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# Increase of heating medium temperature by using HTR mixtures in vapor compression heat pump

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**Abstract**

In this paper the possibility of using vapor-compression heat pumps to increase the temperature of carrier of low-temperature waste energy is assessed. We have studied thermodynamic cycles of heat pumps that use high temperature refrigerant (HTR) and operate within extreme range of evaporation and condensation temperatures.
Due to the limitations imposed by the Second Law of Thermodynamics, it is necessary to artificially increase the potential of the energy absorbed from the low temperature heat source. Either mechanical work (vapor compression) or high temperature heat has to be delivered to the cycle.
From thermodynamic point of view, the most important optimization factor would be the minimization of the work input, that is necessary for specified output. The minimal work input is calculated from the Second Law of Thermodynamics, under the assumption that entropy of the system never decreases. This leads to an efficiency optimized heat pump cycle.
Analyzed systems use natural refrigerants $CO_2$, $N_2O$ and zeotropic mixtures R124/R142b/R600a and R32/R125/R1234yf. Feasible thermodynamic cycles were modelled, compared and discussed in terms of their operation parameters.

*Keywords:* Heat pump; refrigerant; zeotropic mixture

## 1. Heat pump cycle

Conceptual scheme of the heat pump working under the assumption of constant temperature heat sources is presented in Fig. 1a. Refrigerant absorbs certain amount of heat $q_0$ from low temperature source (ambient) at $T_l$. This energy is then released at high temperature $T_h$. Figure 1b shows the case where the temperature of the heating area varies from $T_{h1}$ at the heat exchanger inlet to $T_{h2}$ at the heat exchanger outlet.

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The equation for entropy per 1 kg of refrigerant Δs, J/(kgK) is written as follows:

$$\Delta s = -\frac{q_0}{T_l} + \frac{q_0}{T_h} + \frac{w_{\min}}{T_h} \geq 0 \tag{1}$$

Where $q_0$ is the specific energy absorbed from low temperature heat source (ambient), J/kg, $T_h$ is the temperature of the heat sink (heating area), K, $T_l$ is the temperature of the heat source (ambient), K, $w_{min}$ is the minimized work input, J/kg.

Equation (1) can be rewritten for the work input:

$$w_{\min} \geq q_0 \cdot \frac{(T_h - T_l)}{T_l} \tag{2}$$

Assuming reversibility of the cycle $\Delta s = 0$ and multiplying by the mass flow of refrigerant, equation (2) takes the following form:

$$W_m = Q_0 \left( \frac{T_h}{T_l} - 1 \right) \tag{3}$$

Similarly, the minimal work input $W_{\min}$ for the variable temperature heat sink can be calculated. We have:

$$Q = Q_0 + W_{\min HP} \tag{4}$$

And

$$Q = \dot{m}_h \left( h_{h2} - h_{h1} \right) = T_h \Delta S \tag{5}$$

Where $m_h$ is the mass flow rate of the heat transfer fluid in heat sink, $h_{h1}$ and $h_{h2}$ are the enthalpies at the inlet and the outlet of the heating area.

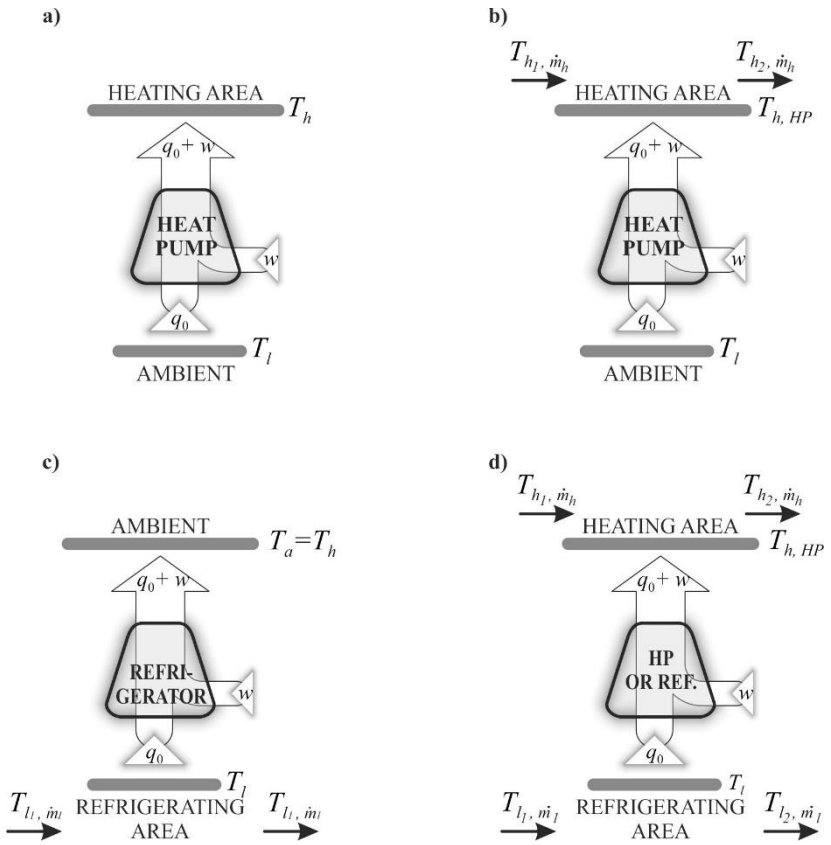



Figure 1. Conceptual scheme of: a) heat pump operating between constant temperature heat source and constant temperature heat sink, b) heat pump operating between constant temperature heat source and variable temperature heat sink, c) refrigerator operating between constant variable temperature heat source and constant temperature heat sink, d) heating/refrigerating system with variable temperature heat sources/sinks.

Considering that:

$$\frac{Q}{T_h} - \frac{Q_0}{T_w} = 0 \tag{6}$$

it is possible to write the equation for minimal work input:

$$W_{\min HP} = \dot{m}_h \left(h_{h2} - h_{h1}\right) - \frac{T_l \cdot \dot{m}_h \left(s_{h2} - s_{h1}\right)}{2} \tag{7}$$

The equation (7) can be written in terms of exergy as follows:

$$W_{\min HP} = \dot{m}_h \left(b_{h2} - b_{h1}\right) \tag{8}$$

Where $b_h$ is the exergy of heat transfer fluid at the inlet (index 1) and the outlet (index 2) of the heating area. By definition the exergy is calculated as:

$$b = \left(h - T_l \cdot s\right) - \left(h_0 - T_0 \cdot s_0\right) \tag{9}$$

Where $h$ and $s$ are correspondingly the enthalpy and the entropy at given temperature and pressure, while $h_0$ and $s_0$ at the reference temperature and pressure.

In heat pumps the expected effect of their work is to release energy of higher potential to the heat sink at the temperature $T_h$. The efficiency of this process $COP_{HP}$ is defined as the amount of heat released $q_h$ divided by the work input $w_{in}$:

$$COP = \frac{q_h}{w_{in}} \tag{10}$$

The efficiency of the optimized heat pump would then be:

$$COP_{HP} = \frac{q}{W_{in\min}} = \frac{\dot{m}_h \left(h_{h2} - h_{h1}\right)}{\dot{m}_h \left(b_{h2} - b_{h1}\right)} \tag{11}$$

Assuming that the change of the heat transfer fluid properties is very small, the fluid can be treated as ideal. Thus the mean fluid temperature during heat rejection $T_{HP}$ can be calculated with logarithmic temperature difference as follows:

$$T_{HP} = \frac{\left(T_{h2} - T_{h1}\right)}{\ln\left(\frac{T_{h2}}{T_{h1}}\right)} \tag{12}$$

## 2. Natural refrigerants

With respect to the environmental and personal safety, natural refrigerants appear to be more attractive than the other synthetic refrigerants. Due to their zero ozone layer depletion potential and low global warming potential, several natural refrigerants are regaining their importance, among which nitrous oxide ($N_2O$) is one of the most promising future refrigerants. While $CO_2$ based systems have already gained large acceptance in refrigeration and heat pump applications, $N_2O$ still remains mostly unexplored. $CO_2$ can be used in refrigeration systems with minimum evaporation temperature of -55°C. Further lowering of temperature cannot be achieved since the triple point of $CO_2$ is about -56.56°C. On the other hand, $N_2O$ has a triple point temperature of -90.82°C with the boiling point temperature of -88.47°C, and hence it can be used in the temperature range below the application limit of $CO_2$. Furthermore, similarity in critical temperature, pressure and molecular weight of $N_2O$ and $CO_2$ causes nearly similar behavior of those two refrigerants with respect to system temperature, pressure, compactness and properties. The main disadvantage of $N_2O$ is its higher GWP compared to $CO_2$, however it is significantly more favorable in terms of toxicity.

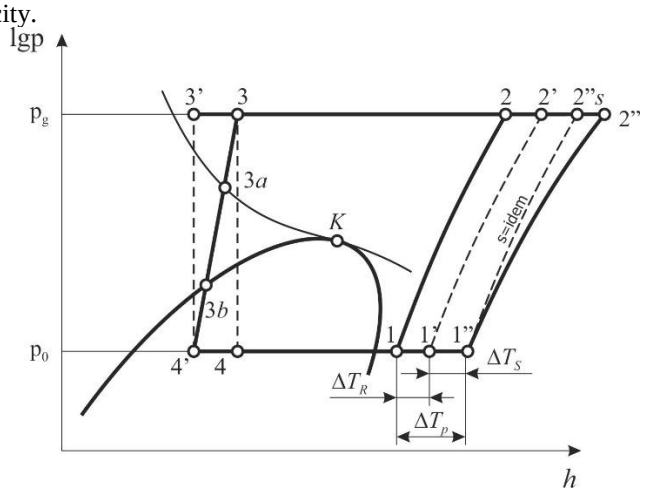


Figure 2. Thermodynamic cycle of heat pump system patented and realized by Lorentzen and Petersen

The refrigerating system patented and executed by Lorentzen and Petersen (Pettersen J., Lorentzen G., 1993) is presented in figure 2. The system features additionalinternal heat exchangers – recuperator and fluid separator. These additional elements assure more effective and, most of all, more stable work of the system.

During the cycle the fluid undergoes several processes described with state points 1”-2”-3’-4’-1”. The differences between the actual and theoretical (1-2-3-4) cycles result from:

– internal heat exchanger, extra gas cooling ($h_3$-$h_{3'}$) and vapor superheating ($h_{1"}$-$h_{1'}$)

– superheating of vapor in the compressor ($h_{1'}$-$h_1$)

– non-isentropic compression of vapor ($h_{2"}$-$h_{2s"}$)

In a heat pump system featuring a capillary tube as a expansion device and an internal heat exchanger of typical construction, the cycle is described with state points 1”-2”-3’-4’-1”. High-pressure refrigerant from the gas cooler exchanges heat with the low-pressure refrigerant leaving the evaporator, which corresponds to processes 3-3’ and 1’-1”respectively. Then the refrigerant enters the capillary tube where it is throttled to low pressure, low temperature and a two-phase state. In practical applications, however, some part of the capillary tube is placed inside the suction line of compressor. A new thermodynamic cycle corresponding to such system is described with state points 1”-2”-3-4’-1”. In this new transcritical cycle the fluid undergoes both beat transfer and expansion processes while flowing through capillary tube. The capillary tube can be assembled together with accumulator or suction line giving a new device with integrated heat exchanger and the capillary tube, where the fluid undergoes processes described with points 3-4’ and l’-1”. The high-pressure refrigerant in an enlarged capillary tube rejects heat to the suction line vapor while being throttled to evaporating pressure. Consequently, the system size and weight could be highly reduced.

For real cycle with heat recuperation:

$$COP' = \frac{h_1 - h_{4'}}{h_{2"} - h_{1"}} \tag{13}$$

Assuming an ideal heat exchanger – recuperator, $h_{4"} - h_{1'} = h_4 - h_{4'}$ and $h_{1'} - h_{4'} = h_{1"} - h_4$.

Taking into consideration the additional vapor superheating, the parameters of the point 1” can be calculated. The vapor heating in compressor before inlet to its cylinder depends on the compression work and final value of temperature $T_{2"}$. It can be determined from dependence for Freon compressors:

$$\Delta T_S = T_{1"} - T_1 = \frac{1}{c_p} \frac{h_{2"} - h_1}{\eta_{is}} \left( \frac{1}{\eta_m} - 1 \right) \tag{14}$$

Rearranging equation (14) yields:

$$h_{1"} - h_1 = c_p \left( T_{1"} - T_1 \right) = \frac{h_{2"} - h_1}{\eta_{is}} \left( \frac{1}{\eta_m} - 1 \right) \tag{15}$$

and further:

$$h_{1"} = h_1 + \frac{h_{2"} - h_1}{\eta_{is}} \left( \frac{1}{\eta_m} - 1 \right) \tag{16}$$

First of all, efficiency $\eta_{is} = l_r / l_s$ depends on the compression degree $p_t/p_0$ for semi-hermetic $CO_2$ compressors. It can be described with the following formula:

$$\eta_{is} = -0,26 + 0,7952\left(\frac{p_g}{p_0}\right) - 0,2803\left(\frac{p_g}{p_0}\right)^2 + 0,0414\left(\frac{p_g}{p_0}\right)^3 - 0,0022\left(\frac{p_g}{p_0}\right)^4 \tag{17}$$

$$\varepsilon_R = \varepsilon_t \cdot \eta_{is} \tag{18}$$

To analyze the feasibility of $CO_2$ and $N_2O$ based compressor heat pumps to increase the water temperature, a model presented in the literature was used. It was assumed that the heat pump system consists of the typical elements of a transcritical cycle. Recuperative heat exchanger and superheating process in the suction line was considered as well (Kim S. G., Kim Y. J. Lee G., Kim M. S., 2005).

The characteristics of transcritical cycle gives the carrier fluid (water) an opportunity to flow directly to gas cooler or to evaporator as a low temperature heat source. Therefore, two types of transcritical cycles were analyzed with the following parameters:

A)

– water temperature at the inlet of the gas cooler $T_{w1}$= 60°C

– water temperature at the outlet of the gas cooler $T_{w2}$= 90°C

– evaporation temperature $T_0$= -10°C

B)

– water temperature at the inlet of the gas cooler $T_{w1}$= 30°C

– water temperature at the outlet of the gas cooler $T_{w2}$ = 90°C

– evaporation temperature change $T_0$= 5÷30°C (35°C for $N_2O$)

In both analyzed cycles we assumed:

– refrigerant superheating in the recuperator $\Delta T_R$= 5K

– refrigerant superheating in the suction line $\Delta T_s$= 5K

Isentropic efficiency of the compression process and the temperature at the end of the compression process were determined assuming that they depend mainly on the compression ratio, which is given by:

$$\eta_{is} = C_1 - C_2\left(\frac{p_t}{p_0}\right) \tag{19}$$

where $C_1$ and $C_2$ are empirical constants. For $CO_2$ piston compressors when the static pressure $p_t/p_0 > 2$ $C_1$ = 93.43, $C_2$ = 0.04478.

The results of COP analysis are shown in Figure 3.

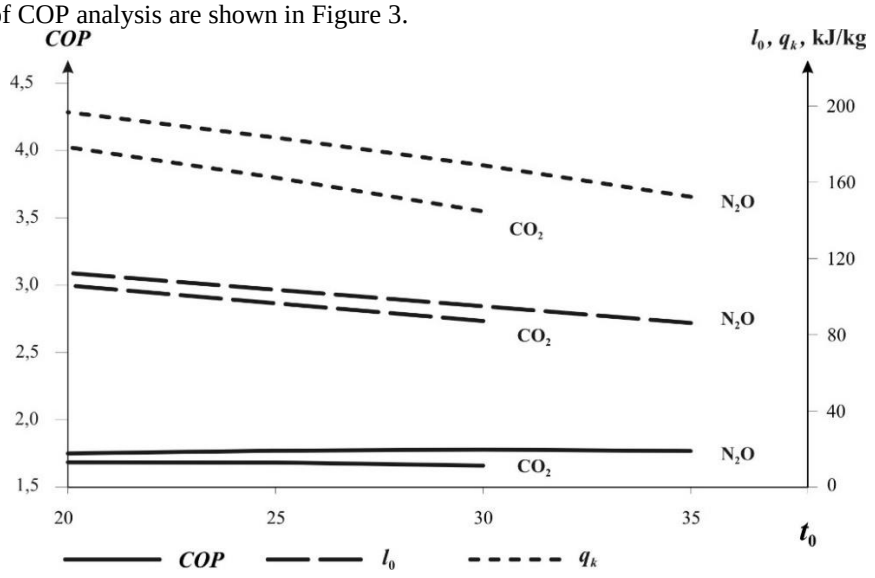



Figure 3. The values of selected parameters of the analyzed cycles for $CO_2$ and $N_2O$

## 3. Refrigerant mixtures

To determine mixture's thermodynamic properties we used a method which allows determination of mixture properties for the mixture that undergoes a process with a change of content. We have also developed a computational program to perform calculations on the basis of the following algorithm. –Starting point for the analysis was the Carnahan-Starling-DeSantis Equation of State:

$$\frac{pv}{RT}=\frac{1+y+y^2-y^3}{1-y^3}-\frac{a}{RT(v+b)} \tag{20}$$

where:
a – equation of state attraction parameter (being a function of temperature);
b – equation of state volume parameter (being a function of temperature).
For a pure component:

$$a(T)=a_0\cdot e^{(a_1T+a_2T^2)};\ b(T)=b_0\cdot e^{(b_1T+b_2T^2)} \tag{21}$$

where:
$a_0$, $a_1$, $a_2$ – coefficients for the temperature;,
$b_0$, $b_1$, $b_2$ - coefficients for the temperature;
Coefficients for the temperature in the case of mixtures:

$$a_{ij}=\sqrt{a_i\cdot a_j}\,(1-k_{ij});\ b_{ij}=\frac{b_i+b_j}{2};\ a=\sum_i\sum_j x_ix_ja_{ij};\ b=\sum_i\sum_j x_ix_jb_{ij} \tag{22}$$

where:
$a_{ij}$ – averaged coefficient equation of state for mixtures *i* and *j*;
$a_i$ – equation's coefficients of state for component *i*;
$a_j$ – equation's coefficients of state for component *j*;
$k_{ij}$ – interaction coefficient for mixtures of component *i* and *j*;
$b_{ij}$ – averaged coefficient b for mixtures of components *i* and *j*;
$a$ – supplementary coefficient of equation of state for mixtures with participations of components $x_i$ and $x_j$;
$b$ – supplementary coefficient of equation of state for mixtures with participations of components $x_i$ and $x_j$;
$x_i$, $x_j$ – participations of components *i* and *j*.
Phase equilibrium criterion for mixtures is defined as a state where chemical potentials of both phases are equal:

$$\mu_{a1}(T,x_1,v_1)=\mu_{a2}(T,x_2,v_2),\ \mu_{b1}(T,x_1,v_1)=\mu_{b2}(T,x_2,v_2) \tag{23}$$

where $\mu_{a1}$ is a chemical potential of component *a* in phase 1 (similarly for index *b* and phase 2). Chemical potentials on the basis of equation of state can be written as:

$$\begin{aligned}\mu(T,p(v),x_i)&=G(T,p(v),x_i)+(1-x_i)\left(\frac{\partial G}{\partial x_i}\right)_{T,p}=\\&=\mu^0(p^*,T,x_i)+RT\ln\left(\frac{RT}{p^*v}\right)+\frac{RT\beta(4v-3\beta)}{(v-\beta)^2}+\\&+\frac{RT\beta(4v^2-2v\beta)}{(v-\beta)^3}+\frac{ab_i}{b^2}\ln\left(\frac{v+b}{v}\right)-\frac{ab_i}{b(v+b)}+\frac{2x_ia_i+2x_ja_{ij}}{b}\ln\left(\frac{v+b}{v}\right)\end{aligned} \tag{24}$$

where: $\beta$ = b/4

### *3.1. Mixtures R124/R142b/R600a and R32/R125/R1234yf*

On the basis of Linde refrigeration cycle calculations were carried out to determine the mixture suitability for the process of increasing water temperature from 30°C to 90°C and from 25°C to 75°C. A mixture composition was selected to maximize the heat pump coefficient of performance and to minimize the compression temperature. The mixture undergoes the processes presented in in Figure 4.

Analysis of the mixture is based on the following assumptions:

– evaporation temperature $t_0$ ranging from 20 to 45 °C
– condensation temperature $t_k$ ranging from 75 to 95 °C
– evaporator superheating - 5K
– isentropic compression process efficiency determined by equation (19)
– superheating in the suction line - 5K
– refrigerant subcooling in the condenser - 10 K.

It was assumed that the cycle implemented in the modeled heat pump system is described with state points 1-2-3-4. The differences between the modeled cycle and the theoretical one are caused by superheating in the suction line 1"-1, liquid subcooling in the condenser 3 '-3 and non-isentropic compression process 1-2. Five mixtures were selected for the anaysis: one proposed in the literature (Nanxin l.,Shi. L.,Lizhong H., 2005) (labeled HTR1) and HTR2, HTR3, HTR4 and HTR5.

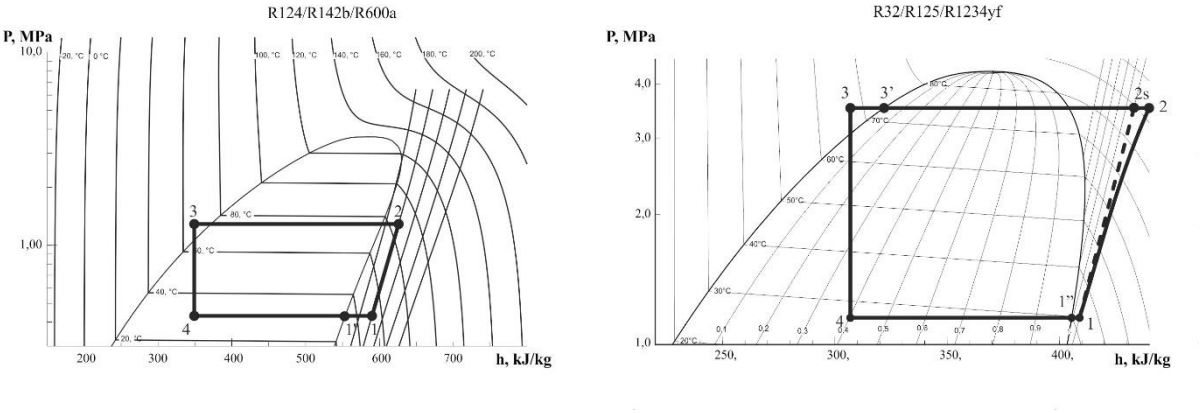



Figure 4. The heat pump cycle for a mixture of R124/R142b/R600a (HTR3) and R32/R125/R1234yf (HTR5)

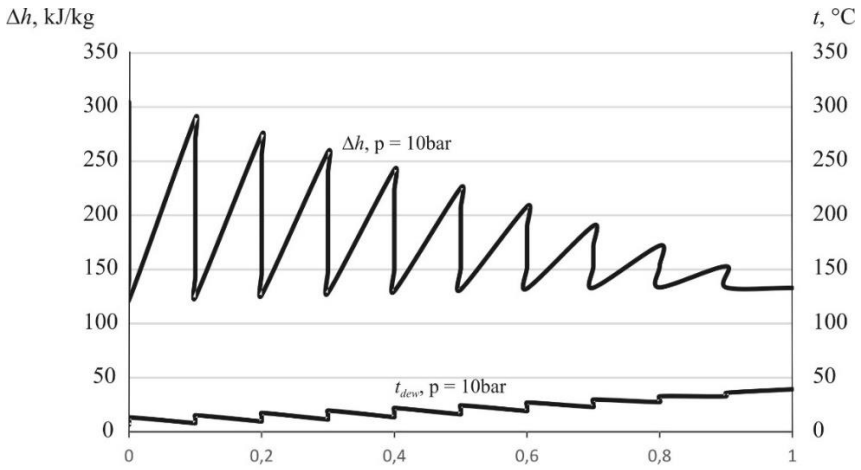



Figure 5. Maximum temperature changes and enthalpy difference in wet vapor area of HTR5 mixture

Selected and analyzed mixtures were:

HTR1 (Nanxin l.,Shi. L.,Lizhong H., 2005) – R124/R142b/R600a – 90/8/2
HTR2 – R124/R142b/R600a – 20/65/15
HTR3 – R124/R142b/R600a – 15/70/15
HTR4 – R124/R142b/R600a – 85/10/5
HTR5 – R32/R125/R1234yf – 23/25/52
The results of modeling the thermodynamic cycles are shown in Fig. 6

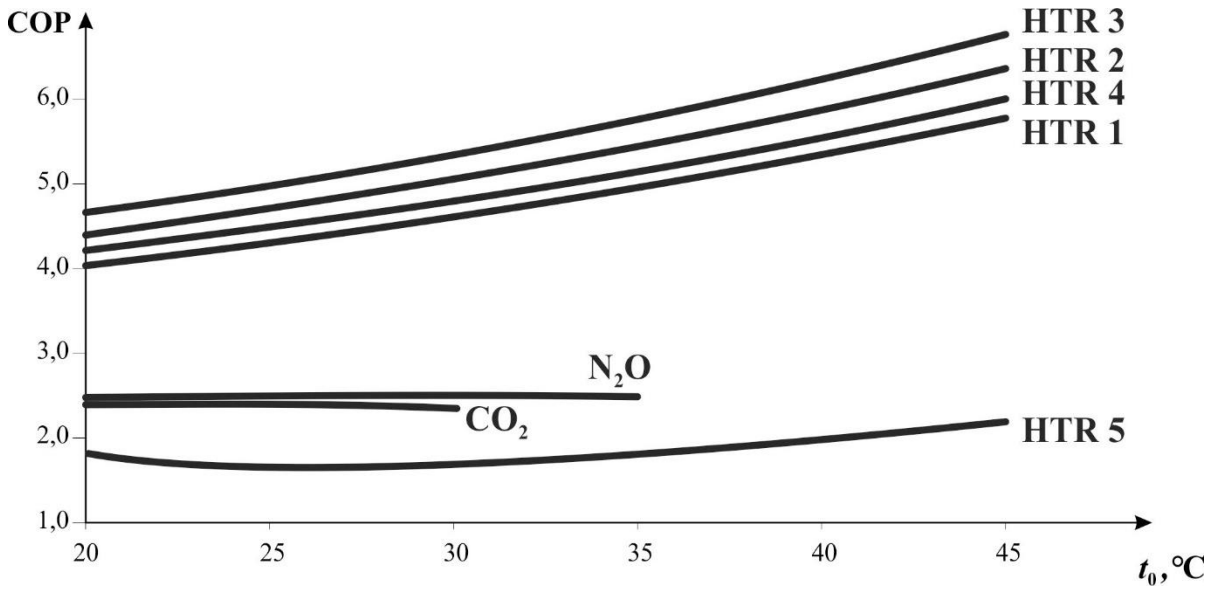



Figure 6. Values of COP for analyzed cycles

## 4. Conclusions

The above analysis shows the potential of using the ternary mixture in high temperature heat pump systems. Under the analyzed conditions, obtained condensation temperature and pressure of the ternary mixture are significantly lower compared to the $CO_2$ and $N_2O$ systems. It shows that application for the mentioned mixtures is a promising solution.

The values of heat pump efficiency coefficients for the analyzed refrigeration cycles show that carbon dioxide and nitrous dioxide are not suitable refrigerants for cycles with evaporation temperature close to their critical point temperatures. Such range of evaporating temperatures result in a significant reduction of the latent heat of evaporation.

Similar results have been obtained for the R407C based mixture, where R134a is replaced by R1234yf. In the analyzed temperature range this refrigerant yields the worst value of COP. These results show that refrigerant blends intended for replacing R134a cannot be always used in a wide range of application.

The values of the coefficient of performance for the proposed mixtures indicate that they are an interesting alternative to traditional refrigerants. Further investigation, involving experimental studies of real-life systems and solving operational problems like oil selection, is needed. Moreover, further studies are necessary for optimization of mixture composition to obtain maximum COP.

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