# THERMODYNAMIC ANALYSIS OF ZEOTROPIC MIXTURES FOR EJECTOR REFRIGERATION CYCLE

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#### Abstract

The conventional refrigeration ejector cycle utilises constant temperature process during motive heat consumption needed for vapour generation. This may be thought as the main restriction concerning application of low-grade heat as a motive source by these systems since it results in required significant mass flow rate with small temperature drop of a heating fluid. In contrary, the large change of temperature and small flow rate of the water in order to provide required heat flux is more economically advantageous. In some cases, however, either requirements cannot be fulfilled. The main reason for this limitation is isothermal evaporation of refrigerant in vapour generator. Because of this the refrigerant with temperature glide is highly recommended. One of the possible approaches to reduce this restriction is application of a zeotropic mixture as the working fluid for the conventional ejector cycle. The paper deals with thermodynamic analysis of low GWP refrigerant mixtures applied for ejection cycle. The results show that depending on the type and proportion of mixed refrigerants the temperature of the heating medium change from 5 to 25 K and more. As an effect COP of the system varies between 5 to 35%.

#### 1. INTRODUCTION

Environmental concerns led to increase of interest in utilising alternative energy sources, like low- and medium-temperature heat sources, such as solar, geothermal or waste heat sources. ORC (Organic Rankine Cycle) is a popular choice for low grade heat utilisation. Many commercial solutions are available, but most of them are large units, suitable for use with high temperature sources (200 - 300 °C).

Another way of using low grade energy sources are ejector refrigeration cycles (ERC) as heat driven systems. COP of these systems is lower than in case of ammonia absorption chillers, but ERC can operate with lower motive heat temperatures as low as  $50 - 70^{\circ}$ C. This makes possible to apply the ejector refrigeration cycles with district heating systems thus increasing overall efficiency of the CHP plant in the summer season by creating a simultaneous demand for utilisable thermal capacity and refrigeration capacity. However, the discussed solution has a major drawback which is low temperature of water circulating in the heating system which is in the most cases app. 65 - 70 °C in summer season. This causes low COP of the ejector refrigeration cycle.

The largest obstacle in utilising this technology is a high drop of heating water temperature at the heat consumer side that is required by district heating CHP system. In most cases the demand for temperature drop is 20 - 30 K that should have to be achieved in vapour generator of the ejector refrigeration system. This requirement can be met by application of the super- or trans-critical cycles, as well as the cycles with use zeotropic mixtures as refrigerants. Due to constant temperature of the phase change process for one-component and azeotropic mixtures as refrigerants the available temperature drop of heating water is very limited. The consequence is requirement for very high demand for heating water flow rate as well as high temperature of heating water at the outflow from the vapour generator. This causes increase of the investment costs as well as limitations in the operation feasibilities of the district heating system. There is a lack of research on ejector refrigeration cycles operating with high temperature glide working fluids employed to provide better fit between the heating water temperature drop and the refrigerant temperature increase in the vapour generator. This paper provides with the results of theoretical analysis of the ejector refrigeration cycle working with a high temperature glide blends composed of the environmentally friendly refrigerants.

Gagan et al. (2018) proved that it is possible to run ejector cycles with low source temperatures, namely around 60°C. They investigated the performance of an ejector cycle with ecological HFO R-1234ze(Z) refrigerant. The system achieved COP = 0.25 for evaporation temperature 0 °C and COP = 0.40 for 6°C. The motive temperature was kept below 65 °C. However, in the discussed cases temperature drop of heating fluid has not exceeded 10 K.

Research on both heat and refrigeration cycles working with zeotropic blends were carried out. Kang et al. (2015) investigated the performance of zeotropic mixtures of HFC/HC and HFO/HC in ORC working with low-to-medium temperature heat source. The performance of R-245fa and R-600a (0.9/0.1) mixture was found to be the best. Hakkaki-Fard et al. (2014) have developed a numerical model of an air-source heat pump to examine how heat pumps work with zeotropic blends of several environmentally friendly refrigerants (CO2, propane, R-32), and R-125. Yang and Zhao (2015) and Yang et al. (2015) investigated of application of the zeotropic mixtures in combined power and ejector cycle. Such systems are created by adding an expander between the vapour generator and the ejector in the standard ejector refrigeration cycle. Chen et al. (2011) have proposed use of zeotropic mixtures was analysed: R32/R134a, R32/R152a, R134a/R142b, R152a/R142b, R290/R600a and R600a/R600. However, in most of the discussed in literature cases the temperature glide was too small for the practical implementation for district heating systems. This is motivation for the further investigations of the suitable mixtures for the ejector refrigeration systems.

#### 2. SELECTION OF WORKING FLUIDS

Regulation of the European Parliament and the EU Council No. 517/2014, enacted on April 16th, 2014 forbids the use of commercial and domestic air conditioning units with more than 3 kg of refrigerant with GWP higher than 150 in EU countries. Hydrocarbons meet the environmental criteria and have been widely used in refrigerators and AC units for years. Extreme flammability of hydrocarbons is not a concern in small devices that contain several dozen grams of refrigerant. However in the case of large systems, comprising significant quantities of working fluid, compliance with regulations and standards regarding operation in an explosive environment is required. Therefore, authors of this paper decided to only consider non-flammable or mildly flammable, low-toxicity fluids (ASHRAE A1 and A2L class) approved for use by the Regulation No. 517/2014.

### 2.1. Fluid requirements

Suitable refrigerant should fulfil the following demands:

- have low critical parameters to avoid high pressures in the system and maximise the temperature drop of the heating water in the vapour generator due to operation of the vapour generator in close proximity to the critical point and low specific enthalpy of evaporation;
- provide as high COP as possible;
- have a positive or infinite saturated vapour line slope (which is classified as dry and isentropic fluids) in order to avoid the additional losses in the ejector due to operation with wet vapour;
- be relatively inexpensive and easily available;
- have GWP lower than 150 in order to comply with restrictive EU regulations;
- be safe, i.e. non-flammable and non-toxic, i.e. fluids of ASHRAE A1 and A2L classes.

Meeting all of the above criteria drastically reduces the list of suitable working fluids. A lot of substances comply with some, or even most of the requirements, but do not provide a high enough drop in water temperature in the vapour generator in the range 20 - 30 K or yield COP too low to consider them as economically feasible ones. Single-component substances that may be thought as appropriate for the transcritical cycle with heat source temperature as low as  $60^{\circ}$ C that would meet all the criteria were not found. Therefore, the most rational solution to the described problem is using the zeotropic refrigerant mixture instead of a pure fluid to meet the above formulated criteria to thermally drive the ejector refrigeration system with district heating system. It should be also noted that Non-isothermal phase change is usually undesirable in the conventional compression systems, so commercially available zeotropic blends, e.g. R-410A have a low or even negligible temperature glide (several K). In the designed system the glide as high as 10 - 15 K is necessary; therefore a new mixture should be developed.

#### 2.2. Properties of selected refrigerants

Four different fluids were selected as mixture components: R-1234yf, R-1234ze(E), R-1234ze(Z) and Novec 649. Table 1 presents their properties. Many refrigerants were rejected during initial selection just because of their high environmental impact even if they were thermodynamically suitable, e.g. R-125.

Fluid name	R-1234yf	R-1234ze(E)	R-1234ze(Z)	Novec 649
Group	HFO	HFO	HFO	N/A
GWP	<1	<1	<1	1
ODP	0	0	0	0
Replacement for	R-134a	R-134a	R-134a	SF6 R-134a R-245fa
ASHRAE class	A2L	A2L	A2L	N/A
Critical temp.	94.7 °C	109.4 °C	150.1 °C	168.7 °C
Critical pressure	3.38 MPa	3.67 MPa	3.53 MPa	1,87 MPa

Table 1. Selected properties of analysed fluids

Four binary blends were selected for analysis, based on their thermodynamic properties and performance in the ejector cycle under considered operation conditions. These blends were listed in Table 2. The properties of the considered fluids and blends were obtained with use of REFPROP 9.1, Lemmon et al. (2013).

Blend	Novec 649 /R-1234ze(E)	Novec 649 /R-1234ze(Z)	Novec 649 /R-1234ze(Z)	Novec 649 /R-1234yf
Composition	0.1/0.9	0.5/0.5	0.1/0.9	0.9/0.1
Critical temp.	115.3	159.4	152	161.2
Critical pressure	3.42	2.41	3.22	1.99

Table 2. Analysed zeotropic blends

### **3.** CYCLE MODELLING

The most important parameters of the proposed cycle, i.e. evaporation, condensation, and motive vapour temperature of the ejector cycle are determined on the basis of the discussed application and temperature range of the heating water. In this case, motive vapour is generated by water circulating in the district heating system, condenser is air-cooled, and the evaporator outlet temperature is set to 0°C or 6°C so the system could be used for low- or high-temperature air conditioning systems. As this is a theoretical study, and geometry of the ejector was not taken into account, some simplifying assumptions were made in order to assess the possibility of the application of the considered zeotropic blends.



Fig. 1. Ejector refrigeration cycle with zeotropic refrigerant: a) schematic of the system;
b) the cycle in p-h coordinates; c) the cycle in T-s coordinates with zeotropic working fluid;
G - vapour generator; EV - evaporator; C - condenser; E - ejector; P- pump; V - expansion valve. IIR Compressors, Slovakia, 13–15 January 2021

Pressure-enthalpy diagram of the cycle is presented in Figure 1 b. The assumed operation parameters are listed below:

- heat source temperature: 65/80/95 °C;
- steam generator pinch point temperature: 5 °C;
- motive vapour temperature: 60/75/90 °C;
- motive vapour superheating: 10 K;
- condenser outlet temperature: 30 °C;
- condensate subcooling: 0 K;
- condenser inlet temperature: 35 °C;
- evaporator outlet temperature: 0/6 °C;
- vapour superheating in the evaporator: 0 K;
- thermal capacity of the vapour generator: 100 kW;
- isentropic expansion and compression in the ejector;
- the ejector overall efficiency: 0.7.

The motive flow inlet temperature  $t_1$  was set at 60, 75, and 90°C. Since 10 K superheating of the motive vapour was assumed, saturated vapour temperature in the vapour generator was assumed at the level of 50/65/80 °C. The following relationships to obtain the state parameters are applied:

$$t_1 = t_{wi} - t_{pp},\tag{1}$$

$$p_1 = f(t_{gs}, x = 1),$$
 (2)

$$s_1 = f(t_1, p_1),$$
 (3)

$$h_1 = f(t_1, p_1),$$
 (4)

$$s_1 = s_2 = s_4$$
, (5)

$$t_5 = 30^{\circ}C,$$
 (6)

$$p_5 = f(t_5, x = 0), \tag{7}$$

$$h_8 = h_5. \tag{8}$$

It was assumed that the increase in enthalpy and refrigerant temperature increase during liquid pumping is negligible, as in eq. (8). The entrainment ratio formula according to Butrymowicz et. al. (2015) may be calculated with use of the following formula:

$$U = k \left( \sqrt{\frac{h_1 - h_2}{h_4 - h_2}} - 1 \right).$$
(9)

Compression ratio is defined as follows:

$$\prod = \frac{p_c - p_e}{p_g - p_e}.$$
(10)

It was assumed that in case of zeotropic mixtures pressure  $p_g$  is equal to vapour saturation pressure in the vapour generator, pressure  $p_c$  is equal to pressure  $p_5$  in the point 5 of the cycle (see Fig. 1), and pressure  $p_g$  is equal to pressure  $p_7$  in the evaporator (see Fig. 1).

The coefficient of performance was calculated with the assumption that power consumption of the liquid pump was neglected:

$$COP = \frac{Uq_e}{q_g}.$$
(11)

Additionally, comparison of power consumption with the conventional vapour compression cycle was performed to evaluate whether the zeotropic mixtures ejector system could be more energy efficient than a conventional vapour compression refrigeration system. This comparison concerns mechanical power needed to drive the pump of the zeotropic ejector system and power of the compressor in a standard vapour compression cycle. The mechanical compressor motive power was calculated for the same operation conditions (condensation and evaporation temperatures) and cooling capacity as for the analysed EFC cycle:

$$P_{comp} = \frac{\dot{m}(h_{c,in} - h_{e,out})}{\eta_{comp}}.$$
(12)

The mechanical compressor isentropic efficiency was assumed as 0.8. The specific enthalpies at the compressor inlet and outlet was determined as  $h_{\text{comp,in}} = h_{\text{e,out}} = h_{\text{sat}}(p_{\text{e}})$  and  $h_{\text{comp,out}} = h_{\text{c,in}} = h(p_{\text{c}}, s_{\text{e,out}})$ , where  $s_{\text{e,out}} = s_{\text{sat}}(p_{\text{e}})$ ,  $p_{\text{e}}$  is evaporation pressure for 0 or 6°C, and  $p_{\text{c}}$  is condensation pressure for assumed condensation temperature 30°C, the same as in calculations for the EFC. Refrigerant mass flow rate  $\dot{m}$  in this equivalent vapour compression cycle was calculated by dividing the refrigeration capacity achieved by the EFC under given conditions by the difference of enthalpy at the outlet and inlet of evaporator in the vapour compression cycle:  $h_{\text{e,out}} - h_{\text{e,in}}$ , where  $h_{\text{e,in}} = h_{\text{c,out}} = h_{\text{sat}}(p_{\text{c}})$ . The relative difference in the liquid pump and the mechanical compressor power consumptions was calculated as follows:

$$\delta_P = \frac{P_{comp} - P_p}{P_{comp}} \times 100\%.$$
<sup>(13)</sup>

#### 4. **RESULTS**

The entrainment ratio (Fig. 2) in case of evaporation temperature 6 °C increases with increase of heat source temperature and varies from 0.08 up to 0.49. The entrainment ratio decreases with temperature glide and is lowest for the blend No. 4 which has the highest glide out of all of the analysed mixtures, see Fig. 4. The highest entrainment ratio U = 0.22 - 0.49 is predicted for the blend No. 3.

The results of the compression ratio calculations are presented in Fig. 2. It is seen that COP decreases with rise of the heat source temperature as heating fluid pressure increases while evaporation and condensation pressures are kept constant. The compression ratio is the highest (0.73 - 0.29) for the blend No. 4, and lowest (0.475 - 0.184) for the blend No. 3. It is also seen that the higher temperature glide is, the higher is the compression ratio.



Fig. 2. The relationship between the entrainment ratio and heating fluid inlet temperature for evaporation temperature 6°C for the zeotropic system



Fig. 3. The relationship between COP, electric power consumption savings and heating fluid inlet temperature for evaporation temperature 6°C for the zeotropic system

Concerning the system efficiency (see Fig. 3), it is seen that COP varies from 0.07 up to 0.18 for the motive heat source temperature 60 °C, the range of COP 0.16 - 0.29 was obtained for 75 °C, and the range 0.23 to 0.36 was obtained for 90 °C. It is seen that COP drops with increase of the temperature glide. The ejector system is the most efficient for the case of the blend No. 3. For the cases of the blends No. 2 and No. 4, the results are similar and the lowest out of the analysed mixtures.

The relative difference in the zeotropic cycle liquid pump and the equivalent compressor power consumptions (Fig. 4) varies from 81% up to 97%. This indicates that the ejector cycles working with the selected blends consume significantly less electrical power than the equivalent conventional refrigeration compression cycle to achieve the same refrigeration capacity. This difference reduces in the case of higher heat source temperatures, as pressure difference between the condenser and the vapour generator is larger, thus the liquid pump power consumption increases. The best blend in this aspect is the blend No. 2 which requires 94-97% less electric power for the system operation than the equivalent compressor. It is closely followed by the blend No. 3 with 93-96% electric power saving. The two other blends perform worse, but they still achieve high electric power savings, i.e. 81-87%. The drop in electric power savings increases with rise in heat source temperature.



Fig. 4. Drop in heating water temperature and temperature glide in the vapour generator for the analysed blends as a function of heating fluid inlet temperature



Fig. 5. The relationship between the entrainment ratio, compression ratio and heating fluid inlet temperature for evaporation temperature 0°C for the zeotropic system



Fig. 6. The relationship between COP, electric power consumption savings and heating fluid inlet temperature for evaporation temperature 0°C for the zeotropic cycle

Temperature drop of the heating fluid (here, water was assumed as the heating fluid) varied significantly, as temperature glides of the analysed blends strongly differ (see Fig. 4). The heating water temperature drop is the highest for the blend No. 4 with 22.8 – 26.3 °C, closely followed by the blend No. 2 with 21.7 – 25.9 °C. IIR Compressors, Slovakia, 13–15 January 2021

Such high values were achieved due to high temperature glide of those blends (9-11°C for the analysed vapour generation pressures), and they are considerably higher than for two other mixtures (temperature glide 2.6 - 5.1 °C). Drop in the heating water temperature and the temperature glide depend on the phase change pressure and properties of the mixture. Those parameters are independent of the evaporation pressure in the ejector cycle; therefore, they were not calculated separately for the discussed evaporation temperature 0 °C.

The relationships of the entrainment ratio and COP with heating fluid inlet temperature for  $t_{evap} = 0^{\circ}C$  (see Fig. 5 and 6) are similar to the case of the evaporation temperature 6°C. The entrainment ratio U varies from 0.07 to 0.41 and these results are 0.01 - 0.07 lower than for  $t_{evap} = 6^{\circ}C$ . The highest values are achieved for the blend No. 3, all of the other blends provide significantly lower entrainment ratio. Compression ratio, compared to  $t_{evap} = 6^{\circ}C$  is higher by 0.02 for 60°C heat source temperature and 0.03 – 0.13 for the motive temperature 90°C. The trends and the order of the selected mixtures in the chart remain unchanged. For the lower evaporation temperature, the COP (Fig. 6) is lower by 0.02 - 0.19, and the difference between 0 and 6°C evaporation temperature is more significant for higher heat source temperatures. The difference in the mechanical motive power saving (see Fig 6.) between the cases of the evaporation temperature 0 and 6°C is negligible. The drop in heating water temperature and the temperature glide are the same as for the case with the evaporation temperature 6°C, see Fig. 4.

# 4. CONCLUSIONS

Based on the presented results the following conclusions can be drawn:

- 1) Regulation of the European Parliament and the EU Council No. 517/2014 was the basis for the selection of working fluids for investigation.
- 2) The ejector refrigeration cycle with zeotropic working fluid applied achieves lower COP compared to the conventional ejector cycles but allows to achieve significantly larger drop in the heating water temperature and thus more efficient utilization of the heat source. Increase in the temperature glide of the analysed refrigerant blends increases the drop of the heating water temperature and decreases of COP, in addition it elevates the ejector pressure ratio due to rise of the condensation pressure.
- 3) The differences of liquid pump power consumption compared to the conventional compression cycle are significant and reach up to 96%. Therefore, application of the ejector refrigeration cycles with zeotropic mixtures as working fluids may be thought as the effective solution in applications where thermal energy is relatively inexpensive and cost of electric energy used to drive the liquid pump is more important (e.g. waste heat utilisation).

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# NOMENCLATURE

COP	coefficient of performance (-)	S	entropy (kJ/kg×K)
h	specific enthalpy (kJ/kg)	Π	compression ratio (-)
q	specific heat (kJ/kg)	t	temperature (Celsius)
D	pressure (MPa)	U	entrainment ratio (-)

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Subscripts:

1-8 c	characteristic points of the ejector cycle condenser	gs pp	vapour generator, saturation pinch point
сотр	compressor	p	pump
e	evaporator	wi	motive source water inlet
g	vapour generator		

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