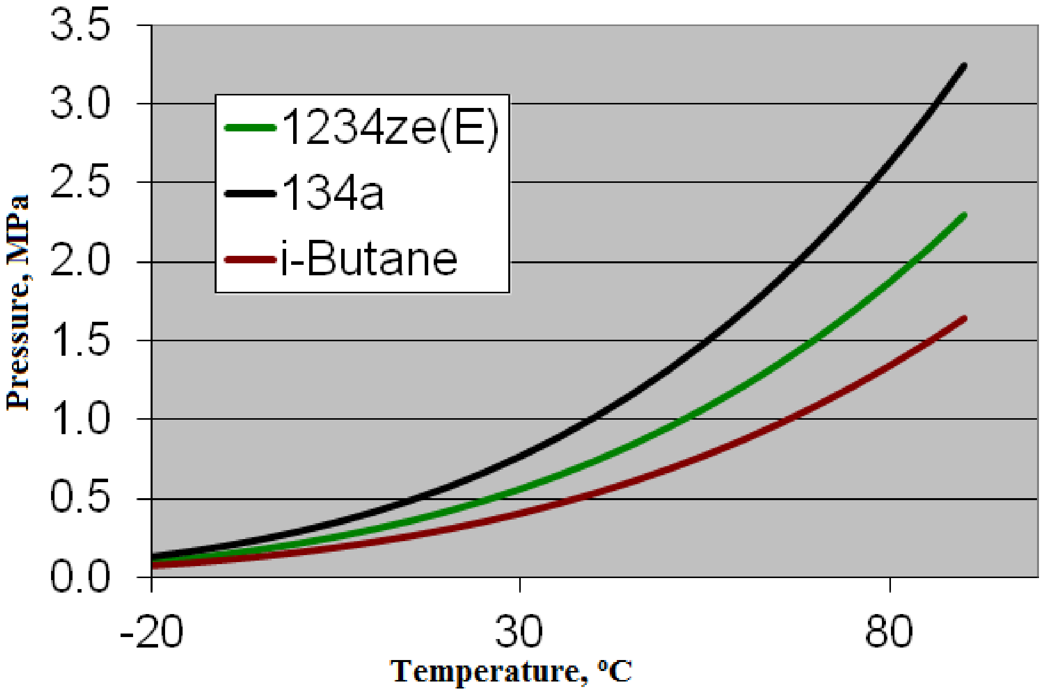


Figure 2.5 shows variation of Vapour Pressure with temperature of HFO-1234ze and HFC-134a

2.4.2. Toxicity

An extensive series of toxicity tests were carried out on HFO-1234ze with excellent results. The toxicity testing program included: acute exposure, repeat exposure, mutagenicity and developmental toxicity studies.

The results of those tests support the conclusion that HFO-1234ze exhibits a very low order of toxicity. A Workplace Environmental Exposure Level (WEEL) of 800 PPM (8-hour time weighted average) has been assigned to HFO-1234ze.

2.4.3. Environmental Effect

The atmospheric lifetime of HFO-1234ze was determined to be approximately 2 weeks. The GWP, which is largely a function of atmospheric lifetime, was determined to be 6 versus CO_2 on a 100-year integrated time horizon. At the University of Copenhagen, it was determined that the atmospheric degradation products of HFO-1234ze have negligible impact on the environment.

Compounds with short atmospheric lifetimes often contribute to the generation of tropospheric, or ground-level, ozone which is one of the components of photochemical smog. That is not the case with HFO-1234ze. The MIR (maximum incremental reactivity) value for HFO-1234ze has been measured and found to be 0.09 g O3/g VOC, which is approximately one-third of the value for ethane. The calculated POCP (photochemical ozone creation potential) of HFO-1234ze is only 6.4. This is roughly half the value for ethane. The very low MIR and POCP values indicate that HFO-1234ze does not contribute in any significant way to tropospheric ozone generation. HFO-1234ze is expected to be classified as a non-VOC in the United States.

Table 2.6: Environmental properties of HFO-1234ze

Property	**HFO-1234ze**	**HFC-134a**	**HFC-152a**	**DME**	**Propane**	**Isobutane**
GWP(versus CO_2, 100 year ITH	6	1320	122	<15	<15	<15
Photochemical Reactivity(MIR g O_3/VOC)	0.09	0.0007	0.0175	0.93	0.57	1.23

2.4.4. Flammability

HFO-1234ze does not exhibit vapour flame limits under standard test conditions. It is therefore classified as non-flammable according to *EC Testing Method A11: Flammability of Gases*, as well as by the U.S. Department of Transportation (DOT) standard (tested according to ASTM E681).

HFO-1234ze is non-flammable in the ASTM flame projection test. When tested against HFC-134a and HFC-152a, its performance was identical to that of HFC-134a, whereas some degree of flame projection was observed with the HFC-152a samples.

HFO-1234ze has also been tested and found to be non-flammable in the ignition distance test and the enclosed space ignition test (closed drum test). The heat of combustion of HFO-1234ze is 10.2 kJ per gram.

2.4.5. Materials Compatibility

2.4.5.1. Miscibility

Honeywell’s HFO-1234ze is miscible with other propellants such as 134a, 152a, DME and the hydrocarbons (butane, isobutane and propane). It is also miscible with many commonly-used solvents such as the lower alcohols, ketones, chlorinated solvents and hydrocarbons. It should thus be possible to formulate a wide range of aerosol products with HFO-1234ze.

2.4.5.2. Stability and dielectric strength

HFO-1234ze has been shown to be thermally and hydrolytically stable. In one experiment, samples of HFO-1234ze, in the presence of water and metals, were stored at 200°C for two weeks. There was no observed effect on the metals and analysis showed no indication of breakdown of the HFO-1234ze. Also, samples stored in steel cylinders for several years have been analyzed and found to be in specification. It is always advisable to confirm the stability of any aerosol formulation containing a new propellant. The dielectric strength of HFO-1234ze vapour has been measured. At ambient temperature and 1 atmosphere pressure, the dielectric strength is 11.7 kV for a 0.25 cm gap. Under the same conditions, the dielectric strength of HFC-134a is 6.6 kV.

2.4.5.3 Compatibility

Honeywell's HFO-1234ze propellant is compatible with copper, steel, aluminium and tinplate aerosol cans. HFO-1234ze is generally compatible with plastics, with the exception of acrylics, and with many elastomers including butyl rubber, natural rubber, silicone and EPDM. It is always recommended that testing be done to confirm compatibility with specific materials of construction.

2.4.5.4 Storage and handling

Honeywell HFO-1234ze should be handled in a manner consistent with materials categorized as "liquefied gases under pressure". As illustrated by the vapour pressure data, Honeywell HFO-1234ze is a moderate pressure gas and containers (bulk storage tanks or packages) should be rated for the pressure of Honeywell's HFO-1234ze. Honeywell HFO-1234ze, in approved packages (containers), should be stored in a cool, well-ventilated area. HFO-1234ze packages (containers) should neither be punctured or dropped, nor exposed to open flames, excessive heat or direct sunlight. Based on industry experience, HFO-1234ze should not be mixed with oxygen at elevated pressures.

Applications necessitating pressurization – exceeding the vapour pressure of HFO-1234ze – should use dry nitrogen.

Table 2.7 shows the thermo-physical properties of refrigerants [54], [57], [58].

Table 2.7: Thermo-physical properties of Refrigerants.

Properties	**HFO-1234yf**	**HFO-1234ze**	**HFC-134a**
Boiling Point, T_b	-29°C	-19°C	-26°C
Critical Point, Tc	94.7°C	109.4°C	101°C
Pvap, MPa (25°C)	0.682	0.500	0.665
Pvap, MPa (80°C)	2.519	2.007	2.635
Liquid Density, kg/m3 (25°C)	1092	1162	1207
Vapour Density, kg/m3 (25°C)	37.94	26.76	32.34

CHAPTER 3: THERMODYNAMICS

Thermodynamics can be defined as the science of *energy*. Energy can be viewed as the ability to cause changes. The name *thermodynamics* stems from the Greek words *therme* (heat) and *dynamis* (power), which is most descriptive of the early efforts to convert heat into power. *Thermodynamics* is the study of energy interactions between *systems* and the effect of these interactions on the system *properties*. Energy transfer between systems takes place in the form of *heat and/or work*. Thermodynamics deals with *systems in equilibrium* [59].

Thermodynamics did not emerge as a science until the construction of the first successful atmospheric steam engines in England by Thomas Savery in 1697 and Thomas Newcomen in 1712. These engines were very slow and inefficient, but they opened the way for the development of a new science [59].

The first and second laws of thermodynamics emerged simultaneously in the 1850s, primarily out of the works of William Rankine, Rudolph Clausius, and Lord Kelvin (formerly William Thomson). The term *thermodynamics* was first used in a publication by Lord Kelvin in 1849. The first thermodynamic textbook was written in 1859 by William Rankine, a professor at the University of Glasgow [59].

3.1. FIRST LAW OF THERMODYNAMICS

The *first law of thermodynamics,* also known as *the conservation of energy principle,* provides a sound basis for studying the relationships among the various forms of energy and energy interactions. The first law of thermodynamics states that *energy can be neither created nor destroyed during a process; it can only change forms.* Therefore, every bit of energy should be accounted for during a process.

In the light of the preceding discussions, the conservation of energy principle can be expressed as follows: *The net change (increase or decrease) in the total energy of the system during a process is equal to the difference between the total energy entering and the total energy leaving the system during that process.* That is,

$$\begin{pmatrix} Total\ energy \\ entering\ the\ system \end{pmatrix} - \begin{pmatrix} Total\ energy \\ leaving\ the\ system \end{pmatrix} = \begin{pmatrix} Change\ in\ the\ total \\ energy\ of\ the\ system \end{pmatrix}$$

Or

$$E_{in} - E_{out} = \Delta E_{system}$$

This relation is often referred to as the **energy balance** and is applicable to any kind of system undergoing any kind of process.

The change in the total energy of the system can be expressed as:

$\Delta E = \Delta U + \Delta KE + \Delta PE$

Where $\Delta U = change\ in\ Internal\ energy$
$\Delta KE = change\ in\ kinetic\ energy$
$\Delta PE = change\ in\ potential\ energy$

3.1.1. Energy balance for closed system

$$Q_{net,in} - W_{net,out} = \Delta E_{system}\ or\ \ Q - W = \Delta E$$

where $Q = Q_{net,in} = Q_{in} - Q_{out}$ is the heat input.
$W = W_{net,out} = W_{out} - W_{in}$ is the net work output.

- *Stationary System:* $Q - W = \Delta U$
  As $\Delta KE = 0, \Delta PE = 0\ and\ \ \Delta E = \Delta U$
- *Per unit mass:* $q - w = \Delta e$
- *Differential form:* $\delta q - \delta w = de$
- *System undergoing cycle:* $Q - W = 0\ or\ Q = W$ (initial and final points are same)

3.1.2. Energy balance for Steady-Flow system

Steady-flow process is the process during which fluid flows through a control volume steadily.

Mass balance: $\sum \dot{m}_{in} = \sum \dot{m}_{out}$

It states that *the total rate of mass entering a control volume is equal to the total rate of mass leaving it.*

Energy balance: $\dot{E}_{in} = \dot{E}_{out}$

It states that *the total rate of energy entering a control volume is equal to the total rate of energy leaving it.*

General *steady-flow energy* equation

$$\dot{Q}_{in} + \dot{W}_{in} + \sum \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) = \dot{Q}_{out} + \dot{W}_{out} + \sum \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right)$$

Applications

- Nozzles and Diffusers.
- Turbines and Compressors.
- Throttling valves.
- Mixing chamber.
- Heat exchangers.
- Pipe and Duct flow.

3.2. SECOND LAW OF THERMODYNAMICS

The *second law of thermodynamics*, which asserts that *processes* occur in a certain direction and that *energy* has *quality* as well as *quantity*. A process cannot take place unless it satisfies both the first and second laws of thermodynamics. The second law of thermodynamics is a limit law. It can be used in determining the *theoretical limits* for the performance of commonly used engineering systems, such as heat engines and refrigerators, as well as predicting the *degree of completion* of chemical reactions [59].

3.2.1. Statements of Second Law of Thermodynamics

3.2.1.1. Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

This statement applies to “**Heat Engine**”. That is, a heat engine must exchange heat with a low-temperature sink as well as a high-temperature source to keep operating.

The Kelvin–Planck statement can also be expressed as *no heat engine can have a thermal efficiency of 100 percent.*

$$W_{net,out} = Q_{in} - Q_{out}$$

$$\eta_{thermal} = \frac{W_{net,out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

3.2.1.2. Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

The Clausius statement is related to **Refrigerators** or **Heat Pumps**.

- **Refrigerator**

  It transfers heat from a low-temperature medium to a high-temperature one with the objective of maintaining the temperature of the medium below the surrounding temperature.

  The *efficiency* of a refrigerator is expressed in terms of the *coefficient of performance (COP)*, denoted by COP_R.

  $$COP_R = \frac{Desired\ output}{Required\ input} = \frac{Q_L}{W_{net,in}}$$

  $W_{net,in} = Q_H - Q_L$

  Where $Q_L = heat\ to\ be\ removed\ from\ the\ refrigerated\ space.$

  $Q_H = heat\ rejected\ at\ higher\ temperature$

- **Heat Pump**

  It transfers heat from a low-temperature medium to a high-temperature one with the objective of maintaining the temperature of the medium above the surrounding temperature.

  The *efficiency* of a heat pump is expressed in terms of the *coefficient of performance (COP)*, denoted by COP_{HP}.

  $$COP_{HP} = \frac{Desired\ output}{Required\ input} = \frac{Q_H}{W_{net,in}}$$

3.2.2 Entropy

Clausius Inequality

It was first stated by the German physicist R. J. E. Clausius (1822–1888), one of the founders of thermodynamics, and is expressed as

$$\oint \frac{\delta Q}{T} \leq 0$$

That is, *the cyclic integral of* δQ*/T is always less than or equal to zero*. This inequality is valid for all cycles, reversible or irreversible. 'δQ' is the heat transfer across the boundary of the system and T is the absolute temperature of the boundary.

For reversible process,

$$\oint \frac{\delta Q}{T} = 0$$

And it is proven that, a quantity whose cyclic integral is zero depends on the *state* only and not the process path, and thus it is a property. Clausius realized in 1865 that he had discovered a new thermodynamic property, and he chose to name this property **entropy.** It is designated *S* and is defined as

$$dS = \left(\frac{\delta Q}{T}\right)_{int\ rev}$$

Entropy is an extensive property of a system and sometimes is referred to as *total entropy*. Entropy per unit mass, designated *s*, is an intensive property and has the unit kJ/kg* K.

The entropy change of a system during a process can be determined by integrating above equation between the initial and the final states:

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{int\ rev}$$

CHAPTER 4: THEORETICAL ANALYSIS

4.1. VAPOUR COMPRESSION REFRIGERATION

In the present work we studied a vapour compression refrigeration system equipped with liquid vapour heat exchanger (lvhe). The purpose of incorporating lvhe is to sub-cool the saturated liquid refrigerant coming out of the condenser exit and to superheat the saturated vapour refrigerant coming out of the evaporator exit.

Schematic line diagram of vapour compression refrigeration system with liquid vapour heat exchanger is shown in figure 4.1.

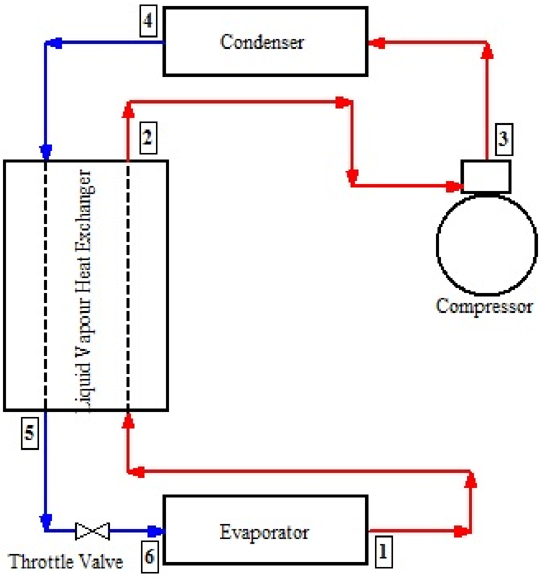


Figure 4.1: vapour compression refrigeration system with liquid vapour heat exchanger (lvhe).

Thus the given system consists of following processes:

- *Process 1-2:* superheating of saturated vapour refrigerant in lvhe
- *Process 2*-3: actual compression of superheated vapour refrigerant in compressor.
- *Process 3*-4: isobaric heat rejection in condenser.
- *Process 4*-5: sub-cooling of saturated liquid refrigerant in lvhe.
- *Process 5*-6: isenthalpic expansion in expansion device.
- *Process 6*-1: isobaric heat extraction in the evaporator.

The above system is represented on the *p-h chart* in the following figure.

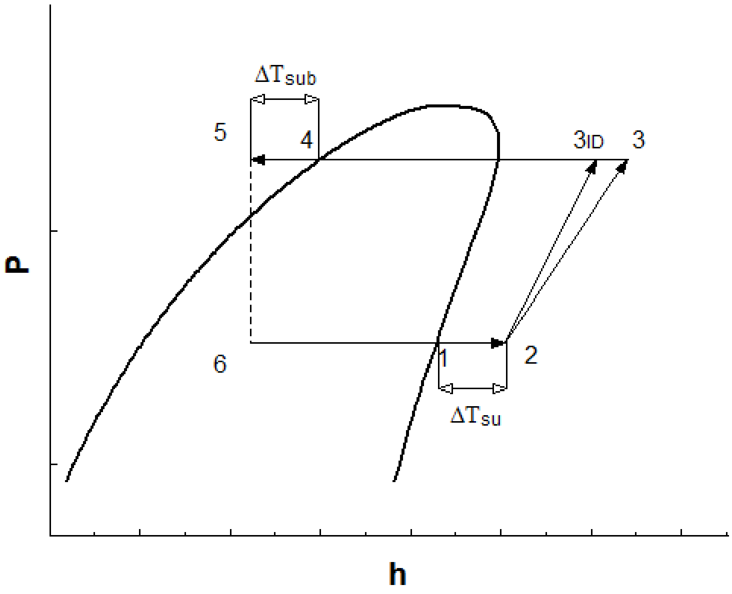


Figure 4.2: represents the vapour compression refrigeration cycle with lvhe on *p-h chart*.

4.2. ENERGY ANALYSIS

The first law of thermodynamics (energy analysis) is related to energy and work losses, while the second law of thermodynamics (exergy analysis) takes entropy into account via irreversibilities [59].

As we can consider each component of the system as open system and applying I_{st} law of thermodynamics i.e. *steady flow energy equation*, we will be able to obtain the energy interaction taking place in each of the component concerned.

Steady-flow energy equation as obtained from equation (1),

$$\dot{Q}_i + \dot{W}_i + \sum \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) = \dot{Q}_e + \dot{W}_e + \sum \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) \quad (1)$$

Applying steady flow energy to various components and neglecting change in Kinetic energy and change in Potential energy, we obtained the following expressions.

- **Evaporator**

  Heat extracted in the evaporator:

  $$\dot{Q}_{6-1} = \dot{Q}_E = \dot{m}_r (h_1 - h_6) \quad (2)$$

- **Compressor**

  Ideal work input to compressor:

  $$\dot{W}_{Ideal} = \dot{m}_r (h_{3ID} - h_2) \quad (3)$$

Isentropic efficiency of compressor: Ratio of ideal (isentropic) work required to the actual work required to do given task.

$$\eta_{isentropic} = \frac{\dot{W}_{ideal}}{\dot{W}_{actual}} \tag{4}$$

also $\dot{W}_{actual}$ can also be written in the terms of enthalpy as

$$\dot{W}_{actual} = \dot{m}_r(h_3 - h_2) \tag{5}$$

- **Condenser**

  Heat rejection in the condenser:

  $$\dot{Q}_{3-4} = \dot{m}_r(h_3 - h_4) \tag{6}$$

- **Liquid vapour heat exchanger**

  Heat transfer taking place between refrigerant coming out of the condenser exit and evaporator exit:

  Effectiveness (ε_{lvhe})of lvhe is defined as ratio of actual heat transfer to the maximum heat transfer taking place in the heat exchanger. It is the measure of the extent to which a heat exchanger approaches to the ideal heat exchanger.

  $$\varepsilon_{lvhe} = \frac{h_2 - h_1}{h_4 - h_1} \tag{7}$$

- **Expansion device**

  The expansion process is an isenthalpic (constant enthalpy) process, hence

  $$h_5 = h_6 \tag{8}$$

Coefficient of performance: obtained from second law of thermodynamics

$$COP_R = \frac{Desired\ output}{Required\ input} = \frac{\dot{Q}_E}{\dot{W}_{actual}} = \frac{\dot{m}_r(h_1 - h_6)}{\dot{W}_{ideal}}\eta_{isentropic}$$

$$= \frac{\dot{m}_r(h_1 - h_6)}{\dot{m}_r(h_3 - h_2)} \tag{9}$$

4.3. EXERGY ANALYSIS

The second law of thermodynamics infer the concept of exergy, a powerful tool for analysing both the quantity and quality of energy utilization. It is defined as the maximum amount of work obtainable when the stream of matter is brought from its initial state to the dead state by the processes during which the stream may interact only with the environment. The exergy balance is similar to an energy balance but has the fundamental difference that, while the energy balance is a statement of a law of conservation of energy, the exergy may be looked upon as a statement of law of degradation of energy [60]

Exergy analysis is a powerful tool in the design, optimization, and performance evaluation of energy systems. An exergy balance applied to a process or a whole plant tell us how much of the usable work potential, or exergy supplied as the inlet to the system under consideration has been consumed (irretrievably lost) by the process. The exergy destruction or irreversibility provides a generally applicable quantitative measure of process inefficiency. Analysing a multi-component plant indicates the total plant irreversibility distribution among the plant components, pinpointing those contributing most to overall plant inefficiency [60]

Exergy analysis is useful for improving the efficiency of energy-resource use, since it quantifies the locations, types and magnitudes of losses [61].

Exergy balance for a control region undergoing a steady-state process is expressed as

$$\dot{\mathrm{X}}_i + \dot{\mathrm{X}}_\mathrm{j}^\mathrm{Q} = \dot{\mathrm{X}}_e + \dot{\mathrm{W}}_\mathrm{j} + \mathrm{E}\dot{\mathrm{D}}_\mathrm{J} \tag{10}$$

$$\dot{\mathrm{X}}_i = \sum_{\mathrm{IN}} \dot{\mathrm{m}}\, x$$

$$\dot{\mathrm{X}}_e = \sum_{\mathrm{OUT}} \dot{\mathrm{m}}\, x$$

$$\dot{\mathrm{X}}_\mathrm{j}^\mathrm{Q} = \sum \left[\dot{\mathrm{Q}}_\mathrm{j} \frac{\mathrm{T} - \mathrm{T_o}}{\mathrm{T}}\right]$$

$$x = (\mathrm{h} - \mathrm{T_o s}) - (\mathrm{h_o} - \mathrm{T_o s_o})$$

where the first term on left hand and right hand side represent physical exergy (neglecting kinetic, potential and chemical exergy component) of stream of matter entering and leaving the control region respectively. The second term on left hand side and right hand side is thermal exergy flow, which gives exergy transfer rate corresponding to the heat transfer rate $\dot{Q}$ when the temperature at the control surface where heat transfer is occurring is T and exergy associated with work transfer to and from the control region. $\dot{ED}$ represents rate of exergy destruction [60].

4.3.1. Exergy Destruction(ED)

Irreversibilities such as friction, mixing, chemical reactions, heat transfer through a finite temperature difference, unrestrained expansion, non-quasi-equilibrium compression or expansion always *generate entropy,* and anything that generates entropy always *destroys exergy.* Exergy destroyed is a *positive quantity* for any actual process and becomes *zero* for a reversible process. Exergy destroyed represents the lost work potential and is also called the *irreversibility* or *lost work.*

- **Evaporator**

$$\dot{ED}_E = \dot{X}_6 + \dot{Q}_E\left(1 - \frac{T_o}{T_r}\right) - \dot{X}_1 = \dot{m}_r[(h_6 - h_1) - T_o(s_6 - s_1)] + \dot{Q}_E\left(1 - \frac{T_o}{T_r}\right) \quad (11)$$

- **Compressor**

$$\dot{ED}_{comp} = \dot{X}_2 + \dot{W}_{comp} - \dot{X}_3 = \dot{m}_r[T_o(s_3 - s_2)] \quad (12)$$

- **Condenser**

$$\dot{ED}_c = \dot{X}_3 - \dot{X}_4 = \dot{m}_r[(h_3 - h_4) - T_o(s_3 - s_4)] \quad (13)$$

- **Liquid vapour heat exchanger**

$$\dot{ED}_{lvhe} = (\dot{X}_4 - \dot{X}_5) + (\dot{X}_1 - \dot{X}_2)$$

$$= \dot{m}_r\big[(h_4 - h_5) + (h_1 - h_2) - T_o[(s_4 - s_5) + (s_1 - s_2)]\big] \quad (14)$$

- **Throttle Valve**

$$\dot{ED}_t = \dot{X}_5 - \dot{X}_6 = \dot{m}_r[T_o(s_5 - s_6)] \quad (15)$$

4.3.2. Total Exergy Destruction

It is the sum of exergy destruction in different components of the system.

$$\dot{\text{ED}}_{\text{total}} = \dot{\text{ED}}_{\text{E}} + \dot{\text{ED}}_{\text{comp}} + \dot{\text{ED}}_{\text{c}} + \dot{\text{ED}}_{\text{lvhe}} + \dot{\text{ED}}_{\text{t}} \tag{16}$$

Second law of thermodynamics provide the means of assigning a quality index to energy. The concept of exergy provides a useful measure of energy quality. Second law efficiency or exergetic efficiency is defined as the ratio of minimum exergy required to do a given task to the actual exergy consumed in performing the same task by (17)[62].

4.3.3. Exergetic Efficiency

$$\eta_{\text{exergetic}} = \frac{\text{minimum exergy required to do given task}}{\text{actual exergy consumed}} \tag{17}$$

For vapour compression refrigeration system, desired task is heat abstraction in to the evaporator from the space to be cooled at temperature T_r and minimum exergy required is the thermal exergy flow between evaporator and space to be cooled, i.e.

$$\dot{X}_{\text{E}}^{\text{Q}} = \dot{Q}_{\text{E}} \left| \left(1 - \frac{T_o}{T_r}\right) \right| \tag{18}$$

and actual exergy consumed is actual compressor work input, $\dot{W}_{\text{comp}}$.

Hence, exergetic efficiency is given by

$$\eta_{\text{exergetic}} = \frac{\dot{Q}_{\text{E}} \left| \left(1 - \frac{T_o}{T_r}\right) \right|}{\dot{W}_{\text{comp}}} = \frac{\text{COP}_{\text{vcr}}}{\text{COP}_{\text{rev}}} \tag{19}$$

where COP_{rev} and COP_{vcr} are coefficient of performance of reversible refrigerator operating between T_O and T_r and of actual vapour compression cycle respectively.

4.3.4. Exergy Destruction Ratio (EDR)

EDR is defined as the ratio of total exergy destruction in the system to minimum exergy required in doing a given task and is given by (20).

$$\text{EDR} = \frac{\dot{\text{ED}}_{\text{total}}}{\dot{X}_{\text{E}}^{\text{Q}}} = \frac{\text{COP}_{\text{vcr}}}{\text{COP}_{\text{rev}}} - 1 \tag{20}$$

EDR in terms of exergetic efficiency can be written as (21).

$$\mathrm{EDR} = \frac{1}{\eta_{\mathrm{exergetic}}} - 1 \tag{21}$$

4.3.5. Efficiency Defect $(\boldsymbol{\delta}_{\mathbf{j}})$

That fraction of the input which is lost through irreversibilities in the different components is called efficiency defect. It gives a direct casual relationship between component irreversibilities and their effect on the efficiency of the plant [60]. It is the ratio between rate of exergy destruction in j-th component to the actual exergy consumed (i.e. actual compressor work) and is given by (22).

$$\delta_{\mathrm{j}} = \frac{\dot{\mathrm{ED}}_{\mathrm{j}}}{\dot{\mathrm{W}}_{\mathrm{comp}}} \tag{22}$$

- **Evaporator**

$$\delta_{\mathrm{e}} = \frac{\dot{\mathrm{ED}}_{\mathrm{E}}}{\dot{\mathrm{W}}_{\mathrm{comp}}} \tag{23}$$

- **Compressor**

$$\delta_{\mathrm{comp}} = \frac{\dot{\mathrm{ED}}_{\mathrm{comp}}}{\dot{\mathrm{W}}_{\mathrm{comp}}} \tag{24}$$

- **Condenser**

$$\delta_{\mathrm{c}} = \frac{\dot{\mathrm{ED}}_{\mathrm{c}}}{\dot{\mathrm{W}}_{\mathrm{comp}}} \tag{25}$$

- **Liquid Vapour Heat Exchanger**

$$\delta_{\mathrm{lvhe}} = \frac{\dot{\mathrm{ED}}_{\mathrm{lvhe}}}{\dot{\mathrm{W}}_{\mathrm{comp}}} \tag{26}$$

- **Throttle Valve**

$$\delta_{\mathrm{t}} = \frac{\dot{\mathrm{ED}}_{\mathrm{t}}}{\dot{\mathrm{W}}_{\mathrm{comp}}} \tag{27}$$

CHAPTER 5: RESULTS AND DISCUSSION

A mathematical computational model is developed for performing the energy and exergy analysis of the system using EES software [63]

The input data assumed for the calculation of results shown in fig. 2-6 are:

1. Mass flow rate of refrigerant($\dot{m}_r$): 1 kg/s
2. Isentropic efficiency of compressor(η_{comp}): 75%
3. Effectiveness of liquid vapour heat exchanger(ε_{lvhe}): 0.8
4. Degree of sub-cooling of liquid refrigerant in lvhe(ΔT_{sub}): 5K
5. Difference between space and evaporator temperature($T_r - T_E$): 15K
6. Evaporator temperature(T_E): 223K to 273K
7. Condenser temperature(T_c): 313K and 323K
8. Ambient state temperature(T_o): 298K
9. It is assumed that pressure drop in evaporator; condenser and liquid vapour heat exchanger is negligible.
10. Effectiveness of liquid vapour heat exchanger is varied from 0 to 1, while discussing its effect on the system performance.
11. Degree of sub-cooling is varied from 0 K to 10 K, while discussing its effect on the system performance.

5.1. RESULTS

An extensive exergy analysis has been performed and the results obtained are arranged in the tabular form. Also the comparison between various parameters calculated, after varying evaporator temperature, ambient state temperature, degree of sub-cooling, and effectiveness of liquid vapour heat exchanger at two different values of condenser temperature, has been represented in graphs.

5.1.1. Variation of Evaporator Temperature

The following tables from table no. 5.1 to 5.5 shows the effect varying evaporator temperature on the various system parameters, corresponding to condenser temperature of 313K and 323K.

Table 5.1: For HFO-1234yf (T_C = 313K)

T_E (K)	T_C (K)	COP	$\eta_{exergetic}$	EDR	δ_{comp}	δ_c	δ_{lvhe}	δ_t	δ_e
223	313	0.7896	0.1991	4.024	0.1877	0.2381	0.08389	0.2263	0.06501
228	313	0.9032	0.2044	3.892	0.1909	0.2375	0.07968	0.2164	0.07105
233	313	1.034	0.2085	3.796	0.194	0.2381	0.07515	0.2064	0.07778
238	313	1.186	0.211	3.74	0.1971	0.2402	0.07025	0.1962	0.08534
243	313	1.364	0.2115	3.729	0.2	0.2438	0.06493	0.1858	0.09393
248	313	1.574	0.2094	3.776	0.2029	0.2494	0.05915	0.1754	0.1038
253	313	1.823	0.2041	3.9	0.2057	0.2572	0.05285	0.1649	0.1152
258	313	2.124	0.1946	4.14	0.2085	0.2678	0.04597	0.1544	0.1288
263	313	2.493	0.1794	4.575	0.2112	0.2821	0.03843	0.144	0.145
268	313	2.952	0.1565	5.39	0.2139	0.301	0.03012	0.1337	0.1648
273	313	3.537	0.1228	7.143	0.2165	0.3263	0.02092	0.1238	0.1896

Table 5.2: For HFO-1234yf (T_C = 323K)

T_E (K)	T_C (K)	COP	$\eta_{exergetic}$	EDR	δ_{comp}	δ_c	δ_{lvhe}	δ_t	δ_e
223	323	0.5895	0.1486	5.728	0.1798	0.2928	0.08144	0.2489	0.04854
228	323	0.6758	0.153	5.537	0.1828	0.2945	0.07753	0.239	0.05317
233	323	0.7744	0.1561	5.405	0.1857	0.2976	0.07335	0.229	0.05825
238	323	0.8876	0.1579	5.334	0.1885	0.3023	0.06888	0.2186	0.06386
243	323	1.018	0.1579	5.334	0.1912	0.3086	0.06408	0.2081	0.07012
248	323	1.17	0.1557	5.422	0.1939	0.317	0.05893	0.1973	0.07717
253	323	1.348	0.1509	5.629	0.1965	0.3277	0.05341	0.1864	0.08518
258	323	1.557	0.1426	6.012	0.199	0.3412	0.0475	0.1753	0.0944
263	323	1.808	0.13	6.69	0.2015	0.3581	0.04117	0.164	0.1051
268	323	2.11	0.1118	7.943	0.2039	0.3794	0.03441	0.1527	0.1178
273	323	2.48	0.08611	10.61	0.2063	0.4062	0.02721	0.1412	0.1329

Table 5.3: For HFO-1234ze (T_C = 313K)

T_E (K)	T_C (K)	COP	$\eta_{exergetic}$	EDR	δ_{comp}	δ_c	δ_{lvhe}	δ_t	δ_e
223	313	0.8562	0.2159	3.633	0.1831	0.2421	0.08309	0.2057	0.0701
228	313	0.9789	0.2216	3.513	0.1867	0.24	0.07884	0.1961	0.07679
233	313	1.119	0.2256	3.432	0.1902	0.2391	0.07467	0.1861	0.0842
238	313	1.281	0.2278	3.39	0.1937	0.2397	0.07047	0.1759	0.09251
243	313	1.469	0.2277	3.392	0.197	0.2418	0.06611	0.1654	0.102
248	313	1.689	0.2248	3.448	0.2002	0.2458	0.06154	0.1548	0.1129
253	313	1.951	0.2184	3.578	0.2033	0.2521	0.05668	0.1439	0.1256
258	313	2.266	0.2075	3.819	0.2064	0.261	0.0515	0.1328	0.1407
263	313	2.651	0.1907	4.244	0.2094	0.2735	0.04598	0.1216	0.1588
268	313	3.128	0.1658	5.031	0.2123	0.2904	0.04015	0.1102	0.1811
273	313	3.735	0.1297	6.712	0.2152	0.3134	0.03402	0.09868	0.209

Table 5.4: For HFO-1234ze (T_C = 323K)

T_E (K)	T_C (K)	COP	$\eta_{exergetic}$	EDR	δ_{comp}	δ_c	δ_{lvhe}	δ_t	δ_e
223	323	0.6591	0.1662	5.018	0.1752	0.2983	0.07649	0.2299	0.05397
228	323	0.7539	0.1706	4.86	0.1785	0.2988	0.07219	0.2207	0.05914
233	323	0.8611	0.1736	4.76	0.1818	0.3007	0.06794	0.2112	0.06478
238	323	0.983	0.1748	4.719	0.185	0.3041	0.06363	0.2015	0.07101
243	323	1.123	0.1741	4.744	0.188	0.3093	0.05916	0.1915	0.07797
248	323	1.285	0.171	4.849	0.191	0.3164	0.05447	0.1813	0.08584
253	323	1.473	0.1649	5.064	0.1939	0.326	0.0495	0.1709	0.09484
258	323	1.695	0.1552	5.442	0.1967	0.3383	0.04421	0.1603	0.1052
263	323	1.959	0.141	6.094	0.1995	0.354	0.0386	0.1495	0.1174
268	323	2.277	0.1207	7.285	0.2022	0.3741	0.03268	0.1386	0.1318
273	323	2.666	0.09256	9.804	0.2048	0.3995	0.02647	0.1275	0.1491

Table 5.5: For HFC-134a (T_C = 313K)

T_E (K)	T_C (K)	COP	$\eta_{exergetic}$	EDR	δ_{comp}	δ_c	δ_{lvhe}	δ_t	δ_e
223	313	0.9041	0.2279	3.387	0.1754	0.2665	0.06753	0.1866	0.07605
228	313	1.023	0.2314	3.321	0.1793	0.2634	0.06511	0.1784	0.08241
233	313	1.159	0.2336	3.281	0.1831	0.2615	0.06241	0.1699	0.08955
238	313	1.316	0.2341	3.271	0.1868	0.2609	0.05941	0.1612	0.09762
243	313	1.5	0.2325	3.3	0.1904	0.2619	0.05612	0.1522	0.1068
248	313	1.716	0.2283	3.38	0.1939	0.2647	0.05253	0.1431	0.1175
253	313	1.972	0.2208	3.53	0.1974	0.2696	0.04865	0.1337	0.1299
258	313	2.28	0.2088	3.789	0.2009	0.2772	0.04446	0.1241	0.1446
263	313	2.656	0.1911	4.233	0.2043	0.2881	0.03996	0.1143	0.1622
268	313	3.123	0.1655	5.041	0.2076	0.3035	0.03516	0.1044	0.1838
273	313	3.716	0.129	6.75	0.2109	0.3247	0.03007	0.09426	0.211

Table 5.6: For HFC-134a (T_C = 323K)

T_E (K)	T_C (K)	COP	$\eta_{exergetic}$	EDR	δ_{comp}	δ_c	δ_{lvhe}	δ_t	δ_e
223	323	0.7116	0.1794	4.574	0.1677	0.3219	0.0623	0.2088	0.05986
228	323	0.8029	0.1817	4.503	0.1713	0.3215	0.05974	0.2011	0.06471
233	323	0.9069	0.1828	4.469	0.1748	0.3224	0.0569	0.1931	0.07009
238	323	1.026	0.1824	4.481	0.1782	0.3248	0.05378	0.1848	0.07608
243	323	1.162	0.1802	4.549	0.1815	0.3288	0.05037	0.1763	0.0828
248	323	1.321	0.1757	4.69	0.1847	0.3349	0.04666	0.1676	0.09042
253	323	1.505	0.1685	4.936	0.1879	0.3432	0.04267	0.1586	0.09911
258	323	1.722	0.1577	5.343	0.1911	0.3542	0.03838	0.1495	0.1091
263	323	1.979	0.1424	6.023	0.1942	0.3686	0.0338	0.1402	0.1209
268	323	2.289	0.1213	7.242	0.1972	0.3871	0.02891	0.1308	0.1347
273	323	2.667	0.09261	9.798	0.2002	0.4109	0.02373	0.1211	0.1514

5.1.2. Variation of Ambient State Temperature (T_0)

Table 5.7: For HFO-1234yf (T_C = 313K)

T_0 (K)	$\eta_{exergetic}$	EDR
298	0.1228	7.143
301	0.1597	5.264
304	0.1965	4.089
307	0.2333	3.286
310	0.2702	2.701
313	0.307	2.257
316	0.3439	1.908
319	0.3807	1.627
322	0.4176	1.395
325	0.4544	1.201
328	0.4912	1.036

Table 5.8: For HFO-1234yf (T_C = 323K)

T_0 (K)	$\eta_{exergetic}$	EDR
298	0.08611	10.61
301	0.1119	7.934
304	0.1378	6.259
307	0.1636	5.112
310	0.1894	4.279
313	0.2153	3.645
316	0.2411	3.148
319	0.2669	2.746
322	0.2928	2.416
325	0.3186	2.139
328	0.3444	1.903

Table 5.9: For HFO-1234ze (T_C = 313K)

T_0 (K)	$\eta_{exergetic}$	EDR
298	0.1297	6.712
301	0.1686	4.932
304	0.2075	3.82
307	0.2464	3.059
310	0.2853	2.505
313	0.3242	2.085
316	0.3631	1.754
319	0.402	1.488
322	0.4409	1.268
325	0.4798	1.084
328	0.5187	0.9279

Table 5.10: For HFO-1234ze (T_C = 323K)

T_0 (K)	**$\eta_{exergetic}$**	**EDR**
298	0.09256	9.804
301	0.1203	7.311
304	0.1481	5.753
307	0.1759	4.686
310	0.2036	3.911
313	0.2314	3.322
316	0.2592	2.859
319	0.2869	2.485
322	0.3147	2.178
325	0.3425	1.92
328	0.3702	1.701

Table 5.11: For HFC-134a (T_C = 313K)

T_0 (K)	**$\eta_{exergetic}$**	**EDR**
298	0.129	6.75
301	0.1677	4.962
304	0.2064	3.844
307	0.2452	3.079
310	0.2839	2.523
313	0.3226	2.1
316	0.3613	1.768
319	0.4	1.5
322	0.4387	1.28
325	0.4774	1.095
328	0.5161	0.9376

Table 5.12: For HFC-134a (T_C = 323K)

T_0 (K)	**$\eta_{exergetic}$**	**EDR**
298	0.09261	9.798
301	0.1204	7.306
304	0.1482	5.749
307	0.176	4.683
310	0.2037	3.908
313	0.2315	3.319
316	0.2593	2.857
319	0.2871	2.483
322	0.3149	2.176
325	0.3426	1.918
328	0.3704	1.7

5.1.3. Variation of Degree of Sub-cooling (ΔT_{sub})

Table 5.13: For HFO-1234yf (T_C = 313K)

ΔT_{sub}	COP	$\eta_{exergetic}$	EDR
0	3.337	0.1159	7.63
1	3.366	0.1169	7.555
2	3.409	0.1184	7.448
3	3.452	0.1199	7.343
4	3.495	0.1213	7.241
5	3.537	0.1228	7.143
6	3.579	0.1243	7.046
7	3.621	0.1257	6.953
8	3.663	0.1272	6.862
9	3.705	0.1286	6.773
10	3.747	0.1301	6.687

Table 5.14: For HFO-1234yf (T_C = 323K)

ΔT_{sub}	COP	$\eta_{exergetic}$	EDR
0	2.302	0.07993	11.51
1	2.338	0.08117	11.32
2	2.374	0.08241	11.13
3	2.409	0.08365	10.95
4	2.445	0.08488	10.78
5	2.48	0.08611	10.61
6	2.515	0.08733	10.45
7	2.55	0.08854	10.29
8	2.585	0.08975	10.14
9	2.619	0.09095	9.995
10	2.654	0.09215	9.852

Table 5.15: For HFO-1234ze (T_C = 313K)

ΔT_{sub}	COP	$\eta_{exergetic}$	EDR
0	3.536	0.1228	7.145
1	3.576	0.1242	7.054
2	3.616	0.1255	6.965
3	3.656	0.1269	6.879
4	3.695	0.1283	6.794
5	3.735	0.1297	6.712
6	3.774	0.131	6.631
7	3.813	0.1324	6.552
8	3.853	0.1338	6.476
9	3.892	0.1351	6.4
10	3.931	0.1365	6.327

Table 5.16: For HFO-1234ze (T_C = 323K)

ΔT_{sub}	COP	$\eta_{exergetic}$	EDR
0	2.502	0.08687	10.51
1	2.535	0.08802	10.36
2	2.568	0.08916	10.22
3	2.601	0.0903	10.07
4	2.633	0.09143	9.938
5	2.666	0.09256	9.804
6	2.698	0.09368	9.674
7	2.73	0.0948	9.548
8	2.762	0.09592	9.425
9	2.795	0.09703	9.306
10	2.827	0.09814	9.189

Table 5.17: For HFC-134a (T_C = 313K)

ΔT_{sub}	COP	$\eta_{exergetic}$	EDR
0	3.532	0.1226	7.154
1	3.569	0.1239	7.069
2	3.606	0.1252	6.986
3	3.643	0.1265	6.906
4	3.679	0.1278	6.827
5	3.716	0.129	6.75
6	3.752	0.1303	6.675
7	3.789	0.1315	6.602
8	3.825	0.1328	6.53
9	3.861	0.134	6.46
10	3.896	0.1353	6.391

Table 5.18: For HFC-134a (T_C = 323K)

ΔT_{sub}	COP	$\eta_{exergetic}$	EDR
0	2.514	0.0873	10.45
1	2.545	0.08838	10.32
2	2.576	0.08944	10.18
3	2.606	0.0905	10.05
4	2.637	0.09156	9.922
5	2.667	0.09261	9.798
6	2.697	0.09365	9.678
7	2.727	0.09469	9.561
8	2.757	0.09573	9.446
9	2.787	0.09676	9.335
10	2.816	0.09778	9.227

5.1.4. Variation of Effectiveness of Liquid Vapour Heat Exchanger (lvhe)

Table 5.19: For HFO-1234yf (T_C = 313K)

ε_{lvhe}	COP	$\eta_{exergetic}$	EDR
0	4.181	0.1452	5.889
0.1	4.076	0.1415	6.066
0.2	3.985	0.1384	6.228
0.3	3.899	0.1354	6.387
0.4	3.818	0.1326	6.543
0.5	3.742	0.1299	6.696
0.6	3.67	0.1274	6.847
0.7	3.602	0.1251	6.996
0.8	3.537	0.1228	7.143
0.9	3.475	0.1207	7.288
1	3.416	0.1186	7.431

Table 5.20: For HFO-1234yf (T_C = 323K)

ε_{lvhe}	COP	$\eta_{exergetic}$	EDR
0	3.058	0.1062	8.419
0.1	2.959	0.1028	8.732
0.2	2.875	0.09981	9.019
0.3	2.796	0.0971	9.299
0.4	2.724	0.09459	9.572
0.5	2.657	0.09226	9.839
0.6	2.594	0.09008	10.1
0.7	2.535	0.08803	10.36
0.8	2.48	0.08611	10.61
0.9	2.428	0.08429	10.86
1	2.378	0.08257	11.11

Table 5.21: For HFO-1234ze (T_C = 313K)

ε_{lvhe}	COP	$\eta_{exergetic}$	EDR
0	4.335	0.1505	5.644
0.1	4.24	0.1472	5.792
0.2	4.157	0.1443	5.929
0.3	4.078	0.1416	6.063
0.4	4.003	0.139	6.196
0.5	3.931	0.1365	6.327
0.6	3.863	0.1341	6.456
0.7	3.797	0.1318	6.584
0.8	3.735	0.1297	6.712
0.9	3.675	0.1276	6.838
1	3.617	0.1256	6.963

Table 5.22: For HFO-1234ze (T_C = 323K)

ε_{lvhe}	COP	$\eta_{exergetic}$	EDR
0	3.211	0.1115	7.968
0.1	3.122	0.1084	8.225
0.2	3.044	0.1057	8.462
0.3	2.971	0.1032	8.694
0.4	2.903	0.1008	8.922
0.5	2.838	0.09855	9.147
0.6	2.778	0.09644	9.369
0.7	2.72	0.09445	9.588
0.8	2.666	0.09256	9.804
0.9	2.614	0.09076	10.02
1	2.564	0.08904	10.23

Table 5.23: For HFC-134a (T_C = 313K)

ε_{lvhe}	COP	$\eta_{exergetic}$	EDR
0	4.335	0.1505	5.643
0.1	4.242	0.1473	5.79
0.2	4.153	0.1442	5.934
0.3	4.07	0.1413	6.075
0.4	3.992	0.1386	6.214
0.5	3.918	0.136	6.351
0.6	3.847	0.1336	6.486
0.7	3.78	0.1313	6.619
0.8	3.716	0.129	6.75
0.9	3.655	0.1269	6.88
1	3.596	0.1249	7.009

Table 5.24: For HFC-134a (T_C = 323K)

ε_{lvhe}	COP	$\eta_{exergetic}$	EDR
0	3.228	0.1121	7.921
0.1	3.14	0.109	8.173
0.2	3.057	0.1062	8.42
0.3	2.981	0.1035	8.66
0.4	2.91	0.1011	8.896
0.5	2.844	0.09875	9.127
0.6	2.782	0.09658	9.354
0.7	2.723	0.09454	9.578
0.8	2.667	0.09261	9.798
0.9	2.614	0.09077	10.02
1	2.564	0.08903	10.23

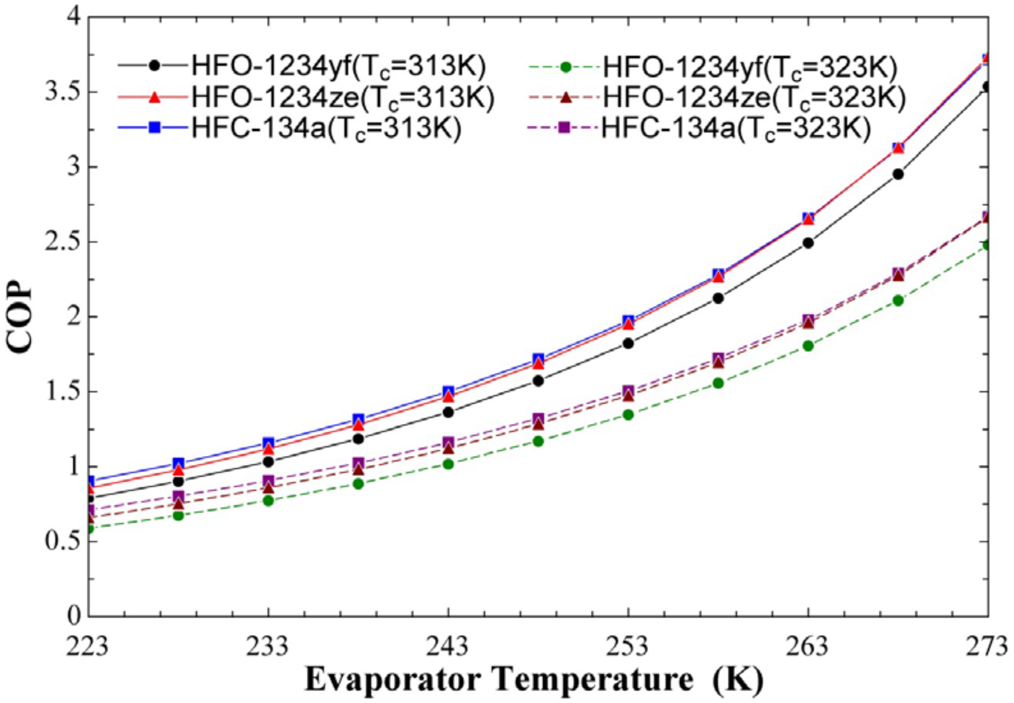


Figure 5.1 variations in COP with evaporator temperature (T_E).

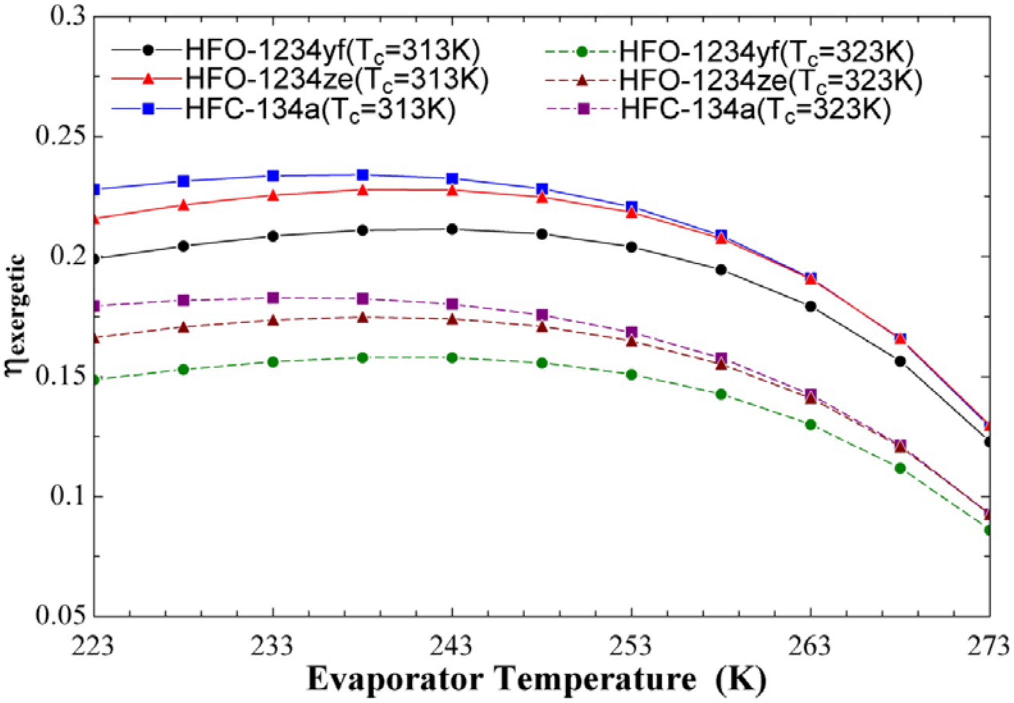


Figure 5.2 variations in exergetic efficiency ($\eta_{exergetic}$) with evaporator temperature (T_E).

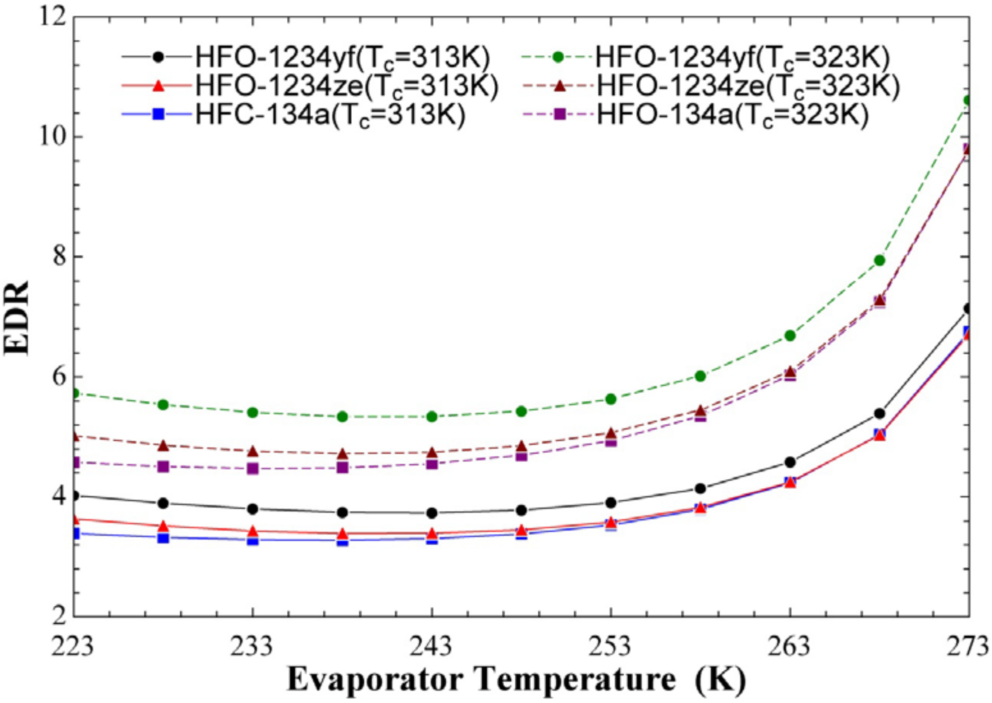


Figure 5.3 variations in Exergy destruction ratio (EDR) with evaporator temperature (T_E).

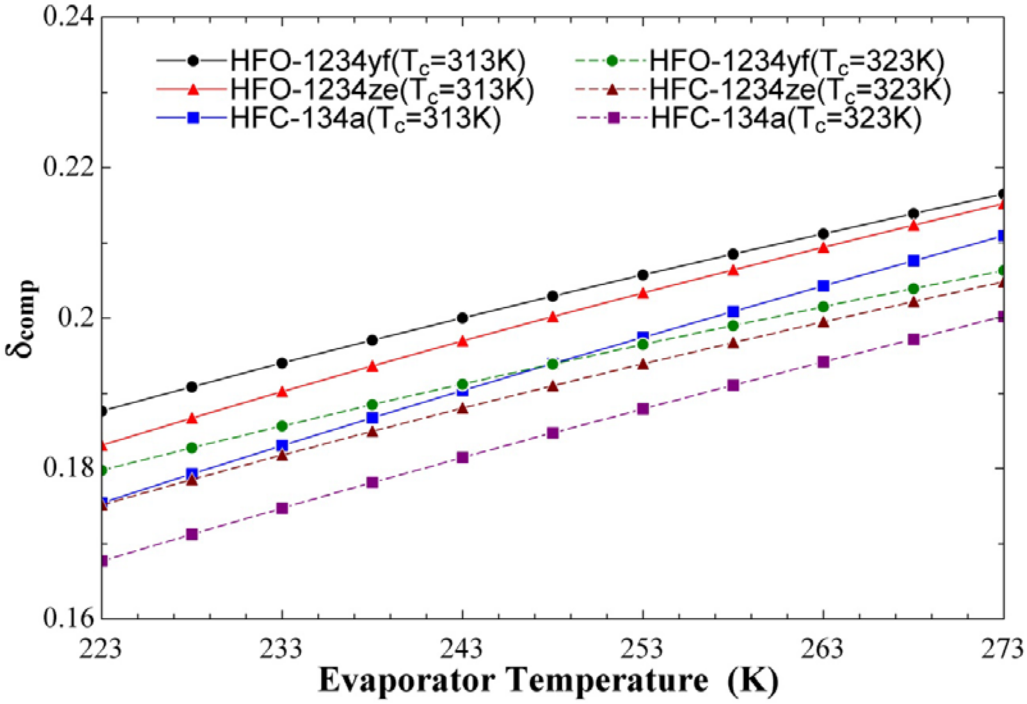


Figure 5.4 variations in efficiency defect in compressor (δ_{comp}) with evaporator temperature (T_E).

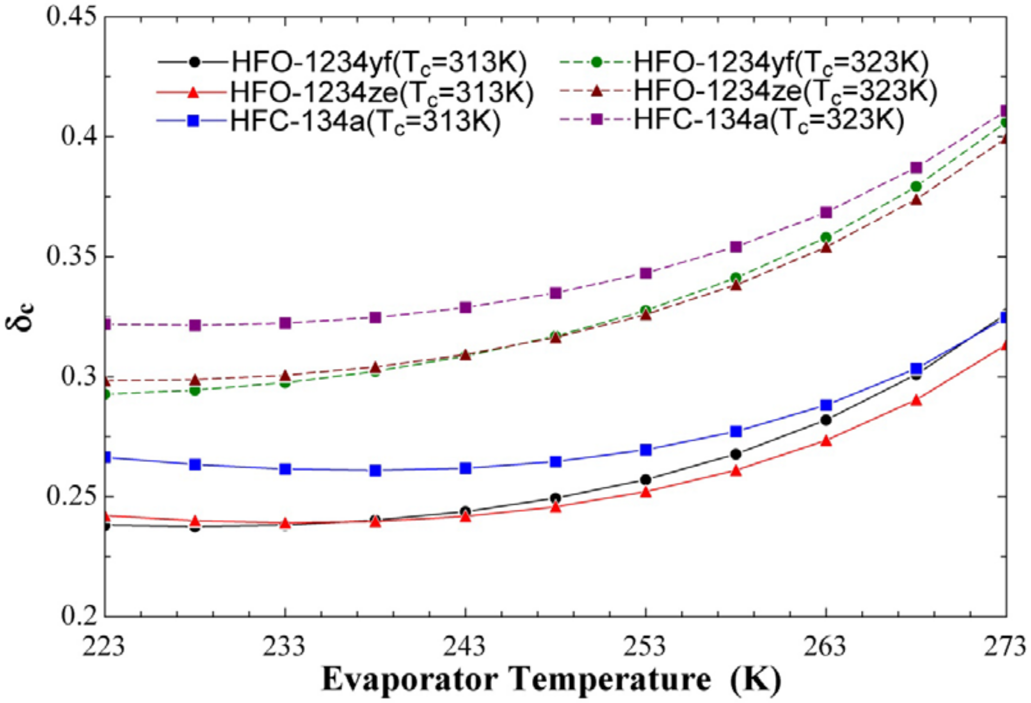


Figure 5.5 variations in efficiency defect in condenser (δ_c) with evaporator temperature (T_E).

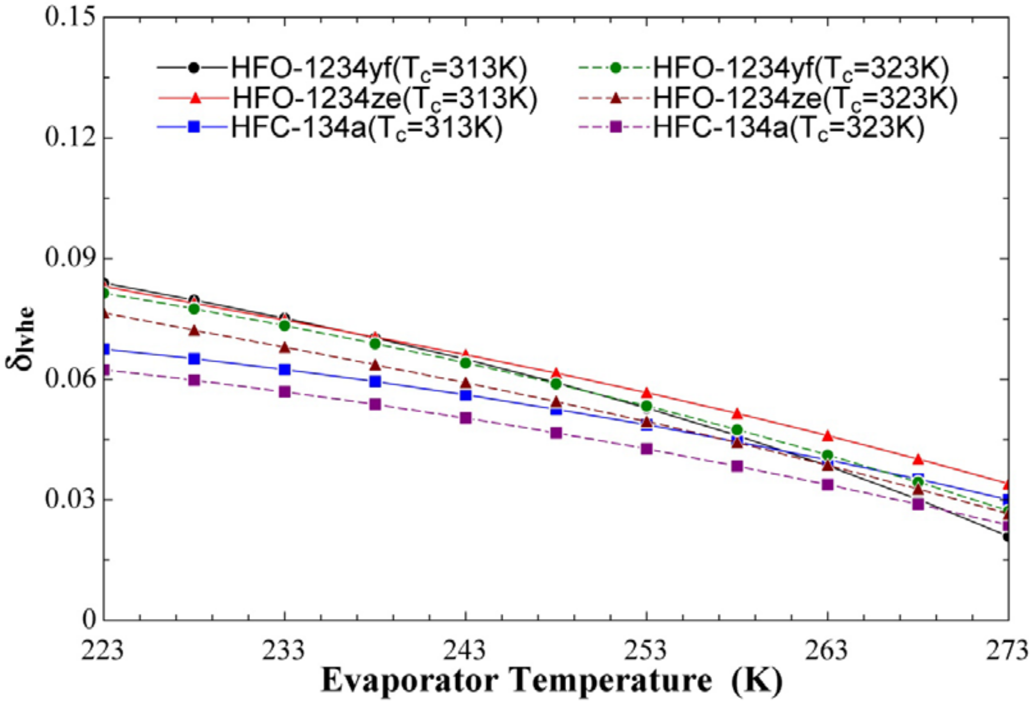


Figure 5.6 variations in efficiency defect in liquid vapour heat exchanger (δ_{lvhe}) with evaporator temperature (T_E).

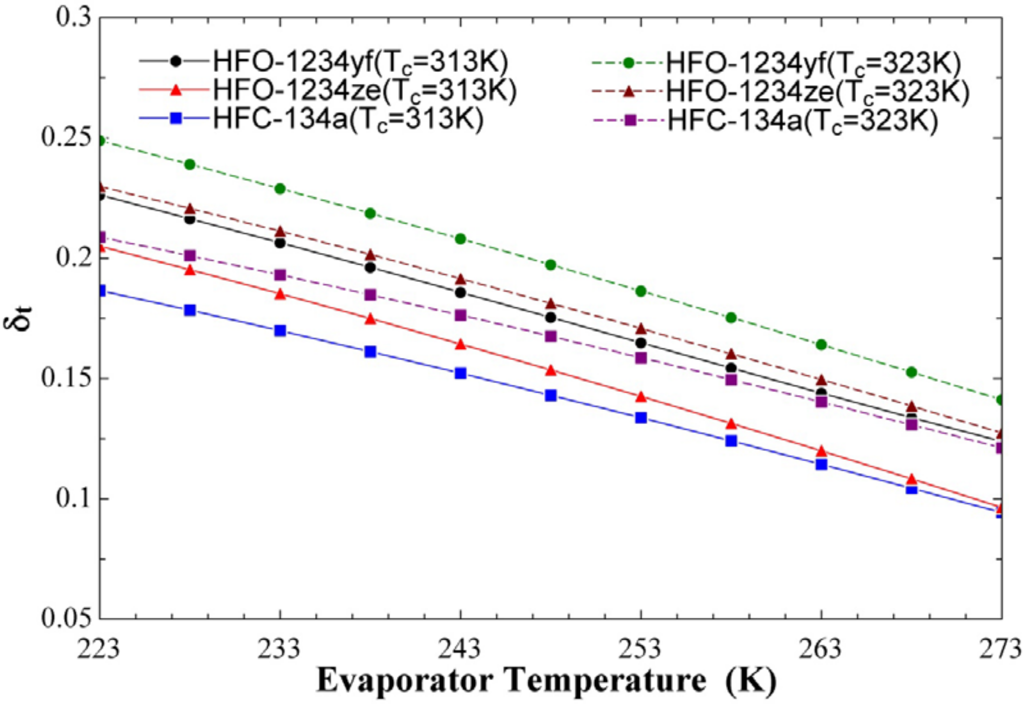


Figure 5.7 variations in efficiency defect in throttle valve (δ_t) with evaporator temperature (T_E).

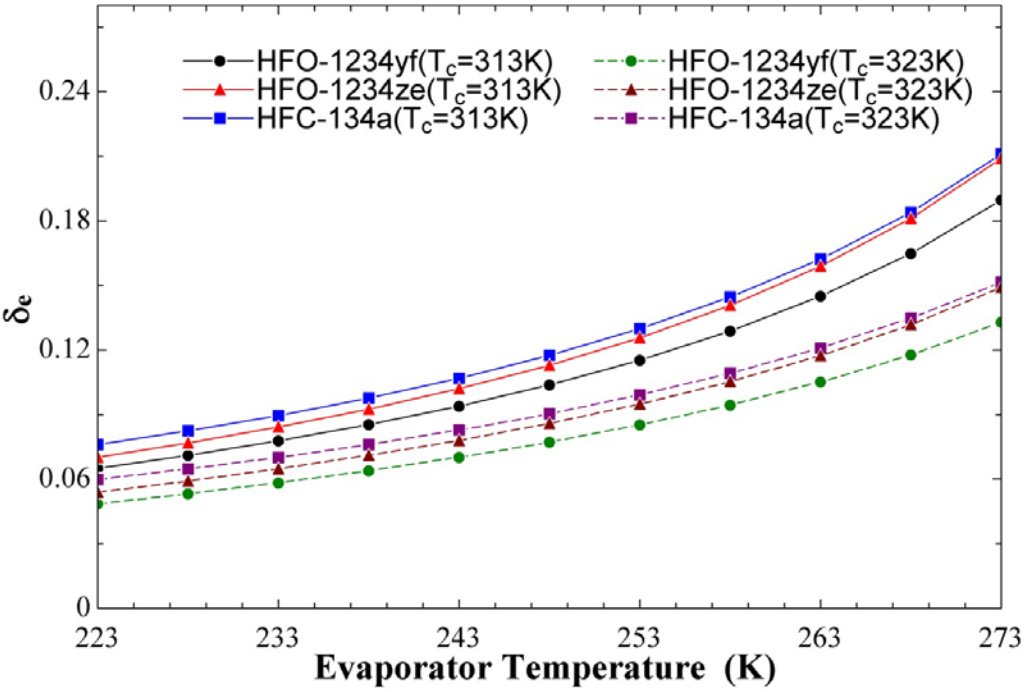


Figure 5.8 variations in efficiency defect in evaporator (δ_e) with evaporator temperature (T_E).

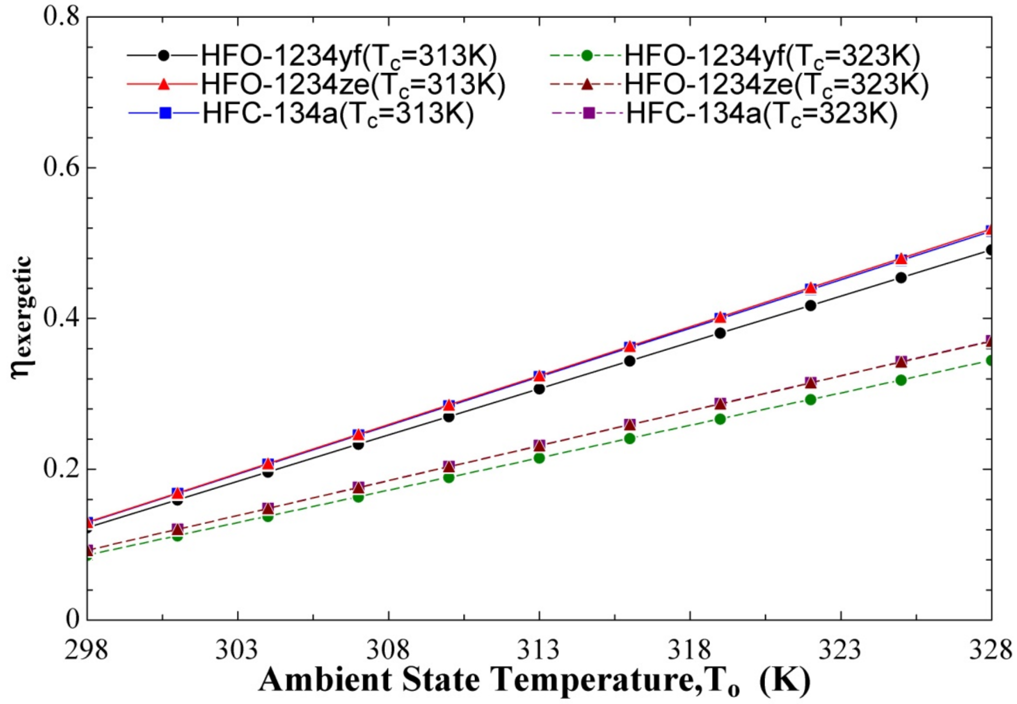


Figure 5.9 variations in exergetic efficiency ($\eta_{exergetic}$) with ambient state temperature (T_E = 273K)

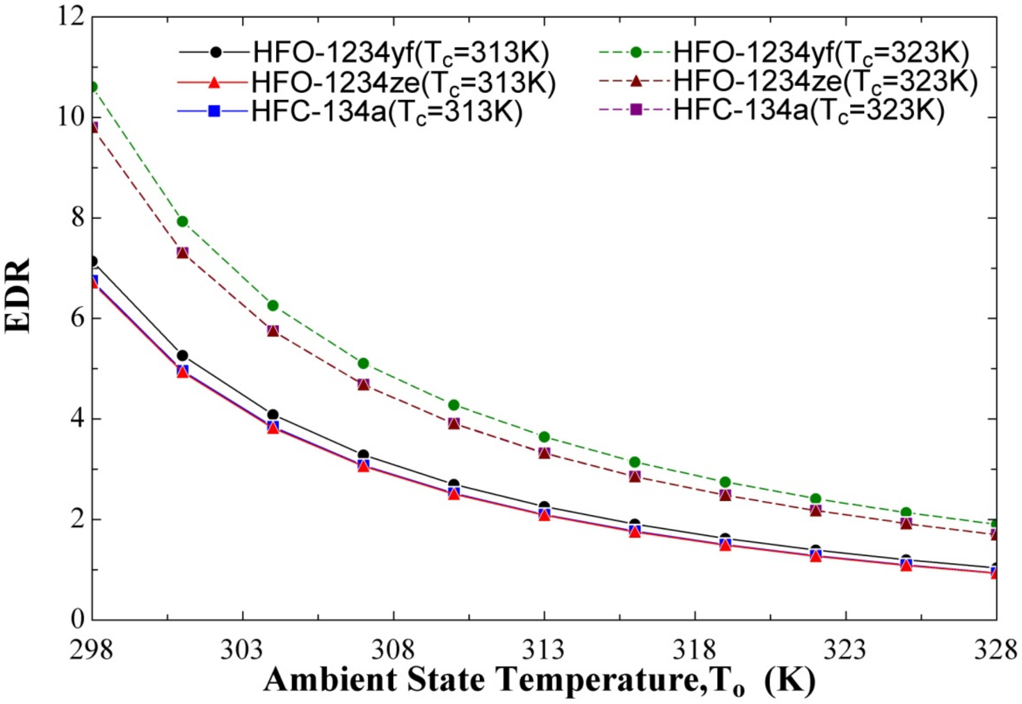


Figure 5.10 variations in EDR with ambient state temperature (T_E = 273K).

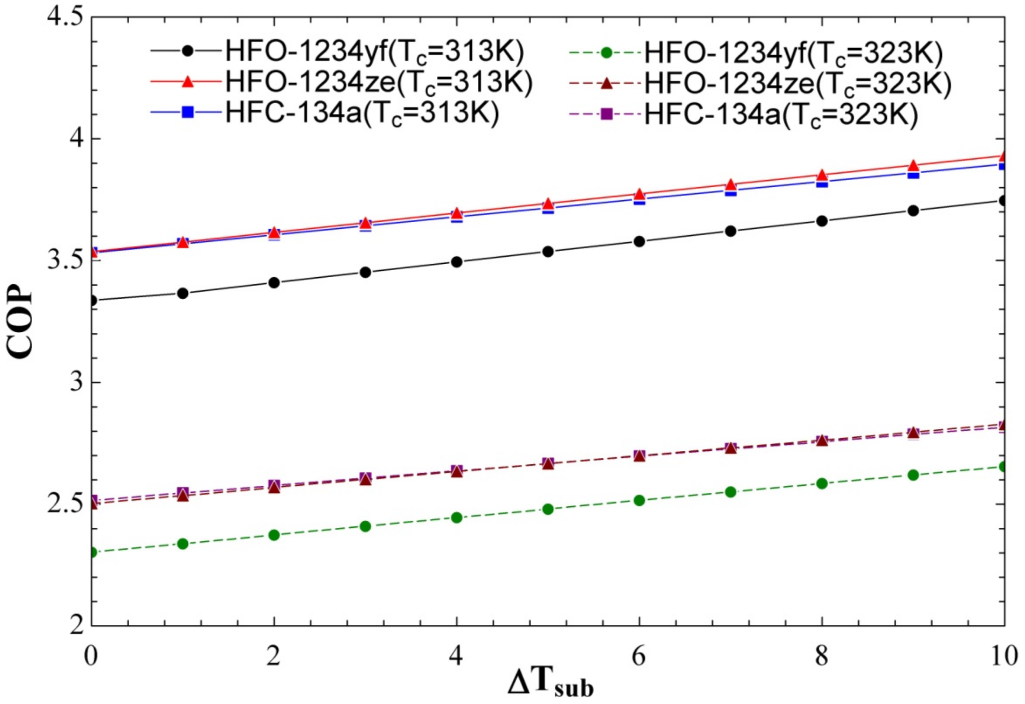


Figure 5.11 variations in COP with degree of sub-cooling (T_E = 273K).

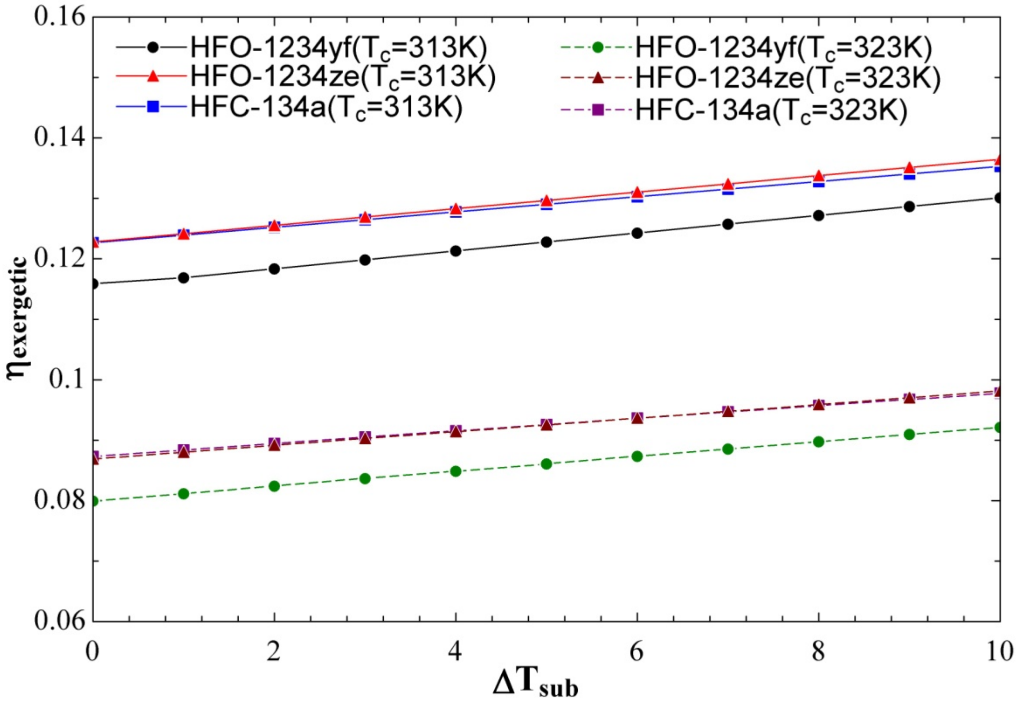


Figure 5.12 variations in exergetic efficiency ($\eta_{exergetic}$) with degree of sub-cooling (T_E = 273K)

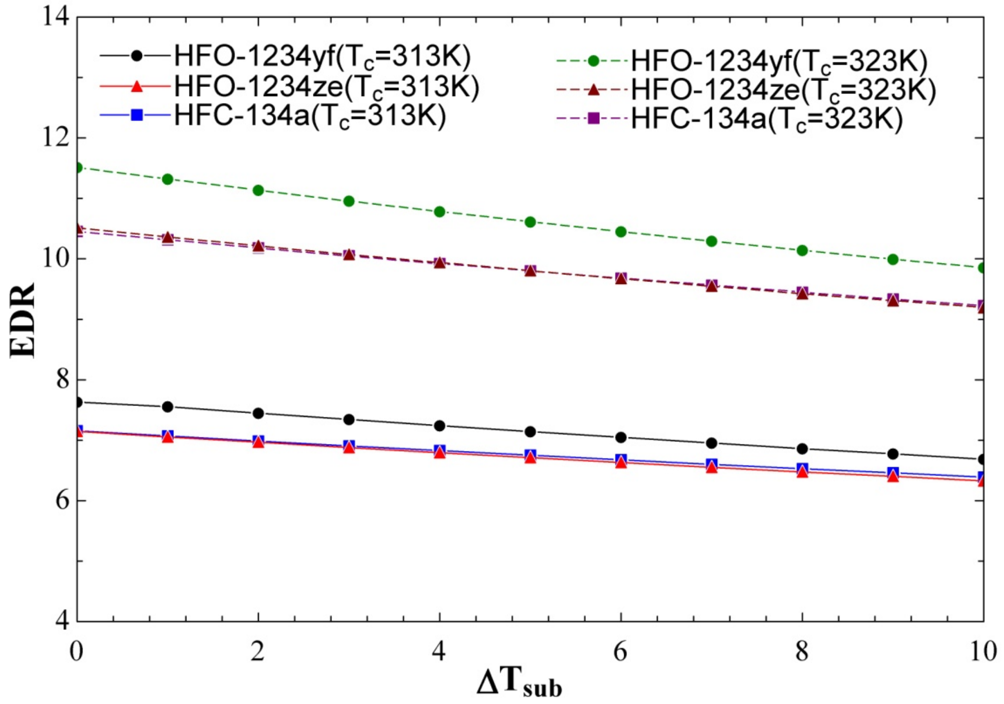


Figure 5.13 variations in EDR with degree of sub-cooling (T_E = 273K)

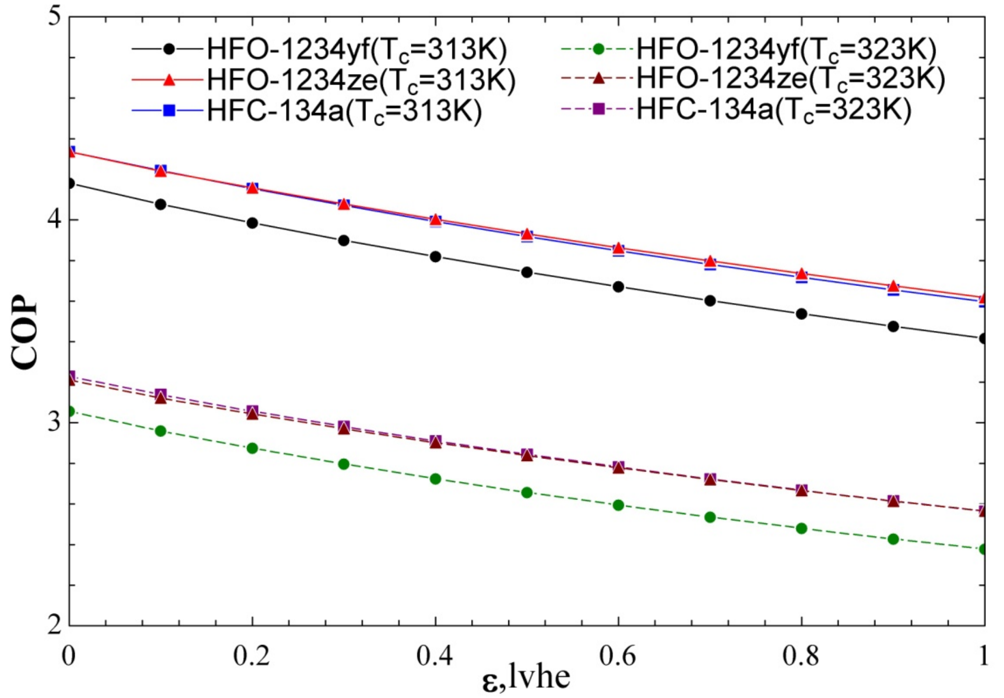


Figure 5.14 variations in COP with effectiveness of liquid vapour heat exchanger (T_E = 273K)

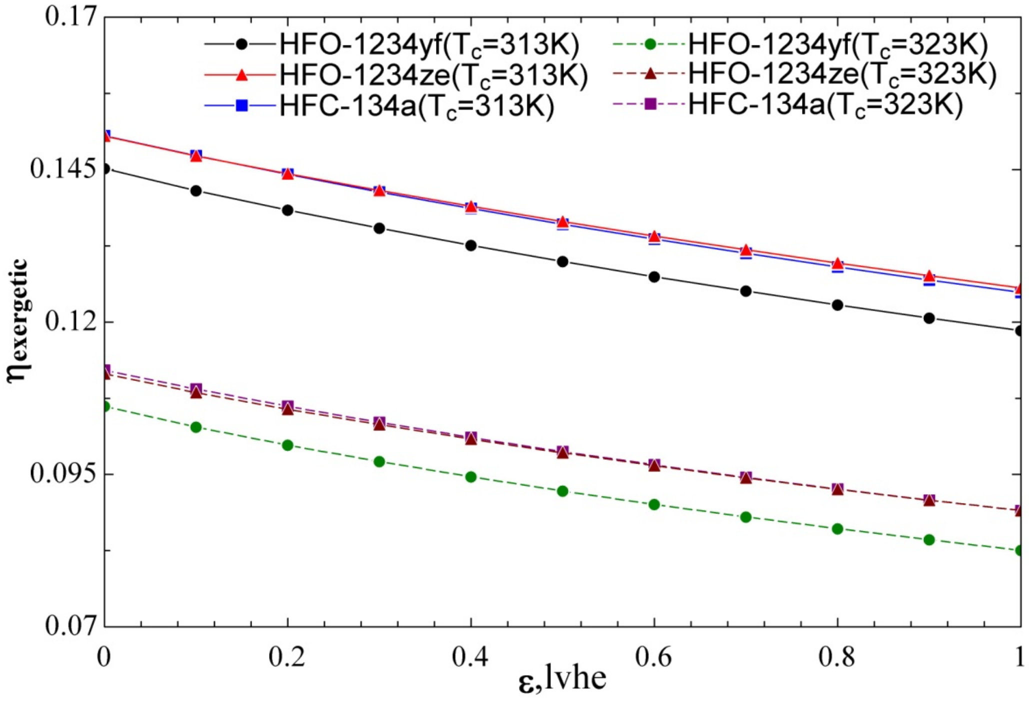


Figure 5.15 variations in exergetic efficiency ($\eta_{exergetic}$) with effectiveness of liquid vapour heat exchanger (T_E = 273K)

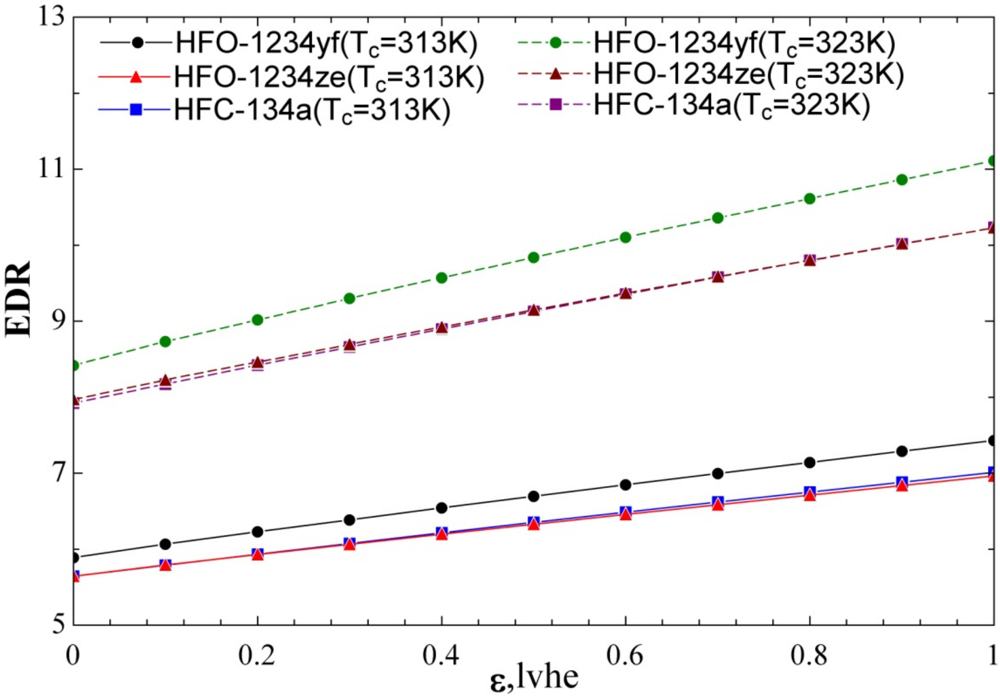


Figure 5.16 variations in EDR with effectiveness of liquid vapour heat exchanger (T_E = 273K)

5.2. DISCUSSION

Fig.5.1 shows variation of COP with evaporator temperature and it can be easily inferred that as the evaporator temperature is increases, pressure ratio decreases causing compressor work to reduce and specific refrigerating effect to increase and hence COP increases.HFC-134a shows highest COP among all the refrigerants, followed very closely by HFO-1234ze which shows almost same COP.HFO-1234yf shows lesser COP then HFC-134a. As the condenser temperature increases, pressure ratio increases causing compressor work to increase and specific refrigerating effect to decrease, hence decrease in COP. The similar trend has been shown by the refrigerants corresponding to the condenser temperature of 323K.The COP of HFC-134a is 14.5-5% and 20.7-7.5% higher than HFO-1234yf for T_C = 313K & 323K respectively, having minimum value at higher end of evaporator temperature, and 5.6% and 8% higher than HFO-1234ze for T_C = 313K & 323K respectively, which diminishes at high value of evaporator temperature.

Fig.5.2 represents the variation of exergetic efficiency with evaporator temperature. Exergetic efficiency first rises and then falls, and this can be attributed to two parameters (refer 19). First parameter is thermal exergy flow in the evaporator i.e. $\dot{\mathrm{Q}}_{\mathrm{e}}\left|\left(1-\frac{\mathrm{T_o}}{\mathrm{T_r}}\right)\right|$, with increase in evaporator temperature, refrigerating effect $\dot{\mathrm{Q}}_{\mathrm{e}}$ increases, however the term $\left|\left(1-\frac{\mathrm{T_o}}{\mathrm{T_r}}\right)\right|$ reduces since Tr approaches To and second parameter is compressor work, which reduces with the increment in the evaporator temperature. The effect of $\dot{\mathrm{Q}}_{\mathrm{e}}$ and $\dot{\mathrm{W}}_{\mathrm{comp}}$ is to increase the exergetic efficiency as opposite to the decreasing effect of$\left|\left(1-\frac{\mathrm{T_o}}{\mathrm{T_r}}\right)\right|$. The combined effect of these two parameters is to increase the exergetic efficiency till it reaches the maximum point and the evaporator temperature corresponding to this efficiency is optimum evaporator temperature, beyond which the combined effect is to decrease the exergetic efficiency. Exergetic efficiency of HFC-134a is 14.4-5% higher than HFO-1234yf for T_C = 313K and 20.7-7.5% for T_C = 323K, having minimum difference at the higher end of evaporator temperature and 5.5%, 7.9% higher than HFO-1234ze at lower end of evaporator temperature, corresponding to T_C = 313K & 323K respectively, which is negligible at higher end of evaporator temperature.

Fig.5.3 represents the variation of exergy destruction ratio (EDR) with evaporator temperature, and it has been observed that trend shown by curves of EDR is reverse of that shown by curves of exergetic efficiency and it can be validated by (21). EDR of HFO-1234yf is higher than HFC-134a and this difference decreases in the range 5.8-18.8% for T_C = 313K and 8.3-25.2% for T_C = 323K as the evaporator temperature increases.

Fig. 5.4-5.8 represents variation of efficiency defect in compressor, condenser, liquid vapour heat exchanger, throttle valve, and evaporator. *Efficiency defect shows that what fraction of the input is lost through irreversibilities in different components of the system*. Thus it assists in determining the worst component in a system. Liquid vapour heat exchanger showing minimum efficiency defect is the most efficient component of a system. In the descending order of efficiency defect the components are arranged as condenser, compressor, throttle valve, evaporator and liquid vapour heat exchanger. From the perspective of refrigerants it has been observed that loss of input energy due to irreversibility in compressor and throttle valve is maximum for HFO-1234yf and minimum for HFC-134a and the difference is decreasing as the evaporator temperature is increasing, however with increase in condenser temperature, efficiency defect in compressor reduces whereas it increases for throttle valve. The trend shown by the curves for the two condenser temperature is same. In condenser and evaporator, HFC-134a gives maximum efficiency defect value, which increases for the condenser and decreases for the evaporator as the condenser temperature increases. HFO-1234yf gives minimum value at lower end of evaporator temperature and HFO-1234ze gives minimum value at higher end of evaporator temperature for condenser. Total of efficiency defects in different components is observed to be minimum for HFC-134a followed by HFO-1234ze and HFO-1234yf in ascending order. HFO-1234yf shows 3.7-0.7% higher than HFC-134a at T_C =313K and 8.5-0.7% higher at T_C =323K, having minimum value at higher evaporator temperature.

Fig. 5.9-5.10 shows the effect of ambient state temperature on exergetic efficiency and EDR. With increase in ambient state temperature, exergetic efficiency increases and EDR reduces, because of the increment in the term $\left|\left(1-\frac{T_o}{T_r}\right)\right|$, while the term $\dot{Q}_e$ and $\dot{W}_{comp}$ remains constant as can be observed from (11) and (13). This can also be attributed to the reason that with increase in the ambient state temperature, the irreversibility due to finite temperature difference decreases and hence EDR reduces and exergetic efficiency increases. HFO-1234ze and HFC-134a show the similar trends and their curves for exergetic efficiency and EDR are almost overlapping. HFO-1234yf shows lesser values for exergetic efficiency and higher values for EDR as compared to HFO-1234ze and HFC-134a for the ambient temperature range considered. As the condenser temperature increases, reduction in exergetic efficiency and increment in EDR is being observed.

It is evident that sub-cooling increases the refrigerating effect whereas there is no change in compressor work, hence COP increases, as illustrated in fig. 5.11 and also increase in exergetic efficiency and decrease in EDR with increase in degree of sub-cooling is shown in fig. 5.12 & 5.13. It can be noticed from the figures that exergetic efficiency and COP obtained for HFO-1234ze is higher than that obtained for HFC-134a, which is almost same at higher condenser temperature of 323K and the trend shown by the curves is similar for both. HFO-1234yf gives lesser values of exergetic efficiency and COP as compare to HFO-1234yf and HFC-134a. The total increase in exergetic efficiency for 10K of sub-cooling is 12.3 & 15.2% for HFO-1234yf, 10.3 & 12% for HFC-134a and 11.1 & 12.9% for HFO-1234ze at condenser temperature of 313K & 323K respectively.

Fig. 5.14-5.16 shows the effect of effectiveness of lvhe on COP, exergetic efficiency and EDR. With the increase in effectiveness of liquid vapour heat exchanger, COP and exergetic efficiency decreases whereas EDR increases for all the refrigerants concerned in the study. This can be explained as with the increase in effectiveness of lvhe, degree of sub-cooling increases and also superheating of suction vapour takes place which results in compression to take place along the isentropes having reduced slope and thus compression work increases. The positive effect of increase in refrigerating effect is belittled by increase in compressor work and hence COP of the system decreases. (20) - (21) demonstrates the effect of COP on exergetic efficiency and EDR. Exergetic efficiency of the system decreases by 18.3 & 22.2% for HFO-1234yf, 17 & 20.5% for HFC-134a and 16.5 & 20.4 for HFO-1234ze at the condenser temperature of 313K and 323K respectively. Similar trend is shown by the curves of COP.

CHAPTER 6: CONCLUSION

During this extensive energy and exergy analysis of HFO-1234yf, HFO-1234ze and HFC-134a in a theoretical vapour compression cycle following conclusions are summarized below.

1. COP and exergetic efficiency of HFC-134a and HFO-1234ze is almost same having a difference of 5.6%, which decreases with the increase in evaporator temperature, whereas it is 14.5-5% higher than HFO-1234yf. Hence HFO-1234yf can be a good ‘drop-in’ replacement of HFC-134a at higher value of evaporator temperature and HFO-1234ze can be a good replacement after certain modification.
2. As the condenser temperature increases, HFC-134a gives 20.7-7.5% higher COP than HFO-1234yf, hence HFO-1234yf can be a drop replacement of HFC-134a at lower condenser temperature.
3. From the irreversibility or exergy destruction viewpoint, worst component is condenser followed by compressor, throttle valve, evaporator and liquid vapour heat exchanger, the most efficient component. Total efficiency defect is more for HFO-1234yf followed by HFO-1234ze and HFC-134a, but the difference is small.
4. Increase in ambient state temperature has a positive effect on exergetic efficiency and EDR, i.e. EDR reduces and exergetic efficiency increases.HFO-1234yf gives lesser values of exergetic efficiency whereas HFO-1234ze gives approximately similar values.
5. HFC-134a gives higher COP and exergetic efficiency than HFO-1234yf but lesser value than HFO-1234ze. However reverse trend is seen when effectiveness of heat exchanger is increased from 0 to 1.

Hence, it can be concluded that even though the values of performance parameters for HFO-1234yf are smaller than that of HFC-134a, but the difference is small, so it can a good alternative to HFC-134a because of its environmental friendly properties. HFO-1234ze can replace the conventional HFC-134a after having slight modification in the design as the performance parameters are almost similar.

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