

## Trade-off working fluid selection for heat pumps

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**Abstract.** Nowadays heat pump systems are used to recover the heat from waste water from different sources and produce hot water for household and communal purposes. In this research comparative thermodynamic analysis of performance for a water-to-water single-stage vapor compression heat pump using several HCs, HCFCs and HFCs which belong to refrigerants of different generations is presented. A multi-criteria approach for optimal selection of refrigerants was used as scientific tool. Results of theoretical experiments of vapor compression heat pump system with the evaporator temperature range 0...25°C and condenser temperature 60°C and 83°C showed that the COP of R1234ze was higher than that of R600a, R152b by about 6.7...17.3%, 8.25...20.5%, and 1.7...14.4%, respectively, at condenser temperature 60 °C; however results are different if at condenser temperature is 83°C: the average COP of R600a was higher than that of R1234ze and R152b by about 7.7...14.7%, 9.3...15.8%, and 7.5...15.6%, respectively. COP displays a positive correlation with the evaporator temperature as well as a negative correlation with the condenser temperature. The complete analysis of all factors, including environmental safety, indicates that R1234ze and R600a refrigerants should be preferred as the working fluids for using in the water-to-water single-stage vapor compression heat pump for the hot water supply and heating purposes in industrial applications.

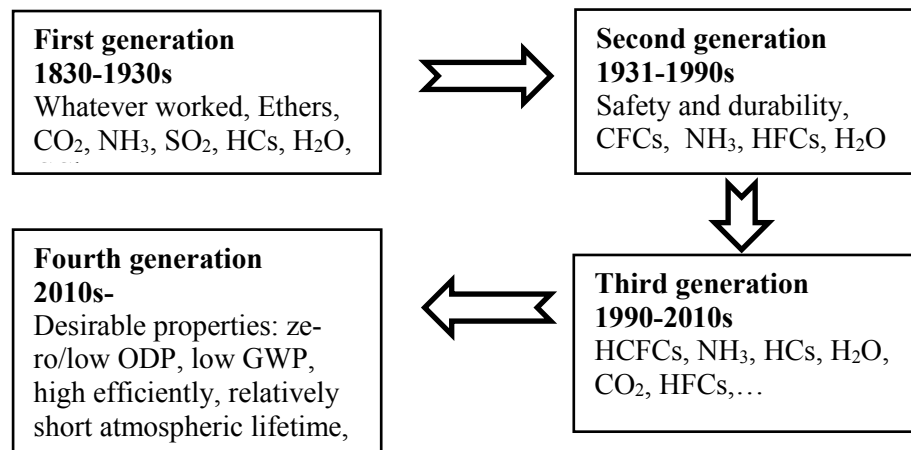
### 1. Introduction

Refrigeration and climate technology in developed countries consume up to 15% or more of produced electricity per year. Today capacity refrigerating and climatic equipment market in the European Union is about 30 billion Euros, and only in Germany - 10 billion Euros. The growth rate of this market in individual countries is 20-30% per year. Russia has a steady growth rate of consumption (25% per year) [1-2].

Refrigerants, coolants and oils - have been and remain the objects of constant thermophysical research throughout the world. Despite the fact that the principle of obtaining artificial cooling based on changing phase state has not changed, the cooling and air-conditioning industry is invariably evolved and expanded, which directly affects the applicability of a particular refrigerant in a certain period of time. Refrigerants have changed over the years, mainly in response to safety and environmental issues (figure 1).



The standards and codes that guide the application of refrigerants in cooling and air-conditioning industry are getting more strict as well [3].



**Figure 1.** Generation of refrigerants.

Since January 1, 2020 the European Union has introduced a ban on the using of refrigerants with a global warming potential (GWP), greater than 2500, and since 01.01.2025 - a ban on refrigerants with GWP<150. D.Sc. Tsvetkov O.B. et al [1-2] have determined the following requirements for any refrigerants in modern conditions, they are:

- Ozone-Depleting Potential (ODP);
- Global Warming Potential (GWP);
- toxicity;
- fire and explosion hazard;
- ease in detecting leaks;
- critical parameters and thermodynamic properties;
- transfer properties;
- heat and mass transfer characteristics;
- freezing and thermal decomposition temperatures;
- solubility in lubricating oils;
- compatibility with the materials used in engineering and water;
- cost.

Nowadays scientists try to understand if climate change causes from direct consequences or from indirect consequences such as energy-related emissions. There are thousand works showing advantages and disadvantages of the certain refrigerant [4-7].

Clearly, future discovery of ideal refrigerant that combines all the desirable properties is highly unlikely. However, algorithms for searching of a refrigerant with desirable combinations of properties have been described and founded application in ejector cooling cycle [8].

The aim of this study is to compare the thermodynamic performances of the high-temperature water-to-water vapor compression heat pump system using several HCs, HCFCs and HFCs which belong to refrigerants of different generations and to recommend more suitable substance based on theoretical calculation and analysis.

## 2. Materials and Methods

In the work we consider the operation of refrigeration system which is simulated by the reverse Rankine cycle. The main processes in the single-stage vapor compression cycle include isentropic compression, isobaric cooling (condensation, subcooling), throttling, and isobaric cooling (evaporation, superheating). The following design specifications are chosen: evaporator and condenser temperatures,  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 60^\circ\text{C}$  and  $t_{cond} = 83^\circ\text{C}$ ; cold carrier temperature at the heat pump inlet/ outlet (temperature of the low potential heat source),  $t_{low1}/t_{low2} = 35/30^\circ\text{C}$ ; hot carrier temperature at the heat pump inlet/ outlet,  $t_{high1}/t_{high2} = 47/57^\circ\text{C}$  and  $70/80^\circ\text{C}$ ; condenser/ evaporator pressure ratio -  $P_r < 9$ . The temperature range of cold space is the most typical of the industrial cooling water system outlet.

The refrigerants used in this analysis are: natural refrigerants, such as R290A, R600a; third generation refrigerants R142b and R152a, and finally, fourth generation refrigerants, such as R1234yf, R1234ze (table 1). The results obtained from the theoretical calculation are presented and commented in this work from the energetic point of view.

**Table 1.** Main Characteristics of Refrigerants [9-12].

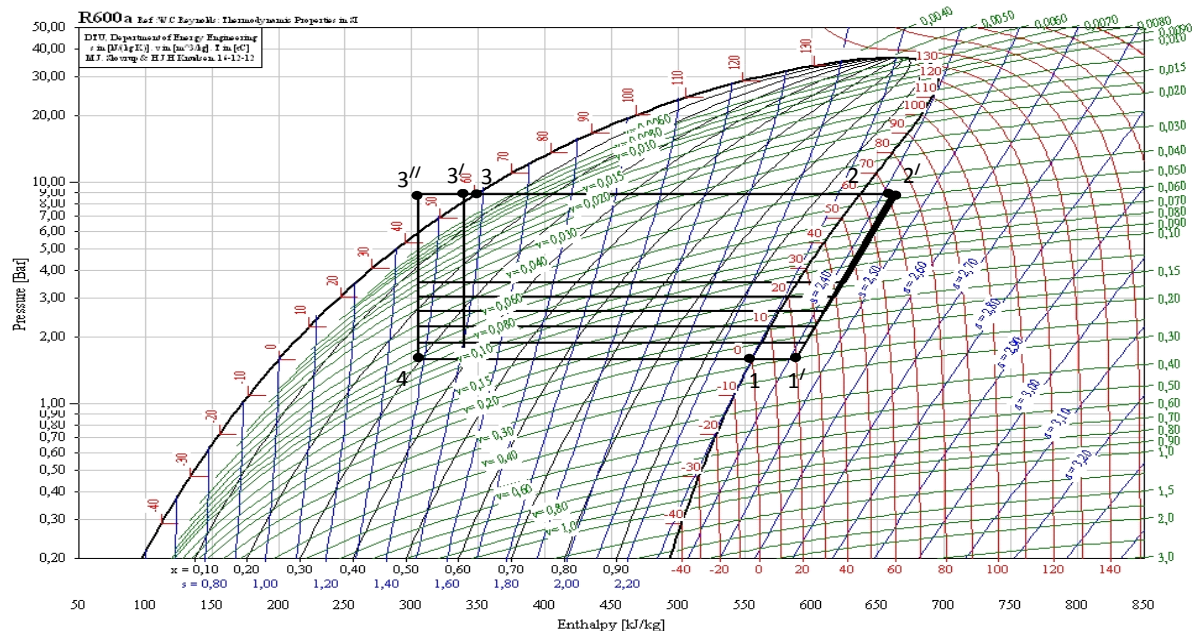
Refrigerant/ parameter	Natural refrigerants		Ethane Series fluids/ third generation refrigerants		Hydrofluoroolefins fluids/ fourth generation refrigerants	
	R290	R600a	R142b	R152a	R1234yf	R1234ze
Chemical formula	$\text{C}_3\text{H}_8$	$\text{C}_4\text{H}_{10}$	$\text{CH}_3\text{CClF}_2^*$	$\text{CHF}_2\text{-CH}_3$	$\text{CF}_3\text{CF=CH}_2$	$\text{CF}_3\text{-CH=CHF}$
Molecular mass, kg/kmol	44.1	58.1	100.5	66.05	114.04	114.04
Normal Boiling Point at $p=1\text{atm}$ , K	230.91	261.2	283.15	249.05	243.66	254.17
Critical Tempera- ture, K	370	407.98	410.26	386.41	94.7	109.4
Critical Pressure (absolute), $p_{cp}$ , bar	42.7	36.846	41.4	45.16	33.82	36.4
Critical Density, $\text{kg/m}^3$	220.48	225.5	446.0	368	475.55	470.0
Ozon Depletion Potential, ODP	0.0	0.0	0.065	0	0	0
Global Warming Potential, GWP	3	0.01	2000	140	4	7
Safety class <sup>a</sup>	A3	A3	A2	A2	A2L	A2L

<sup>a</sup>Classification: A2 – non-toxic, mildly-flammable with high velocity of flammability; A2L – non-toxic, mildly-flammable with low velocity of flammability; A3 – non-toxic, flammable.

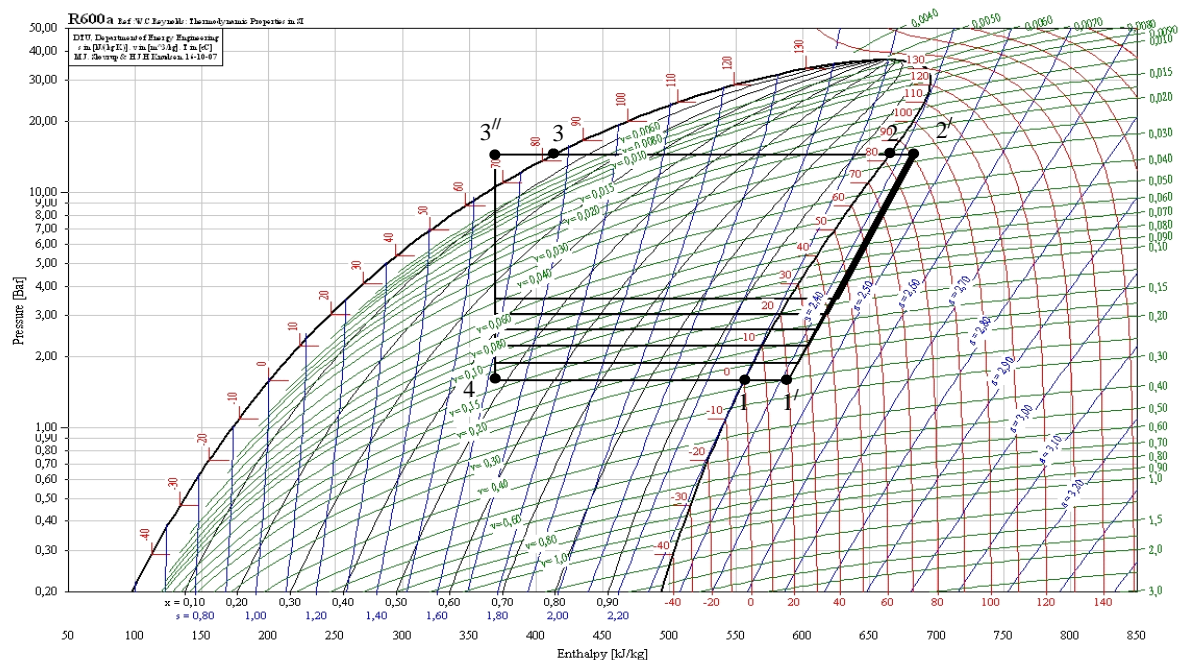
The temperature range of hot space is set basing on the most typical values for municipal and industrial high-temperature heating and hot water supply system inlet.

The heat pump thermodynamic cycles diagrams were prepared in the  $\log(p)$ - $h$  for each of the selected refrigerants. All calculations and diagrams were carried out with the help of freeware CoolPack ("CoolPack– IPU," n.d.) ver. 1.46, freeware REFPROP ver.8 (NIST Standard Reference Database 23) [11-12] and Microsoft Excel 2010.

The thermodynamic cycle for R600a is shown in the Log(p)-h diagram at  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 60^\circ\text{C}$  (figure 2) and at  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 83^\circ\text{C}$  (figure 3) as an example. The thermodynamic cycles for the other selected refrigerants have the same order except values of parameter for each state point.



**Figure 2.** The log(p)-h diagram for R600a at variable evaporation temperature, including  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 60^\circ\text{C}$ .



**Figure 3.** The log(p)-h diagram for R600a at variable evaporation temperature, including  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 83^\circ\text{C}$ .

The performance and efficiency of the water-to-water single-stage vapor compression heat pump were estimated as described in [13].

Basing on the parameters from diagrams all the necessary data were calculated for all refrigerants and presented in table 2.

In this work we have tried to adapt a multi-criteria optimization for making comparative analysis in order to choose “desirable” refrigerant for our heat pump system. For the multi-criteria problems the local criteria usually have a different physical meaning, and consequently, they have incomparable dimensions. It complicates the solution of a multi-criteria problem and makes it necessary to introduce the procedure of normalizing criteria or making these criteria dimensionless. There is no unique method for the criteria normalizing and choice of method depends on statement of problem having a subjective character [8].

**Table 2.** Calculated parameters for using refrigerants at  $t_{ev}=20^{\circ}\text{C}$ ,  $t_{cond}=60^{\circ}\text{C}$ .

Refrigerant/parameter	R290	R600a	R142b	R152a	R1234yf	R1234ze
Vaporizer specific heat load, $q_{vap}$ , kJ/kg	269.5	279.0	176.0	251.29	100.0	120.0
Condenser specific heat load, $q_{cond}$ , kJ/kg	316.1	315.0	200.0	283.27	116.0	136.0
Subcooler specific heat load, $q_{s\ cool}$ , kJ/kg	8	8	8	8	8	8
Total heat pump specific heat load, $q_{hp}$ , kJ/kg	324.1	323.0	208	291.27	124.4	144.0
Compressor specific work, $l_{comp}$ , kJ/kg	48.2	44.0	32.0	45.83	20.4	18.0
Exergy efficiency ratio, $\eta_e$	0.45	0.48	0.4	0.43	0.42	0.52
Coefficient of performance COP, $\mu$	6.72	7.34	6.5	6.36	6.1	8.0
Heat equivalent of the electric power, consumed by compressor, $q_{cpower}$ , kJ/kg	53.41	48.75	44.44	50.78	22.6	19.94

Multi-criteria comparative analysis algorithm is realized in the following way.

- Thermodynamic properties and design characteristics of vapor compression cycle are calculated for specified external conditions.
- The “desirable” value of criterion  $D_i=D_{max}$  and  $D_i=D_{min}$  have been chosen for each of the criterion. The value of  $D_i$  depended on thermodynamic mean of each parameter, e.g. for “total heat pump specific heat load”  $D_{max}=q_{hp}=324.1\text{kJ/kg}$  and  $D_{min}=q_{hp}=124.41\text{kJ/kg}$  were chosen as data.

If the absolute value of parameter should strive for a minimum value, than  $D^0_{absREF_i}$  can be obtained as (1)

$$D^0_{absREF_i} = \frac{D_i - D_{min}}{D_{max} - D_{min}}. \quad (1)$$

If the absolute value of parameter should strive for a maximum value, than  $D^0_{absREF_i}$  can be obtained as (2)

$$D^0_{absREF_i} = \frac{D_{max} - D_i}{D_{max} - D_{min}}. \quad (2)$$

- The best value of design characteristics  $D_{absREF}$  is chosen for each criterion among all concurrent refrigerants.
- Composite criterion  $D_{absREF}$  is defined by

$$D_{absREF} = \sum_{i=1}^n D_{absREF_i}^0 \quad (3)$$

- Minimum value of  $D_{absREF}$  – criterion corresponds to best refrigerant among concurrent working fluids.

Trade-off search of working fluid control variables  $X$  is formulated as a fuzzy nonlinear programming problem with  $n$  non-compatible criteria (economic, environmental, and thermodynamic),  $m$  decision variables, and  $k$  nonlinear constraints:

$$\text{Optimize } K [K_{th}(X), K_{ec}(X), K_{en}(X)] \quad (4)$$

subject to

$$G_{Li} \leq G_i(X) \leq G_{Ui}, I = 1, 2, \dots, k \quad (5)$$

$$X_{Li} \leq X_i \leq X_{Ui}, i = 1, 2, \dots, m \quad (6)$$

where  $K_{th}(X)$ ,  $K_{ec}(X)$ ,  $K_{en}(X)$  represent the fuzzy local criteria of thermodynamic, economic, and environmental efficiency;  $X (X_1, X_2, \dots, X_m)$  is a vector of control variables;  $G_{Li}$ ,  $G_{Ui}$ , are respectively the lower and upper limits for the constraints  $G_i(X)$  and  $X_{Li}$ ,  $X_{Ui}$  are respectively the lower and upper bounds for the control variables.

There are several methods of finding “good” solutions to the above problem in thermoeconomic analysis based on scalar optimization. However, as example, the attempts to resolve the CGAM problem [14, 15] via single objective paradigm illustrate a conflict among different approaches and lack of compromise decision [8]. Multicriteria approach is based on synergetic combination of formal and informal making-decision procedures to select a trade-off solution of problem. There are no entirely formal mathematical tools to resolve a multicriteria problem and additional exogenous information is needed.

In the present study, a next sequence of decision-making steps in fuzzy thermoeconomic analysis of refrigeration system is applied [8, 16].

- Determination of the Pareto optimal (or compromise, or trade-off) set  $X_P$  as the formal solution of multicriteria problem to minimize a conflict source of uncertainty;
- Fuzzification of goals as well as constraints to represent an ill-structured situation;
- Informal selection of convolution scheme to switch over a vector criterion  $K[K_{th}(X), K_{ec}(X), K_{en}(X)]$  into scalar combination of the  $K_{th}(X)$ ,  $K_{ec}(X)$ , and  $K_{en}(X)$ ;

Evaluation of the final decision vector  $X_{opt} \hat{=} X_P$  to minimize a vagueness source of uncertainty.

### 3. Results

The complete set of design criteria is considered in table 3 where calculation results for R290A, R600a; R142b, R152a, R1234yf, R1234ze are given.

Results of comparison are shown in figure 4(column a) where thermodynamic advantages of such refrigerants as R600a, R152a and R1234ze are demonstrated obviously. R142b has the worst value of the Global Warming Potential; it was taken into account during the calculation procedure.

The similar calculation stages were made for the same groups of the refrigerants at another condition, videlicet  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 83^\circ\text{C}$ . Diagram with multi-criteria selection of refrigerants for water-to-water single-stage vapor compression heat pump is shown in figure 4 (column b). In fact theoretical results indicate the preservation of the trend in refrigeration choice. Both natural refrigerant R600a and new fourth generation's refrigerant R1234ze have obvious advantages.

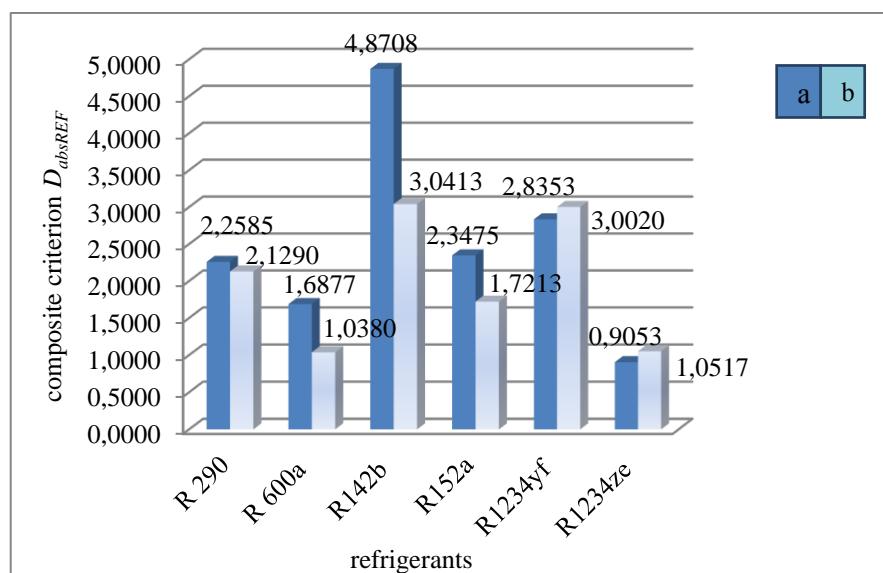
In order to obtain the results in the theoretical assessment of a water-to-water single-stage vapor compression heat pump using three chosen refrigerants, two different condenser temperatures were set as  $60^\circ\text{C}$  and  $83^\circ\text{C}$  versus a wide range of evaporator temperatures (range between  $0^\circ\text{C}$  and  $25^\circ\text{C}$ ).

**Table 3.** Assessment of design criteria for using refrigerants.

Refrigerant/ parameter	K	R290A	R600a	R142b	R152a	R1234yf	R1234ze	Dmax	Dmin	$\Delta D$
Total heat pump specific heat load, $q_{hp}$ , kJ/kg	K1	324.1	323.0	208	291.27	124.4	144.0	324.1	124.4	199.7
Exergy effi- ciency ratio, $\eta_e$	K2	0.45	0.48	0.4	0.43	0.42	0.52	0.52	0.4	0.12
Coefficient of performans COP, $\mu$	K3	6.72	7.34	6.5	6.36	6.1	8.0	8.0	6.1	1.9
Ozon Deple- tion Potential, ODP	K4	0.0	0.0	0.065	0	0	0	0.065	0.0	0.065
Global Warm- ing Potential, GWP	K5	3	0.01	2000	140	4	7	2000	0.01	1999.99
Flammability index <sup>a</sup>	K6	1.0	1.0	0.5	0.5	0.0	0.0	1.0	0.0	1.0

<sup>a</sup>Flammability index based on the refrigerant's safety class

It was obtained that the average COP of R 1234ze was higher than that of R600a, R152b by about 6.7-17.3%, 8.25-20.5%, and 1.7-14.4%, respectively, at condenser temperature 60 °C (figure 5a). However results are different if at condenser temperature is 83 °C: the average COP of R600a was higher than that of R1234ze and R152b by about 7.7-14.7%, 9.3-15.8%, and 7.5-15.6%, respectively (figure 5b). COP displays a positive correlation with the evaporator temperature as well as a negative correlation with the condenser temperature.

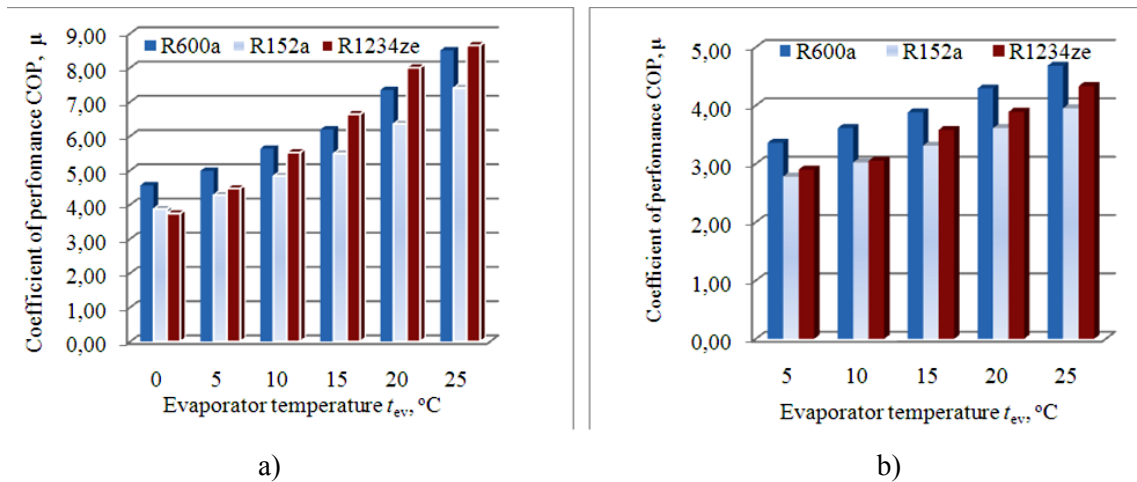


**Figure 4.** Multi-criteria selection of refrigerants for water-to-water single-stage vapor compression heat pump: a) at  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 60^\circ\text{C}$ ; b)  $t_{ev} = 20^\circ\text{C}$ ,  $t_{cond} = 83^\circ\text{C}$ .



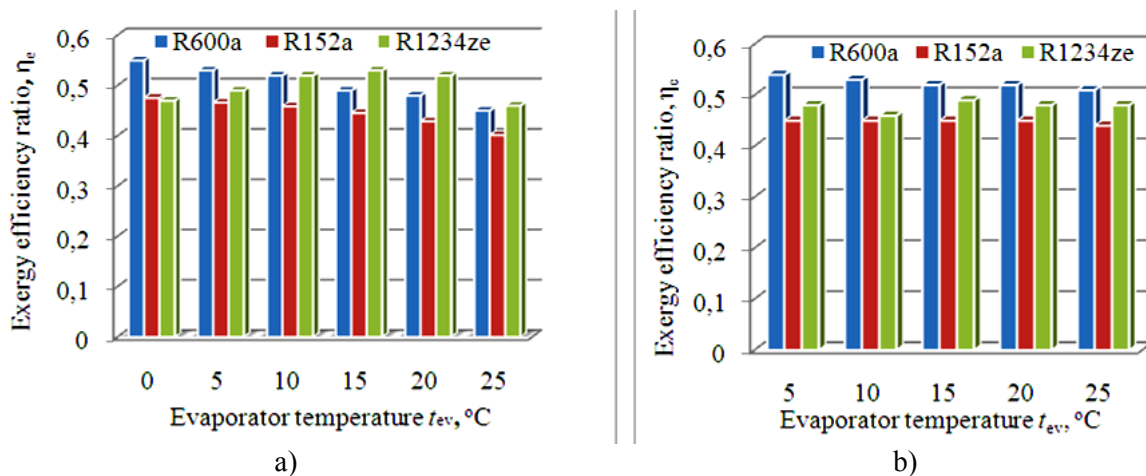
When the evaporating temperature and the condensing temperature are 20°C and 60°C,  $COP_h$  of R600a and R1234ze are 7.37 and 8.0 respectively, so this theoretical cycle is becoming more closer to ideal Carnot cycle. When the evaporating temperature and the condensing temperature are 20°C and 83°C,  $COP_h$  of R600a and R1234ze are 4.3 and 3.89 respectively.

The change in exergy efficiency ratio  $\eta_e$  as a function of evaporator temperature for R600a, R152a and R1234ze is demonstrated in figure 6.



**Figure 5.** Variation of coefficient of performance with evaporator temperature: a) for  $t_{cond} = 60^\circ\text{C}$  b) for  $t_{cond} = 83^\circ\text{C}$ .

It was obtained that exergy efficiency ratio  $\eta_e$  doesn't change a lot for each temperature value and  $\eta_e$  difference between R600a, R152a and R1234ze is 7.7-13.5%.  $\eta_e$  of R600a and R1234ze were higher than that of R152a for a range of condenser and evaporator temperatures. It also slightly decreases with the evaporator temperature increase (2-5%).



**Figure 6.** Variation of exergy efficiency ratio  $\eta_e$  with evaporator temperature: a) for  $t_{cond} = 60^\circ\text{C}$  b) for  $t_{cond} = 83^\circ\text{C}$ .

#### 4. Conclusion

To find balance between high performance and environmental safety of working fluids for HPS is an extremely important goal for heating and cooling industries. In fact, a refrigerant that combines all the desirable properties and has no undesirable properties does not exist.



Thermodynamic analysis based on a multi-criteria approach to optimum selection of refrigerants is useful tool for engineering calculations.

Theoretical results indicate that both the natural working fluid R600a and new fourth generation's refrigerant R1234ze have good cycle performances in a water-to-water single-stage vapor compression heat pump cycle. Therefore the complete analysis of all factors, including environmental safety, allows us to draw a conclusion that the R-1234ze and R600a refrigerants should be preferred as the working fluids for using in the water-to-water single-stage vapor compression heat pump for the hot water supply and heating purposes in industrial applications.

### Nomenclature

HFC: Hydrofluorocarbon;  
 HFO: Hydrofluoroolefin;  
 ODP: Ozone Depletion Potential;  
 GWP: Global Warming Potential,  
 COP: Coefficient of Performance;  
 $p$ : Pressure (kPa);  
 $t$ : Temperature (°C);

### References

- [1] Tsvetkov O B, Laptev YU A, Galahova N A and Timofeev B D 2016 Parizhskie ideologemy` i e`nergoe`ffektivny`e rabochie veshhestva tekhniki nizkix temperatur [Parisian ideologems and energy-efficient working substances of low temperature technology] *Nauchny`j zhurnal NIU ITMO. Seriya "Xolodil`naya tekhnika i kondicionirovanie"* **2** 6-11 [In Russian]
- [2] Tsvetkov O B, Baranenko A V, Laptev YU A, Sapozhnikov S Z, Khovalyg D M and Pjatak G L 2014 Ozonobezopasny`e xladagenty` [Ozone layer-safe refrigerants] *Nauchny`j zhurnal NIU ITMO. Seriya "Xolodil`naya tekhnika i kondicionirovanie"* **3** 98-111 [In Russian]
- [3] 2015 New refrigerants Impact Standards and Code *Carrier Engineering Newsletter* vol 3 is 2 URL [https://dms.hvacpartners.com/docs/1001/Public/0E/ENG\\_NEWS\\_3\\_2.pdf](https://dms.hvacpartners.com/docs/1001/Public/0E/ENG_NEWS_3_2.pdf)
- [4] Karnaukh V V, Biryukov A B, Mazur V A and Rzheshik K A 2017 Comparative analysis of different refrigerants used in a high-temperature vapor-compression heat pump *J. of Energy for a Clean Environment* **18(2)** 161-74
- [5] Meng Z, Zhang H, Qiu J and Lei M 2016 Theoretical analysis of R1234ze(E), R152a, and R1234ze(E)/R152a mixtures as replacements of R134a in vapor compression system *Int. J. of Advances in Mechanical Eng.* **8 (11)** 1-10
- [6] Ansari N A, Yadav B and Kumar J 2013 Theoretical exergy analysis of HFO-1234yf and HFO-1234ze as an alternative replacement of HFC-134a in simple vapour compression refrigeration system *Int. J. of Scientific & Eng. Research* **4(8)** 137-44
- [7] Gao Y, Zhao H, Peng Y and Roskilly T 2013 Analysis of Thermodynamic Characteristic Changes in Direct Expansion Ground Source Heat Pump Using Hydrofluoroolefins (HFOs) Substituting for HFC-134a *Int. J. Energy and Power Eng.* **5** 11-7
- [8] Mazur V A 2003 Optimum Refrigerant Selection for Low Temperature Engineering *Low Temperature and Cryogenic Refrigeration* (Dordrecht: Kluwer Academic Publishers) 101-18
- [9] 2019 Designation and Safety Classification of Refrigerants. ASHRAE Standard, ANSI/ASHRAE Standard 34-2010 URL <https://www.ashrae.org/technical-resources/standards-and-guidelines/ashrae-refrigerant-designations>
- [10] Calm J M 1999 *Arti refrigerant database. Primary and recently-added citations* (Arlington: Air-Conditioning and Refrigeration Technology Institute)
- [11] Lemmon E W, Huber M L and McLinden M O 2009 *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties* (Gaithersburg: National Institute

- of Standards and Technology)
- [12] Bell I H, Wronski J, Quoilin S, Lemort V 2014 Pure and Psedo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Propety Library Cool Prop *Industrial & Engineering Chemistry Research* **53(6)** 2498-508
  - [13] Trubaev P A and Grishko B M 2010 *Teplovy'e nasosy`* [Heat Pumps] (Belgorog: BGTU im V G Shukhova)
  - [14] McLinden M O, Domanski P A, Kazakov A, Heo J and Brown J S 2012 Possibilities, limits, and tradeoffs for refrigerants in the vapor compression cycle *ASHRAE/NIST Refrigerants Conference* (Gaithersburg)
  - [15] Kazakov A, McLinden M O and Frenkel M 2012 Computational Design of New Refrigerant Fluids Based on Environmental, Safety, and Thermodynamic Characteristics *J. Ind. Eng. Chem. Res.* **51(38)** 12537-48
  - [16] Kazakov A, Muzny C D, Diky V, Chirico R D and Frenkel M 2010 Predictive correlations based on large experimental datasets: Critical constants for pure compounds *J.Fluid Phase Equilib* **298** 131-42