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Evaluation of Performance of HFC-R134a/HFO-1234yf Binary Mixtures Used as Refrigerant in a Heat Pump System

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Abstract: The use of heat pumps is increasing day by day. So, various refrigerants have been used in the heat pump systems so far. Therefore many studies and arrangements have been made to reduce the environmental effects of refrigerants. The refrigerant mixtures that obtaining from the hydrofluorocarbons (HFCs) and the hydrofluoroolefins (HFOs) are started to be used to reduce of global warming potential of the HFCs and remove flammability of the HFOs in these days. In this study, the performance of the R134a/R1234yf (HFC/HFO) mixture in the heat pump was theoretically investigated for different R1234yf mass fractions (from 0.0 to 1.0). The analysis of R134a/R1234yf mixture for different R1234yf mass fraction has made for three different evaporator temperatures (-10 ^{o}C, -5 ^{o}C and 0 ^{o}C) and a constant condenser temperature (35 ^{o}C). When the R1234yf mass fraction increases from 0.0 to 1.0 the COP value decreases by 2.44% (at the -5 ^{o}C evaporator temperature). The R1234yf mass fraction must be 0.9 for the R134a/R1234yf mixture to have a lower GWP than 150. Because R134a has high GWP.

Keywords: Global warming, climate change, R134a/R1234yf mixtures, Refrigerant blends

Bir Isı Pompası Sisteminde Soğutucu Olarak Kullanılan HFC-R134a / HFO-1234yf İkili Karışımların Performansının Değerlendirilmesi

Öz: Isı pompalarının kullanımı gün geçtikçe artmaktadır. Bu nedenle, şimdiye kadar ısı pompası sistemlerinde çeşitli soğutucu akışkanlar kullanılmıştır. Bu yüzden, soğutucu akışkanların çevresel etkilerini azaltmak için birçok çalışma ve düzenleme yapılmıştır. Hidroflorokarbonlardan (HFC) ve hidrofloroolefinlerden (HFO) elde edilen soğutucu akışkan karışımları, HFC'larin küresel ısınma potansiyelini azaltmak ve HFO'lerin yanıcılığını gidermek için bu günlerde kullanılmaya başlanmıştır. Bu çalışmada, bir ısı pompasında R134a/R1234yf (HFC / HFO) karışımının performansı teorik olarak farklı R1234yf kütle karışım oranı (0.0 - 1.0) için araştırılmıştır. Farklı R1234yf kütle karışım oranı için R134a / R1234yf karışımının analizi, üç farklı evaporatör sıcaklığı (-10 ^{o}C, -5 ^{o}C ve 0 ^{o}C) ve sabit bir kondenser sıcaklığı (35 ^{o}C) için yapılmıştır. R1234yf kütle karışım oranı 0.0'dan 1.0'e yükseldiğinde, COP değeri % 2.44 azalmaktadır (-5 ^{o}C evaporatör sıcaklığında). R134a / R1234yf karışımının 150'den düşük GWP oranına sahip olması için R1234yf kütle karışım oranı 0.9 olmalıdır. Çünkü R134a yüksek GWP oranına sahiptir.

Anahtar Kelimeler: Küresel ısınma, iklim değişikliği, R134a/R1234yf karışımları, soğutucu akışkan karışımları

1. Introduction

Heat pumps operate according to the vapor compression cycle. In the vapor compression cycle, a working fluid (refrigerants) is used to transport heat. Refrigerants used in heat pump systems are

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required to be environmentally friendly [1]. For many reasons (changing conditions, environmental effects, legal regulations, etc.), many refrigerants have been developed since 1830 [2].

As seen in Figure 1, Calm (2008) divided refrigerants into four generations. When looking at the refrigerants classified as 1st generation, every useful fluid was used as refrigerants. In the 2nd generation, features such as security and permanence came to the fore. In the 3rd generation, the protection of the ozone layer has been brought to the agenda, and refrigerants that will not damage the ozone layer have been used. In today's 4th generation refrigerants, due to increasing global warming concerns, conditions such as refrigerants with zero ozone depletion potential (ODP) and low global warming potential (GWP) values, high performance, and disappearing in the atmosphere in a short time have become necessary [3].

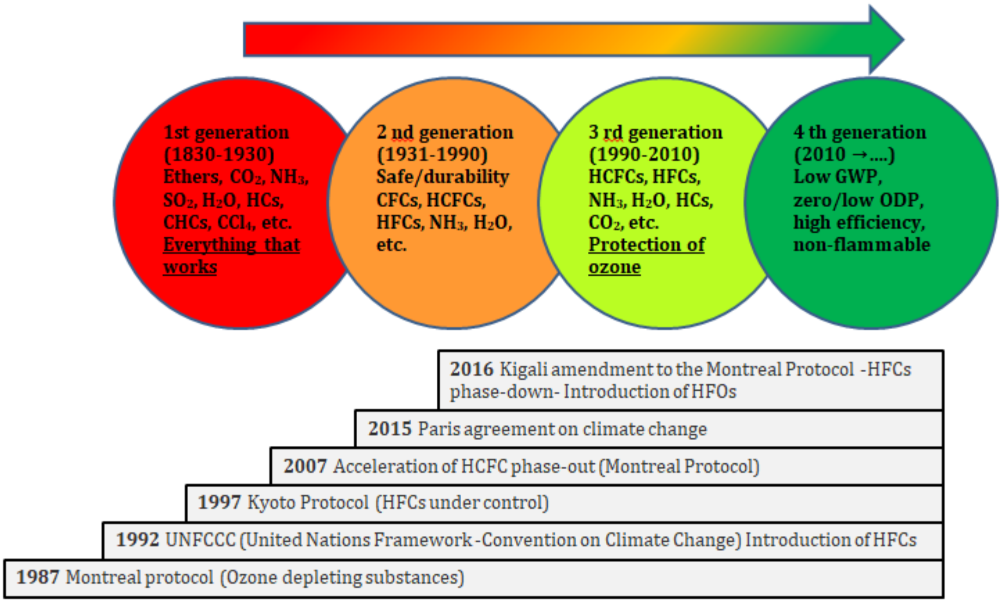

Figure 1. The progression of refrigerants [3] and the list of specific agreements by years [4]

In 1834, Perkins used ether as the refrigerant in its first refrigeration machine. In the cooling industry, carbon dioxide (CO_2) was first used in 1866, and ammonia (NH_3) was used in 1873. The use of natural substances such as air, water (H_2O), NH_3, CO_2, ether, sulfur dioxide (SO_2) as refrigerants continued until the presence of artificially obtained chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC). CFCs and HCFCs obtained in laboratories have been used extensively by replacing some of these natural refrigerants. However, these refrigerants harm the environment due to their properties such as GWP, ODP. Therefore, many studies have been conducted on refrigerants with zero ODP and low GWP ratio [5].

The use of substances that deplete the ozone is prohibited by the Montreal protocol (1987). Thus, hydrofluorocarbons (HFCs) appeared thanks to the Montreal protocol. Because there were no restrictions on the use of F - gases at that time. The use of HFCs as an alternative to CFCs started nearly at the same time as the climate change congress (UNFCCC). HFCs (F-gases) have a high GWP rate. Therefore, it was taken to the controlled greenhouse gas list with the Kyoto protocol (1997). The HFCs should be phased out according to the Kigali's amendment to the Montreal protocol (2016). Because using HFCs instead of CFCs wasn't a sustainable solution [4], [6],[7].

In this context, various researches on alternative refrigerants (zero ODP and low GWP) have been made. Hydrofluoroolefins (HFOs) and hydrocarbons (HCs) are good candidates for alternative refrigerants [8]. R1234yf and R1234ze (E) refrigerants are the first low GWP synthetic refrigerants developed to replace R134a. R1234yf and R1234ze (E) refrigerants in the HFO group have a low GWP ratio (less than 1) and zero ODP. However, these refrigerants have low flammability [9], [10].

Refrigerants with a low GWP ratio are required to reduce the impact of cooling systems on climate change. HFC/HFO mixtures are thought to replace HFCs in systems operating according to the vapor compressing cycle. R134a/R1234yf mixtures can overcome particular of the drawbacks of pure refrigerants and improve thermophysical properties. Some studies on the R134a / R1234yf mixtures in the literature are given below and are summarized in Table 1.

Table 1. Literature summaries

Author	**Year**	**Refrigerants**	**Analyzes**		
			Energy	**Exergy**	**Environmental**
Lee et al. [10]	2013	R134a R1234yf R134a/R1234yf (15/85) R134a/R1234yf (10/90) R134a/R1234yf (05/95)	☑	☐	☐
Aprea et al. [11]	2017	R134a R1234yf R134a/R1234yf (10/90)	☑	☐	☐
Mota-Babiloni et al. [12]	2017	R134a R513a	☑	☐	☐
Llopis et al. [13]	2017	R134a R513a R450a R507a	☑	☐	☐
Mota-Babiloni et al. [9]	2018	R134a R513a	☐	☑	☐
Aprea et al. [14]	2018	R134a R1234yf R1234ze (E) R134a/R1234yf (10/90) R134a/R1234ze (E) (10/90)	☑	☐	☑
Meng et al. [15]	2018	R134a R134a/R1234yf (11/89)	☑	☐	☐
Yang et al. [16]	2019	R134a R513a	☑	☐	☐

R1234yf and R1234ze (E) have some disadvantages when using them in R134a systems, such as low flammability and insufficient cooling capacity [10], [11]. To reduce the disadvantages of HFOs and keep the GWP ratio low, refrigerants consisting of HFC/HFO mixtures have been developed recently (such as R513A and R450A). R513A refrigerant consists of mixing R134a/R1234yf by 44/56 percent by mass. R513A refrigerant is an azeotropic mixture. R513A has zero ODP and 573 GWP rates (about half of R134a) [12].

Meng et al. [13] experimentally investigated both the heating and cooling performance of the R134a/R1234yf (11/89 by mass) mixture in an air conditioning systems of cars. They stated that R134a/R1234yf mixture has a lower cooling COP (nearly 4% - 9%) than R134a. In the case of heating, the COP value of the R134a/R1234yf mixture has lower (nearly 4% - 16%) than R134a. Aprea et al. [14] experimentally examined and compared the energy performance of the R134a, R1234yf and R134a/R1234yf (10/90 by mass) refrigerants as used a working fluids in the household refrigerator. They stated that the R134a/R1234yf mixture has similar thermophysical properties with R134a and consumes 16% less energy than R134a and 14% less energy than R1234yf. They also stated that the R134a/R1234yf mixture becomes non-flammable, when added 10% of R134a to R1234yf. In another study, Aprea et al. experimentally investigated energy and environmental analysis of refrigerants with low GWP ratios such as R134a, R1234yf, R1234ze (E), R134a/R1234yf(10/90 by mass), R134a/R1234ze (E) (10/90 by mass). They stated that R134a/R1234yf (10/90) reduced the emission value by 17% compared to R134a [14]. Lee et al. [15] examined the effects of R1234yf and R134a/R1234yf mixtures (5/95, 10/90, 15/85 mixing rates in mass) on COP, heating and cooling capacity, discharge temperatures, and stated that the R134a/R1234yf mixtures gave similar results with R134a refrigerant. They also emphasized that R1234yf and R134a/R1234yf mixtures need to charge more refrigerant (approximately 11%) than R134a.

When we examine the studies related to HFC/HFO mixtures in the literature, there are few studies, and these studies are made for similar R1234yf mass fractions (such as 0.85, 0.89, 0.9 and 0.95). Unlike the studies in the literature, this study used many R1234yf mass fractions (0.0 - 1.0). It is important that researching new generation refrigerants that have a low GWP and zero ODP and environmentally friendly. Therefore, this study could be made significant contributions to the literature.

2. Materials and Methods

2.1. Properties of Refrigerants

The pure refrigerants thermophysical properties much affect the properties of the mixture refrigerants. The properties of R134a and R1234yf are given in Table 2. ODP of both pure refrigerants is zero. R1234y has a very low GWP rate. However, it is not possible to say the same for R134a. The GWP ratio of R134a is very high when compared to R1234yf. R134a/R1234yf mixtures can considerably reduce of GWP of refrigerants.

Table 2. Thermodynamic properties of R134a and R1234yf [11]

	R134a	**R1234yf**
ASHRAE safety classification	A1	A2L
ODP	0	0
GWP	1300	<1
Critical temperature (^{o}C)	101.1	94.7
Normal boiling temperature (^{o}C)	-26.1	-29.5

The mass fraction of R1234yf greatly effect of the mixtures refrigerant properties. So, the thermophysical properties of R134a/R1234yf mixtures are obtained under many R1234yf mass fractions (from 0.0 to 1.0). The R134a/R1134yf mixture properties have obtained from Refprop.

The vapor-liquid equilibrium (VLE) behaviors of R134a/R1234yf mixtures under different R1234yf mass fractions and temperatures are given in Figure 2. It is seen that almost all R134a/R1234yf mixtures have an azeotropic/near-azeotropic behavior. An azeotropic behavior states that the boiling point and condensing point overlap, as showed by the concurrence point of the liquid line and vapor line. The R134a/R1234yf indicates an azeotropic behavior when R1234yf mass fraction nearly between 0.4 and 0.7. This situation clearly can be seen in the inspect picture for 0 ^{o}C.

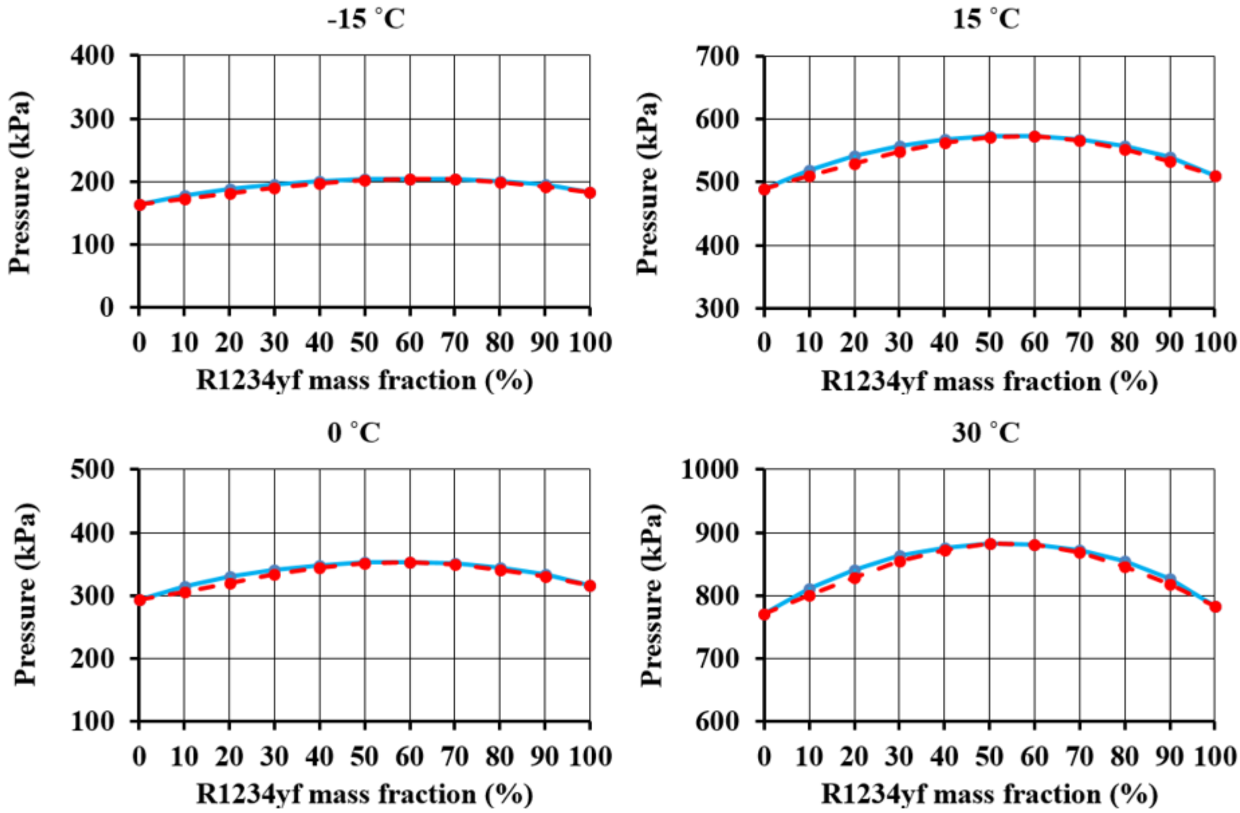

Figure 2. VLE behaviors of R134a/R1234yf mixtures

The pressure (P) - enthalpy (h) diagram of R134a/R1234yf mixtures for different R1234yf mass fractions (%0, %50 and %100) is shown in Figure 3. The many important properties such as saturated liquid line, saturated vapor line and latent heat of evaporation, etc. can be observed through the P - h diagram.

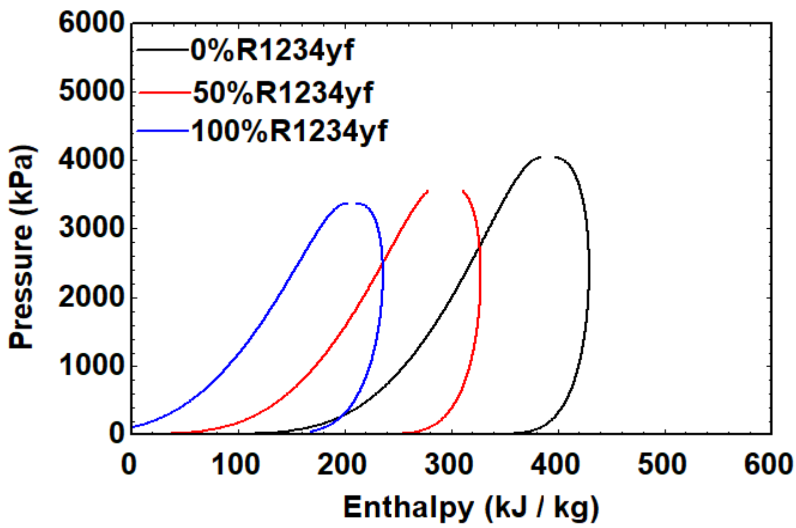

Figure 3. The P-h diagram of R134a/R1234yf mixtures for different R1234yf mass fractions

2.2. Thermodynamics Model of the Heat Pump

The schematic diagram and the temperature (T) - entropy (s) diagram of the single-stage vapor compressing heat pump cycle are seen in Figure 4 and Figure 5, respectively. The refrigerant enters the compressor in the form of saturated/superheated vapor and is compressed up to the condenser pressure (1-2). The refrigerant comes to the condenser in the form of superheated vapor and condenses by transferring heat to the surrounding environment (produce a heating effect) in the condenser (2-3). The refrigerant passes to the expansion valve after condensation and thanks to the expansion valve, the pressure and temperature of the refrigerant are significantly reduced (3-4). After the expansion valve, the refrigerant passes to the evaporator in vapor and liquid phases. It takes heat from the heat source in the evaporator and evaporates (produce a cooling effect). The evaporated refrigerant passes to the compressor again and so the cycle is completed (4-1).

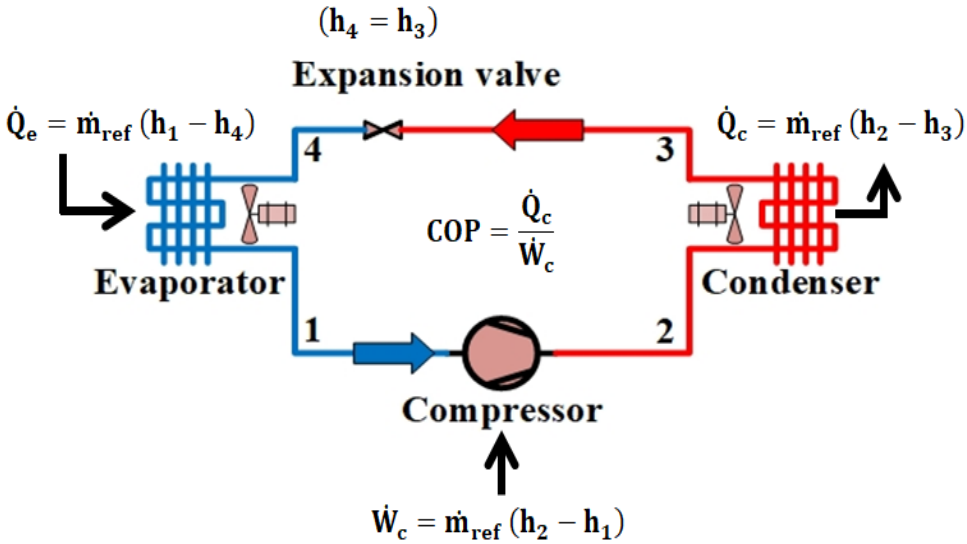

Figure 4. The schematic view of the heat pump

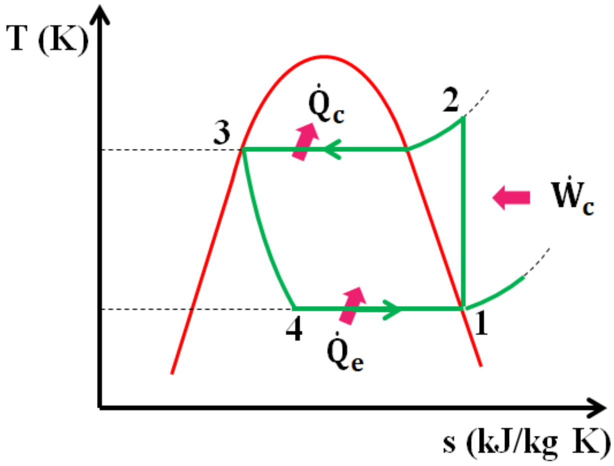

Figure 5. T-s diagram of the heat pump

The energy analysis of the heat pump was made according to the first law of thermodynamics. The energy consumed of compressor ($\dot{W}_c$), the heat rejected from the condenser ($\dot{Q}_c$), the heat taken from the evaporator ($\dot{Q}_e$) and the coefficient of performance of the heat pump (COP) are given in Figure 4. Here, h shows the enthalpy value of the related reference point (kJ/kg) and $\dot{m}_{ref}$ is the mass flow rate of refrigerant (kg/s). The assumptions made for energy analysis of the heat pump are given below:

- ✓ The heat pump system works in a steady-state.
- ✓ There is no heat loss and pressure drops.
- ✓ The compressor isentropic efficiency is constant and 0.7.
- ✓ The superheat and subcooling are taken 5 ^{o}C.

✓ $h_3 = h_4$

For the standard heating conditions, the evaporator section (heat source) and condenser section (heat rejection) temperatures are 7 ^oC and 20 ^oC, respectively. The temperature difference is usually taken from 10 ^oC to 15 ^oC for an effective heat transfer. So, temperatures of the evaporator are taken 0 ^oC, -5 ^oC and -10 ^oC, and the condenser temperature is taken 35 ^oC. The heating capacity of the heat pump is taken 1 kW.

3. Results and Discussion

In this study, the performance of R134a / R1234yf mixture in different R1234yf mass fractions (from 0.0 to 1.0) for the heat pump was investigated. The mass flow rate of refrigerant, compressor energy consumption, COP value, discharge temperature, volumetric heating capacity and GWP rate were conducted for a heat pump.

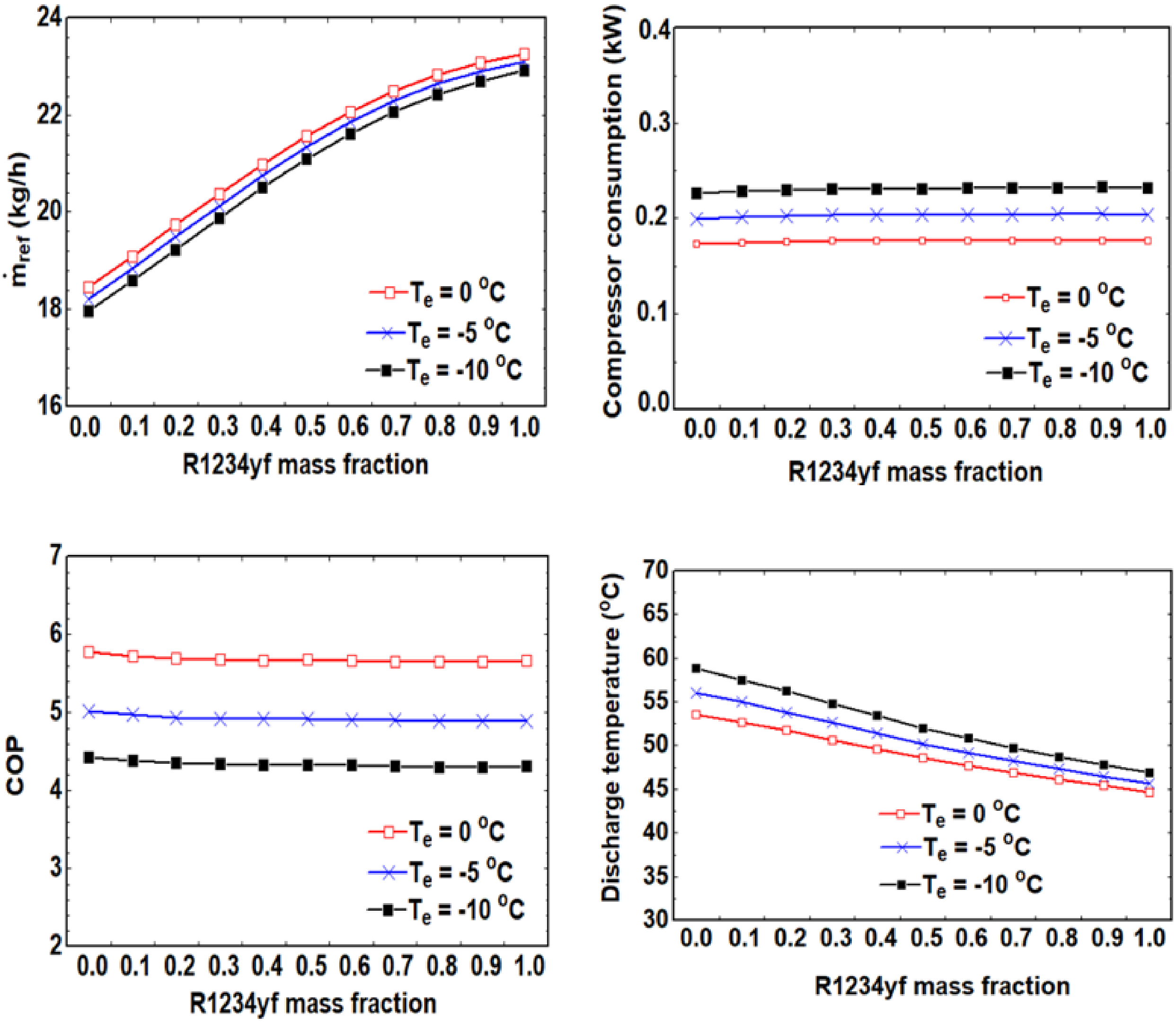

Figure 6. The mass flow rate of refrigerant, compressor consumption, COP and discharge temperature for different R1234yf mass fractions

The analysis results of refrigerant mass flow rate, compressor energy consumption, COP and discharge temperature for different R134a/R1234yf mixtures are shown in Figure 6. It is seen that the refrigerant mass flow rate tends to increase as the R1234yf mass fraction is increment. The refrigerant mass flow rate rises from 18.21 kg/h to 23.09 kg/h for R1234yf mass fraction 0.0 – 1.0 at the -5 °C evaporator temperature. This is because the density of the refrigerant mixture increases as R1234yf mass fraction raises.

The compressor energy consumption increases very little as R1234yf mass fraction increases. The compressor energy consumption changes between 199.35 W and 204.33 W within R1234yf mass fraction 0.0 – 1.0 at -5 °C evaporator temperature. So the compressor energy consumption is almost the same for all R1234yf mass fraction (from 0.0 to 1.0).

As R1234yf mass fraction increases the COP value slightly decreases. At the -5 °C evaporatör temperature, when R1234yf mass fraction 0.0, 0.5 and 1.0 the COP value are 5.02, 4.91 and 4.89, respectively. When the R1234yf mass fraction increases from 0.0 to 1.0 at the -5 °C evaporator temperature, the COP value decreases by 2.44%.

The compressor discharge temperature is one of the significant factors to selection refrigerant. If the discharge temperature is too high, it will reason the compressor to break down. Figure 6 clearly shows that the discharge temperature decreases as R1234yf mass fraction increases. When R1234yf mass fraction 0.0, 0.5 and 1.0 at the -5 °C evaporator temperature, the discharge temperature are 56.05 °C, 50.24 °C and 45.73 °C, respectively. Increasing the R1234yf mass fraction from 0.0 to 1.0 at the -5 °C evaporator temperature decreases the discharge temperature by 18.41%.

The volumetric heating capacity (VHC) of R134a/R1234yf mixture for different R1234yf mass fraction is given Figure 7. The volumetric heating capacity first increases and then decreases depend on the R1234yf mass fraction increases. At the -5 °C evaporator temperature; If the R1234yf mass fraction increases from 0.0 to 0.6, the volumetric heating capacity increases from 2329 kJ/m^3 to 2570 kJ/m^3, and if the mass fraction of R1234yf continues to increase, the volumetric heating capacity decreases. When the R1234yf mass fraction is 1.0, the volumetric heating capacity is decreases to 2269 kJ/m^3.

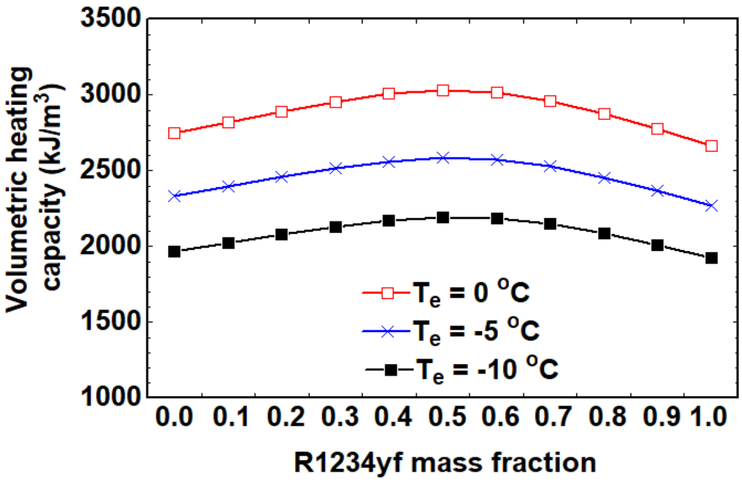

Figure 7. The VHC of R134a/R1234yf mixture for different R1234yf mass fractions

The GWP of mixtures depends on GWP and mass fraction of refrigerants which used to compositions. The GWP of R134a/R1234yf mixtures according to R1234yf mass fraction is given figure 7. Since 2011, the refrigerants with a GWP rate of higher than 150 in Europe are prohibited use in mobile air conditioning (MAC) systems by the European Union's MAC instruction 2006/40/EC. Therefore, the GWP rate of 150 is selected as the maximum limit. Due to the GWP ratio of R134a is very high the R1234yf mass fraction must be 0.9 for the R134a/R1234yf mixture to have low GWP. Also, the mixture obtained by adding 10% R134a to R1234yf eliminates the flammability of R1234yf [14].

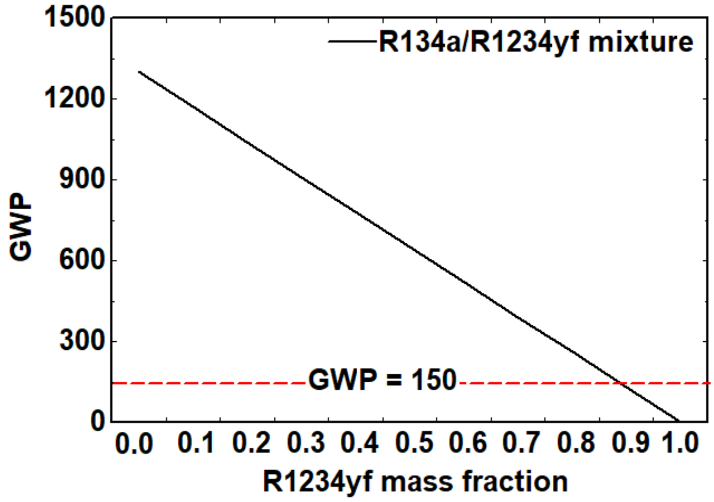

Figure 8. Effect of R1234yf mass fraction on GWP of R134a/R1234yf mixtures

4. Conclusions

Investigation of environmentally friendly refrigerants with lower GWP and zero ODP is necessary for the reduction of global warming, ozone depletion and other environmental problems. In this study, the performance of R134a/R1234yf mixture in the heat pump was theoretically investigated for different R1234yf mass fractions (from 0.0 to 1.0). The main results obtained from the study are as follows:

- It is seen that general R134a/R1234yf mixtures have an azeotropic behavior.
- The mass flow rate of R134a/R1234yf mixture increases as the R1234yf mass fraction rises.
- The compressor energy consumption of R134a/R1234yf mixture is almost the same for all R1234yf mass fractions.
- As R1234yf mass fraction increases the COP value slightly decreases. When the R1234yf mass fraction increases from 0.0 to 1.0 the COP value decreases by 2.44% (at the -5 ^{o}C evaporator temperature).
- The discharge temperature decreases as R1234yf mass fraction increases.
- If the R1234yf mass fraction increases from 0.0 to 0.6, the volumetric heating capacity raises, and if the mass fraction of R1234yf continues to increase, the volumetric heating capacity is beginning to decrease.
- The R1234yf mass fraction must be 0.9 for the R134a/R1234yf mixture to have a lower GWP than 150. Because R134a has high GWP.

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