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PERFORMANCE STUDY OF THE ECO-FRIENDLY HYDROFLUOROOLEFINS AND DIMETHYL-ETHER REFRIGERANTS IN REFRIGERATION SYSTEMS

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SUMMARY: This paper presents theoretical investigation of the performance of eco-friendly hydrofluoroolefins (R1234yf and R1234ze) and dimethyl-ether (RE170) refrigerants as substitutes for R134a in a standard vapour compression refrigeration system. The results showed that the vapour pressure of R1234yf and RE170 is very close to that of R134a, while the vapour pressure of R1234ze in the temperature range of -30 to 40°C deviated by 25.3% high. Very high refrigerating effect and condenser duty were obtained using RE170, which shows that it will equally excellently perform as a heat pump refrigerant. The condenser duty obtained using R1234yf and R1234ze is slightly lower, by 17.2 and 9.9%, than that of R134a, respectively. RE170 and R1234yf exhibited very close volumetric refrigerating capacity with R134a. The average coefficient of performance (CO_{Pref}) obtained using RE170 is 6.2% higher than that of R134a, while the CO_{Pref} obtained for R1234yf and R1234ze is slightly lower, by 6.1 and 0.9%, respectively. Generally, the performance of the three alternative refrigerants is quite similar to that of R134a, but the best overall performance is obtained using RE170.

Key words: *eco-friendly, performance, alternative refrigerant, hydrofluoroolefins, dimethyl-ether*

INTRODUCTION

Most refrigeration and air-conditioning systems are based on the vapour compression cycles which depend on the performance of refrigerants that are safe, chemically stable, have good thermodynamic and thermo-physical properties. Chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs) have been applied extensively as refrigerants in these systems from 1930s, as a result of their outstanding thermodynamic, thermo-physical and safety properties. These refrigerants largely replaced the toxic sulphur dioxide and ammonia, the less cyclically efficient carbon dioxide, and the flammable hydrocarbons used earlier in the century *(Pham and Sachs, 2010; Bolaji and Huan, 2012)*.

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Since 1987 refrigerants are experiencing new constraints due to global environment concerns. These chlorine containing fluorinated hydrocarbon refrigerants (CFCs and HCFCs) were found to diffuse up into the stratosphere. The chlorine content of the refrigerants was the principal cause of destruction of the stratospheric ozone which absorbs the sun's high energy ultraviolet rays and protects both humans and other living things from exposure to ultraviolet radiation. The hazard is represented by the refrigerant ozone depletion potential (ODP) number *(McMullan, 2002; Padilla et al., 2010; Kim et al., 2011)*.

The protection of stratospheric ozone under the Montreal Protocol has led to the phase-down and then the phase-out of CFCs and HCFCs. CFCs have been banned in the refrigeration industry all over the world since January 1, 2010. HCFCs, despite their low 0.05 ODP, have been banned from new equipment as of 1 January 2010, and they will also be phased out internationally, in the developed countries by 2020, in the developing countries by 2030. Many chemicals have been considered as alternative refrigerants over the decades and the selection of replacement refrigerants has been encouraged to avoid the shortcomings of the previous ones. CFCs and HCFCs, which were the two most used groups of refrigerants, were replaced in most applications with hydro-fluorocarbons (HFCs) such as R134a, and HFC blends such as R404A, R407C and R410, due to their zero ODP, which is appealing. *(Sivasakthivel and Siva-Kumar, 2011; Bolaji and Huan, 2013).*

However, HFCs have come under scrutiny for their contribution to greenhouse gases. While they were entirely harmless to the ozone layer, they did have large global warming potential (GWP). It is known that halocarbons (CFCs, HCFCs and HFCs) accounted for 12% of the radiative forcing produced by the increased levels of globally mixed long-lived greenhouse gases from 1750 to 2009. Due to the phase-out of CFCs, their atmospheric concentrations are diminishing, while those of HCFCs and HFCs are increasing speedily *(WMO, 2011; Kauffeld, 2012, UNEP, 2013)*. Although HFCs have a lower GWP than many of the CFCs and HCFCs they are replacing, their GWP is still very high *(Baskaran and Mathews, 2012)*. Fluorine (F) atoms are the heat trapping part of the HFCs. The number of the fluorine atom determines the stability of the molecule, and the greater the stability, the higher the atmospheric lifetime and the GWP. In 1997, HFCs were considered as greenhouse gases and currently they are target compounds for greenhouse gases emission under the Kyoto Protocol *(UNFCC, 1997; Park and Jung, 2009; Del-Col et al., 2010)*. One of the HFC refrigerants (R134a) was initially assessed as having a GWP of 1300 *(IPCC, 2001)* and later assessed to have a GWP of 1430 *(IPCC, 2007)*.

The global concern about the increasing impact of mankind on the warming of our atmosphere has forced the industry to begun searching for alternatives with a lower GWP. The researchers have to revisit the use of long-term alternative refrigerants, such as hydrocarbons, that are favourable for the environment. Many studies have considered hydrocarbons as a replacement for HCFCs and HFCs due to their zero ODP and relatively low GWP. Lee and Su *(2002)* conducted an experimental study on the use of iso-butane as refrigerant in domestic refrigerators. The performance was comparable with those systems using R12 and R22 as refrigerants. Wongwises and Chimres *(2005)* presented an experimental study on the application of a mixture of propane, butane and isobutene to replace R134a in domestic refrigerators. The results showed that the 60%/40% propane/butane mixture was the most appropriate alternative refrigerant.

Sattar et al. *(2007)* compared the performance of a domestic refrigerator using pure iso-butane, butane, and their blends as refrigerants with that of HCFCR134a. Their results showed that the compressor consumed 3% and 2% less energy than that of R134a when iso-butane and butane were used as refrigerants, respectively. Mani and Selladurai *(2008)* conducted an experimental study on the replacement of R12 and R134a by R290/R600a refrigerant mixture without any modification to the system components. The result showed that R290/R600a consumed 6.8 to 17.4% more energy than R12. The coefficient of performance (COP) of R290/R600a was 25.1% and 17.6% higher than that of R12 at lower and higher evaporating temperatures, respectively.

Sarkar and Bhattacharyya *(2009)* assessed the performance of blends of CO_2 (R744) with butane (R600) and iso-butane (R600a) as alternative working fluids for CFC R114 in heat pump application. Their results showed that the R744/R600a blend can be the best alternative to R114 for high-temperature heating due to superior COP compared to pure R600 and R600a. Some investigations performed on domestic refrigerators working with R290, R600 and R600a as drop-in replacements for R134a revealed that propane has a higher saturation pressure at a given temperature compared to R134a, while butane and iso-butane have lower pressures *(Fatouh and El-Kafafy, 2006)*.

As a result of the need to find more suitable substitutes for the existing higher global warming potential refrigerants, two new low global warming molecules were identified (R1234yf and R1234ze). These hydrofluoroolefins (HFO) refrigerants have extremely low GWPs of only 4 and 6 due to their very short atmospheric life times of 11 and 18 days respectively as compared to

GWP of 1430 for R134a with atmospheric life time of 12 years *(Spatz et al., 2010; Bitzer, 2012).* Therefore, in this study, the performance of two HFOs and dimethyl-ether refrigerants was investigated theoretically and compared with that of R134a in a vapour compression refrigeration system. Dimethyl-ether (DME or RE170) is a hydrocarbon refrigerant with zero ODP and very low GWP. The environmental and thermo-physical properties of investigated refrigerants are shown in Table 1.

Table 1. Environmental and thermo-physical properties of investigated refrigerants

Tablica 1. Ekološka i termofizikalna svojstva istraženih rashladnih tvari

Properties	Refrigerants			
	R134a	R1234yf	R1234ze	RE170
Molar mass (kg/kmol)	102.03	114.04	114.04	46.07
Normal boiling point, (°C)	-26.07	-29.45	-18.95	-24.78
Critical temperature (°C)	101.06	94.70	109.37	127.23
Liquid density, kg/m^3 at 25°C	1373	1092	1310	661
Vapour density, kg/m^3 at 25°C	5.51	7.17	4.43	12.44
Latent heat, kJ/kg at (-15°C)	209.49	172.37	193.17	453.67
ODP	0	0	0	0
GWP	1430	4	6	4

(Source: Restrepo et al., 2008; Calm, 2007; Calm, 2011).

MATERIALS AND METHODS

Cycle Analysis

Vapour compression refrigeration, air-conditioning and heat pump systems are systems whose operational cycle is based on the principles of reversed Rankine cycle, requiring work input to accomplish their purpose of transferring heat from a lower temperature source to a higher temperature sink. These systems use a circulating fluid refrigerant which absorbs and removes heat from the refrigerating chamber and subsequently rejects that heat at the condenser. In their simplest form, a vapour compression refrigeration system (VCRS) consists of two heat exchangers, an expansion valve, and a compressor. The ideal VCRS is shown on the Pressure-Enthalpy diagram in Figure 1. It consists of four processes: isobaric heat rejection and condensation in the condenser, a constant enthalpy expansion process in the expansion device, isobaric heat absorption and evaporation in the evaporator, and an isentropic compression process in the compressor. The heat transferred to the refrigerant in the evaporator is termed the refrigerating effect. For the purpose of rating the system's performance either for heating or cooling application, the efficiency term is the coefficient of performance (COP). It is the ratio of desired output (the refrigerating effect for refrigerating system or heating effect for heat pump system) to the work input which, in this case, is the work input to the compressor.

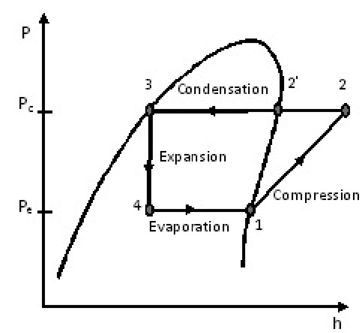

Figure 1. Conventional refrigeration cycle on p-h diagram

Slika 1. Konvencionalni rashladni ciklus na p-h dijagramu

Different refrigerants provide the desired product with more or less effectiveness. The desired product for a cooling application is the heat entering the evaporator. Considering the refrigeration system on p-h diagram in Figure 1, the following assumptions are made *(Bolaji and Huan, 2012)*:

(a) Process from point 1 to point 2 represents isentropic compression in the compressor and the work input is:

$$W_{comp} = (h_2 - h_1) \qquad [1]$$

where, W_{comp} = compressor and the work input (kJ/kg); h_1 = specific enthalpy of refrigerant at the outlet of evaporator (kJ/kg); and h_2= specific enthalpy of refrigerant at the outlet of compressor (kJ/kg).

(b) Process from point 2 to point 3 represents de-superheating at constant pressure (P_c) from compressor discharge temperature (T_2) at point 2 to condenser temperature (T_c) at point 2′, followed by a condensation at both constant temperature (T_c) and constant pressure (P_c) from point 2′ to point 3. The heat rejected in the condenser (Q_{cond}, kJ/kg) is:

$$Q_{cond} = (h_2 - h_3) \quad [2]$$

where, h_3 = specific enthalpy of refrigerant at the outlet of condenser (kJ/kg).

(c) Process from point 3 to point 4 represents expansion at constant enthalpy (isenthalpy) in the throttling valve. Therefore,

$$h_3 = h_4 \quad [3]$$

where, h_4 = specific enthalpy of refrigerant at the inlet of evaporator (kJ/kg).

(d) Process from point 4 back to point 1 represents evaporation at constant pressure (P_e) and constant temperature (T_e) in the evaporator. The heat absorbed by the refrigerant in the evaporator or refrigerating effect (Q_{evap}, kJ/kg) is given as:

$$Q_{evap} = (h_1 - h_4) \quad [4]$$

For refrigeration application, the coefficient of performance (COP) is the refrigerating effect produced per unit of work required; therefore, CO_{Pref} is obtained as the ratio of Eq. [4] to Eq. [1]. It can be expressed as:

$$COP_{ref} = \frac{Q_{evap}}{W_{comp}} \quad [5]$$

For heat pump application, the coefficient of performance (COP) is the heating effect produced per unit of work required; therefore, CO_{Php} is obtained as the ratio of Eq. [2] to Eq. [1]. It can be expressed as:

$$COP_{hp} = \frac{Q_{cond}}{W_{comp}} \quad [6]$$

The pressure ratio (P_R) of the cycle is obtained as:

$$P_R = \frac{P_{cond}}{P_{evap}} \quad [7]$$

where, P_{cond} = absolute condensing pressure (MPa) and P_{evap} = absolute evaporating pressure (MPA). The volumetric refrigerating capacity (VRC, kJ/m³) is calculated as follows:

$$VRC = \rho_1 . Q_{evap} \quad [8]$$

where, ρ_1 = density of the refrigerant at the exit of evaporator (kg/m³).

Thermodynamic Properties of Refrigerants

Thermo-physical properties of the hydrofluoroolefins and iso-butane refrigerants were obtained to study and compare their performance with that of R134a. The pressure-volume-temperature (PvT) in an equilibrium state are the most fundamental of a working fluid's thermal properties that are needed for the prediction of a refrigerant system's performance. Other properties, such as enthalpy and entropy as well as the Helmholtz and Gibbs functions, may be derived from a PvT correlation, that is an equation-of-state, utilizing specific heat. There exists a myriad of equations-of-state, which have been classified into families. Today, the most widely used refrigerant database is REFPROP *(Lemmon et al., 2002)*. It was developed and is maintained by The National Institute of Standards and Technology and is currently in its ninth edition. It uses several equations-of-state to correlate 33 single component refrigerants and 29 predefined mixtures, along with the ability to construct virtually any desired mixture of up to five components *(Kumar and Rajagopal, 2007)*. This software was used to compute the properties of investigated refrigerants. Cycle data was calculated based on fluid properties and used to predict the basic performances of the new refrigerants (R1234yf and R1234ze) and compare them to other known refrigerants (R600a and R134a).

RESULTS AND DISCUSSION

The saturation vapour pressure curves for the hydrofluoroolefin refrigerants (R1234yf and R1234ze) and dimethyl-ether (RE170) compared with the base refrigerant (R134a) are shown in Figure 2. As shown in this figure, the saturation vapour pressure curves for R1234yf and RE170 are very close to that of the base refrigerant (R134a). With only 4.1% higher and 10.6% lower deviations than that of R134a, respectively. This indicates that these refrigerants can exhibit similar properties and could be used as substitute for R134a. The average saturation vapour pressure for R1234ze in the temperature range of -30 to 40°C, deviated by 25.3% higher than that of R134a.

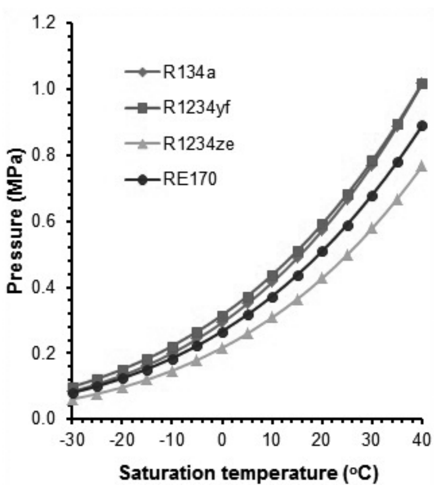

Figure 2. Variation of pressure with saturated liquid temperature

Slika 2. Promjena tlaka i temperatura zasićene tekućine

The effect of evaporating temperature on the refrigerating effects at condensing temperature of 40°C for R134a and its three low GWP alternatives is shown in Figure 3. As shown in the figure, the refrigerating effect increases as the evaporating temperature increases for all the investigated refrigerants. The latent heat of refrigerant increases as its evaporating temperature increases; hence, the refrigerating effect increases. Very high latent heat energy is desirable, since the mass flow rate per unit of capacity is less. When the latent value is high, the energy efficiency and capacity of the compressor are greatly increased. RE170 exhibited a much higher refrigerating effect than R134a, as is clearly shown in Figure 3. This is due to the much higher latent heat of RE170 (Table 1). The average refrigerating effects obtained using the hydrofluoroolefin refrigerants (R1234yf and R1234ze) were 25.3 and 10.1% lower than that of R134a, respectively.

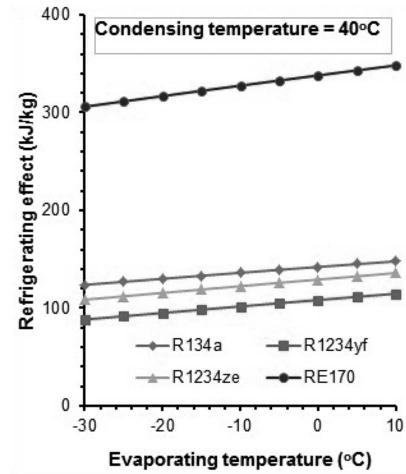

Figure 3. Influence of the evaporating temperature on the refrigerating effect

Slika 3. Utjecaj temperature isparavanja na rashladni učinak

The variation of the condenser duty with evaporating temperature for R134a and the three investigated alternative refrigerants at condensing temperature of 40°C is shown in Figure 4. This figure shows that the condenser duty slightly decreases as the evaporating temperature increases. Very high condenser duty was obtained using RE170. This is also due to the much higher latent heat of RE170 (Table 1), which shows that it will perform excellently as heat pump refrigerant. Compared to R134a, R1234yf and R1234ze exhibited slightly lower condenser duty, with average values of 17.2 and 9.9% lower than that of R134a, respectively.

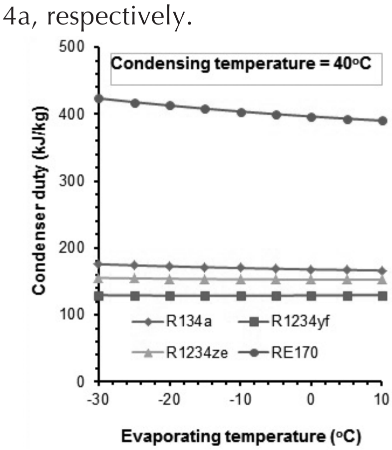

Figure 4. Variation of the condenser duty with evaporating temperature

Slika 4. Varijacije u radu kondenzatora i temperatura isparavanja

Figure 5 shows the variation of the compressor work input with evaporating temperature for R134a and the three investigated alternative refrigerants at condensing temperature of 40°C. This figure shows that the compressor work input decreases as the evaporating temperature increases. The compressor work input obtained using RE170 was higher than those obtained using the other three investigated refrigerants, but it also produced significantly higher refrigerating effect (Figure 3) and condenser duty (Figure 4) than the other three refrigerants.

The coefficient of performance (COP) reflects the cycle performance and is the major criterion for selecting a new refrigerant as a substitute. Figure 6 shows the variation of coefficient of performance for refrigeration (COP_{ref}) and heat pump (COP_{hp}) with evaporating temperature at condensing temperature of 40°C for R134a and the three alternative refrigerants. As shown in this figure, the COP increases with increase in the evaporating temperature. The COPs obtained for the three alternative refrigerants were very close to that of baseline refrigerant (R134a). Again, this result reveals RE170 as the refrigerant with the best performance in the system with slightly higher COP_{ref} and COP_{hp}, with average values of 6.2 and 5.1% higher, respectively, than those of R134a, while the average COP_{ref} for R1234yf and R1234ze are slightly lower, by 6.1 and 0.9%, respectively, than that of R134a.

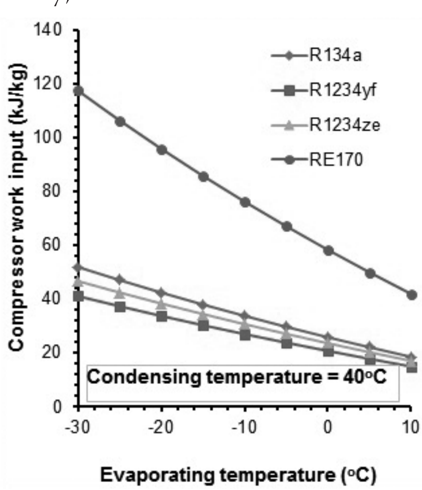

Figure 5. Compressor work input versus evaporating temperature

Slika 5. Ulazni rad kompresora i temperatura isparavanja

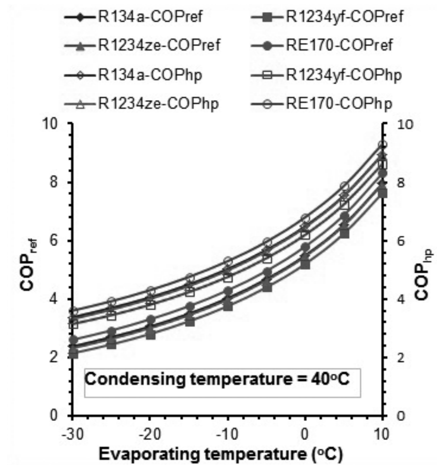

Figure 6. Variation of the coefficient of performance of refrigeration (COP_{ref}) and heat pump (COP_{hp}) with evaporating temperature

Slika 6. Varijacije koeficijenta performanse hlađenja (COP_{ref}) i toplinske crpke (COP_{hp}) pri promjenama temperature isparavanja

The effect of the evaporating temperature on the pressure ratio at condensing temperature of 40°C for R134a, RE170 and the two hydrofluoroolefin refrigerants is shown in Figure 7. From this figure, it is evident that the pressure ratios for the investigated refrigerants dropped with the increase in evaporating temperature. Increased evaporating temperature will simultaneously increase the evaporating pressure, which will reduce the pressure ratio since condensing pressure is constant [Eq. 7]. Low pressure ratio is desirable in the system. The three alternative refrigerants exhibited similar pressure ratio with R134a. The lowest pressure ratio was obtained using R1234yf. The average pressure ratio obtained for RE170 and R1234yf is slightly lower, by 6.1 and 11.2%, respectively, than that of R134a, while the average pressure ratio of R1234ze is slightly higher, by 3.2%, than that of R134a.

The variation of the volumetric refrigerating capacity (VRC) with evaporating temperature at condensing temperature of 40°C for R134a, RE170 and the two hydrofluoroolefin refrigerants is shown in Figure 8. As shown in this figure, the VRC increases as the evaporating temperature increases for all the investigated refrigerants. This is due to the increase in the volume of refrigerant vapour at the exit of the evaporator. A high cooling capacity can be obtained from a high volumetric capacity refrigerant for given swept volume in the compressor. RE170 and R1234yf exhibited very close VRC with R134a, while the VRC of R1234ze is very low. The average VRCs for RE170R1234yf and R1234ze are 2.9, 6.6 and 26.6% lower than that of R134a.

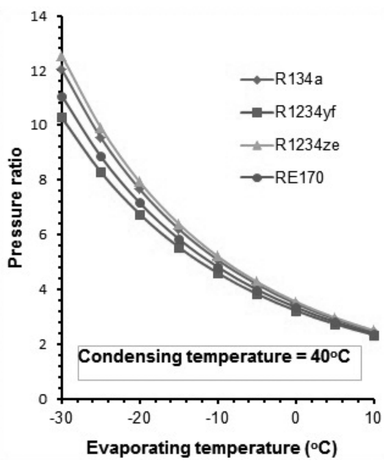

Figure 7. Effect of the evaporating temperature on the pressure ratio

Slika 7. Učinak temperature isparavanja na omjer tlaka

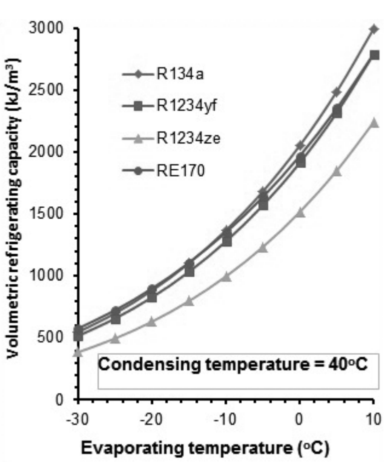

Figure 8. Effect of the evaporating temperature on the volumetric refrigerating capacity

Slika 8. Učinak temperature isparavanja na sposobnost volumetrijskog hlađenja

CONCLUSIONS

Ozone depletion and the atmospheric greenhouse effect due to refrigerant emissions have led to drastic changes in the refrigeration and air-conditioning technology. Therefore, in this study, the performance of eco-friendly hydrofluoroolefins (R1234yf and R1234ze) and dimethyl-ether (RE170) refrigerants as substitutes for R134a was investigated theoretically in a standard vapour compression refrigeration system. The following conclusions can be drawn from the analysis and discussion of the results:

- The saturation vapour pressure curves for R1234yf and RE170 are very close to that of the base refrigerant (R134a), which indicates that these refrigerants can exhibit similar properties and could be used as substitute for R134a, while the vapour pressure of R1234ze in the temperature range of -30 to 40°C deviated by 25.3% higher than that of R134a.
- RE170 exhibited much higher refrigerating effect than R134a, while the average refrigerating effects obtained using the hydrofluoroolefin refrigerants (R1234yf and R1234ze) are 25.3 and 10.1% lower than that of R134a, respectively.
- Very high condenser duty was obtained using RE170, which shows that it will perform excellently as heat pump refrigerant. The condenser duty obtained using R1234yf and R1234ze is slightly lower, by 17.2 and 9.9%, than that of R134a, respectively.
- The coefficients of performance (COP) obtained for the three alternative refrigerants are very close to that of baseline refrigerant (R134a). The average COPref obtained using RE170 is 6.2% higher than that of R134a, while the values obtained for R1234yf and R1234ze are slightly lower, by 6.1 and 0.9%, respectively.
- The three alternative refrigerants exhibited similar pressure ratio with that of R134a. The average pressure ratio obtained for RE170, R1234yf and R1234ze is 6.1 and 11.2% lower, and 3.2% higher than that of R134a, respectively.
- RE170 and R1234yf exhibited very close volumetric refrigerating capacity (VRC) with R134a, while the VRC of R1234ze is 26.6% lower.

Generally, the performance of the three alternative refrigerants is quite similar to that of R134a. RE170 performed better than the other two alternatives in that it exhibited highest COP, refrigerating effect, condenser duty and very high VRC.

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ISTRAŽIVANJE KARAKTERISTIKA EKOLOŠKI PRIHVATLJIVIH RADNIH TVARI HIDRO-FLORO-OLEFINA I DIMETIL ETERA U RASHLADNIM SUSTAVIMA

SAŽETAK: Članak predstavlja teoretsko istraživanje karakteristika ekološki prihvatljivih radnih tvari hidro-floro-olefina (R1234yf i R1234ze) i dimetil etera (RE170) kao zamjene za R134a u standardnim parnim kompresijskim rashladnim sustavima. Rezultat pokazuje da je tlak pare kod R1234yf i RE170 vrlo blizu tlaku kod R134a, dok je kod R1234ze pri temperaturma između -30 i 40°C devijacija 25.3%. Vrlo visok rashladni i kondenzacijski učinak postignut je uporabom RE170 što dokazuje da će jednako izvrsno poslužiti kao radna tvar u toplinskoj crpki. Kondenzacija pri uporabi R1234yf i R1234 ze nešto je niža, 17.2 i 9.9% nego kod R134a. RE170 i R1234yf pokazali su vrlo sličnu volumetrijsku rashladnu sposobnost kao i R134a. Prosječan koeficijent performanse (COP_{ref}) dobiven pri uporabi RE170 viši je za 6.2% nego kod R134a, dok je COP_{ref} za R1234yf i R1234ze nešto niži, 6.1 i 0.9%. Zaključak je da je učinak (performansa) triju radnih tvari vrlo sličan onom kod R134a, a najbolji učinak postignut je uporabom RE170.

Ključne riječi: *ekološki prihvatljiv, performansa (učinak), alternativna radna tvar, hidro-floro-olefini, dimetil eter*

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