Current research trends in the process of using zeotropic mixtures in energy installations; Lorenz's comparative cycle

Aktualne kierunki badań w procesie stosowania mieszanin zeotropowych w instalacjach energetycznych; Cykl porównawczy Lorenza

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This paper is devoted to modern research directions and the development of the use of zeotropic mixtures in compact heat exchangers presents selected problems regarding the use of zeotropic mixtures in the implementation of refrigeration cycles in heat pumps. The phenomenon of temperature glide occurring in phase transitions has a significant impact on the selection of an appropriate reference circuit. For homogeneous refrigerants and for azeotropic mixtures, the reference cycle is the Carnot cycle with constant source temperature levels. In the case of zeotropic mixtures, due to temperature glide, there is a system with variable values of the temperature of the heat sources, for which the Lorenz cycle is an appropriate pattern. The method of calculating the coefficient of performance of a heat pump operating according to such a cycle and the criteria for assessing the approximation of the real cycle to the model cycle is given.
Keywords: Temperature glide; Lorenz cycle; zeotropic mixtures; condensation; heat pumps; mixture composition

W artykule omówiono współczesne kierunki badań i rozwój zastosowań mieszanin zeotropowych w kompaktowych wymiennikach ciepła. Przedstawiono wybrane zagadnienia dotyczące zastosowania mieszanin zeotropowych w realizacji obiegów chłodniczych w pompach ciepła. Zjawisko poślizgu temperaturowego występujące w przejściach fazowych ma istotny wpływ na dobór odpowiedniego obiegu porównawczego. W przypadku jednorodnych czynników chłodniczych i mieszanin azeotropowych cyklem referencyjnym jest cykl Carnota ze stałym poziomem temperatury źródła. W przypadku mieszanin zeotropowych, ze względu na poślizg temperaturowy, istnieje układ o zmiennych wartościach temperatury źródeł ciepła, dla którego właściwym wzorcem jest cykl Lorenza. W artykule podano sposób obliczania współczynnika wydajności pompy ciepła pracującej według takiego cyklu oraz kryteria oceny przybliżenia cyklu rzeczywistego do cyklu wzorcowego.
Słowa kluczowe: Poślizg temperaturowy; cykl Lorenza; mieszaniny zeotropowe; kondensacja; pompy ciepła; skład mieszaniny

Introduction

Zeotropic mixtures, similarly to azeotropic ones, are mixtures with a certain percentage composition of several single-component refrigerants with significantly different volatility (the volatility of the refrigerant determines its ability to change from the liquid phase to the vapor phase when heated; it is the higher the lower its boiling point at a given pressure), changing their composition with changing boiling and condensing temperatures – at constant saturation pressure. The total change in saturation temperature with the phase change of these refrigerants at constant pressure is called temperature glide. This temperature glide occurring in these mixtures can be beneficial in some cases, and sometimes harmful in others. The change in the composition of the refrigerant during evaporation can be used, for example, for continuous control of a refrigeration device (which requires intervention in its construction). Currently, new zeotropic refrigerants are being composed by selecting appropriate mass fractions of components, so as to obtain the lowest GWP (Global Warming Potential) and ODP (Ozone Depletion Potential) coefficients with similar thermodynamic properties. Zeotropic mixtures can bring significant energy benefits with large temperature glides, even above 50K, when the fluids are cooled in the evaporator or heated in the condenser in counter-current. Such conditions occur, for example, in large heating heat pumps used to heat water in central heating systems and for hygienic and sanitary purposes, as well as in evaporators of the food, chemical, and petrochemical industries and in plants for liquefaction and separation of gas mixtures by distillation [57]. These benefits are unattainable in typical refrigeration devices, where the temperature differences in the heat exchangers do not exceed 10K. According to many authors, adopting the Carnot cycle as the basic comparative cycle and assessing and analyzing the implemented refrigeration cycles on this basis is not correct. The basic reference circulation should be one with component transformations as close as possible to the

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processes occurring in real refrigeration devices. For left-rotating (refrigeration) cycles using zeotropic refrigerants, the basic comparative cycle should be a reversible cycle with variable source temperature, i.e. the so-called Lorenz cycle. In such a case, the heat exchange processes in the lower and upper heat exchangers are non-isothermal (t ≠ const.), unlike the Carnot cycle, where they occur at a constant temperature of the lower and upper sources. In the Lorenc cycle, the temperature of the medium changes during evaporation and condensation, and the heat exchange process takes place during isobaric transformations (p = constant). The processes of compression and expansion of the medium occur isentropically (s = const.), similarly to the Carnot cycle. In recent years, working fluids in mixtures, including zeotropic mixtures, have become increasingly popular. This is due to the need to look for refrigerants that are more energy efficient and have less undesirable impact on the surrounding natural environment. It is expected that due to their use in place of previously used refrigerants, greenhouse gas emissions and the destruction of the ozone layer around the Earth will be reduced. Therefore, it is important to conduct research in the search for new mixtures of refrigerants, including zeotropic ones. It is equally important to conduct research on their thermodynamic properties, achieved energy indicators, and behavior in operating conditions. Below are some examples of commonly used zeotropic mixtures.

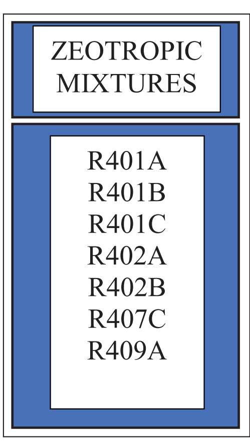


Fig. 1. Commonly used zeotropic mixtures with significant temperature glide [58,59]
Rys. 1. Powszechnie stosowane mieszaniny zeotropowe charakteryzujące się znacznym poślizgiem temperaturowym

These refrigerants have good thermodynamic properties i. e. relatively low pressure at given phase transition temperatures. Zinc, magnesium, lead, and aluminum alloys should not be used in the installations. Some of them show high reactivity towards alkaline earth metals, powdered metal salts of aluminum, zinc, and beryllium. They show high compatibility of materials and plastics. They are generally non-explosive substances and do not have a harmful effect on the human body. The undoubted advantage of zeotropic refrigerants obtained by mixing a certain number of homogeneous refrigerants with their specific percentage is the relatively low Global Warming Potential and Ozone Depletion Potential index, which proves the environmentally friendly nature. Zeotropic refrigerants are used in devices such as heat pumps, compressor refrigeration devices, absorption refrigeration devices and other refrigeration systems, mainly of low and medium power.

In the summary of Part 1 of this series [1], it was stated that the phenomenon of temperature glide that occurs during phase transitions (especially boiling and condensation) of zeotropic mixtures is generally regarded as undesirable. This was confirmed in paper [2], where it was stated directly that such mixtures are unsuitable for direct use in installations. However, this does not mean that it is impossible to use various methods to extend the introduction of zeotropic mixtures into the installation. This applies in particular to the implementation of thermodynamic cycles with zeotropic mixtures [3–5], including refrigeration cycles (refrigerating devices, heat pumps) and right-handed cycles (ORC cycles). The number of papers published so far in which analyzes of related problems are presented is very large. It is noteworthy, however, that in recent years there has been an increasing interest in topics treated as fully recognized. In this regard, publications presenting a new look at the implementation of the Lorenzo cycle [6] should be seen, the foundations of which have been known for many years, e.g. [7].

Limiting the issue to the counter-clockwise rotation of thermodynamic cycles, it should be stated that the assessment of its efficiency requires the adoption of a certain reference cycle against which the comparison is made. Such a reference cycle is a reversible cycle that meets the following basic criteria in light of the 2nd law of thermodynamics:

1. circuit is in thermal contact with at least two heat sources with different temperature levels,
2. all changes in the cycle are reversible,
3. heat exchange between the medium in the cycle and the heat sources is carried out at an infinitely small temperature difference (within dT = 0).

If the heat exchange takes place at a finite temperature difference (dT > 0), then it is treated as an irreversible transformation. In real processes, the transport of energy by heat is the most common cause of irreversibility. According to [8] circulation, in which all transfor-mations are reversible and the heat exchange at the sources is irreversible is called a pseu-do-reversible cycle (for example, a pseudo-reversible Carnot cycle can be such) it means that there is an external irreversibility.

As it was rightly stated in [9,10], the model (ideal) cycles have the disadvantage that they do not precisely take into account the changes taking place in real systems, usually irreversible. Therefore, a second type of circulation is introduced, the so-called comparative circuits, which are treated as a substitute circuit. In some cases (e.g. in the Linde cycle) irreversible transformations are introduced in the comparative circuits (isenthalpic throttling transformation) and then the equivalent comparative circuit becomes an irreversible one. There-fore, the effects obtained in real cycles refer to either model or comparative cycles. For steam, compressor cycles, in which the thermodynamic medium is a homogeneous, one-component refrigerant, there are no major problems, because the reversible, Carnot cycle is the reference cycle. If the refrigerant is a zeotropic mixture, then giving the correct answer is not the same.

The comparative analysis of the irreversible real cycle depends on the correct selection of the reference refrigeration circuit. In the practice of steam and compressor cycles, two basic variants of ideal comparative cycles are considered:

Variant 1 – in the comparative cycle there is a reversible heat exchange of the refrigerant with heat sources of infinitely high heat capacity, the temperature of which remains at a constant, unchanging level of each source;

variant 2 – heat exchange between the circulating medium and the sources is reversible, with the temperature levels of the sources being variable.

- If phase transformations of boiling and condensation of the refrigerant are carried out as isobaric-isothermal, then variant 1 of the analysis is selected. In particular, it applies to homogeneous refrigerants, for which phase transitions boil and condensation takes place at the saturation temperature, which depends on the satura-tion pressure.
- If phase transformations of boiling and condensation of the refrigerant are carried out isobarically, without maintaining isotherm, then it is recommended to use variant 2 of the analysis. The problem concerns, in particular, circulating media in the form of zeotropic binary [11–13] or

multi-component mixtures, when the phenomenon of "temperature glide" occurs in phase transformations.

In accordance with the previously set limitations, the possibilities of analyzing real cycles in relation to the cycles recognized as comparative have been discussed.

The boiling and condensation of zeotropic solutions does not take place at a constant temperature (for p=const), but in a certain temperature range resulting from the opening of the boiling and condensation curves. This temperature range is called temperature glide. The glide depends on both the type of solution components and the proportion of their mixing [14–16]. In the boiling process, both the temperature and the share of the liquid and vapor phases of the solution change. Experimental data [17,18] indicate that at the beginning of the evaporation process, the composition of the liquid phase has a certain value and the appearance of the first vapor bubbles changes the composition of the vapor phase with a given concentration. In this process, the temperature of the refrigerant increases. Chisholm and Sutherland [19] studied the influence of the nature of the refrigerant flow on concentration gradient. During laminar flow, a linear concentration gradient can develop from the interface to the vapor bulk. For turbulent flows, the vapor and liquid phases have a more uniform concentration as a result of turbulent mixing. For homogeneous refrigerants, the dependence of temperature on pressure is clearly defined [20–23], while in the case of zeotropic mixtures, it is also conditioned by the composition of the solution. The phenomenon of tem-perature glide plays an essential role in the boiling process in the flow of zeotropic solutions (e.g. in evaporator tubes), because in this process there is a temperature change resulting from the temperature glide ΔT_G as well as from the pressure drop in the flow $\Delta T(\Delta p)$. These values may vary. Few studies on zeotropic mixtures have been devoted to the problem of heat and mass transfer the condensation and boiling process [24–27]. Most of the studies on zeotropic mixtures condensation proved that there is a strong influence of concentration of the zeotropic mixture on the condensation process [18,25,28–31]. The refrigerants' heat transfer coefficient decreases when the concentration of one component rises. Moreover when it reaches a minimum value, reverses trend with was noted [32]. Authors found that heat transfer coefficient is strongly related to the heat flux density level. Study [33] indicated several differences between pure fluids and the zeotropic mixtures. The noted that the condensation process intensity is strongly affected at low values of heat flux density levels during the stratified flow of the refrigerant. It is also known that the effect of channels diameter affects the condensation proces [34].

Carnot reference cycle

According to [35], the analysis of the reference cycle in variant 1 concerns reversible Carnot cycle, assuming that the temperature of the heat sources and the refrigerant exchanging heat with them is constant, unchanging. The temperature of the upper source T_G is equal to the condensation temperature T_k in the isothermal-isobaric phase tran-sition. For the lower source, the determination of the lower source temperature T_d equal to the evaporation temperature To of the homogeneous refrigerant in the isothermal-isobaric phase transition of evaporation was introduced. Fig.2 shows two possibilities of implementing such a reference cycle.

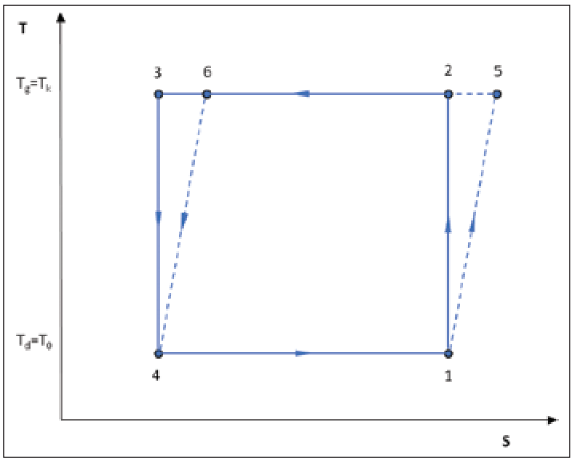


Fig. 2.
Reversible refrigeration reference cycles at constant unchanging temperature levels of heat sources; 1 – 2 – 3 – 4 – 1 Carnot cycle, 1 – 5 – 6 – 4 – 1 circulation with ideal regeneration
Rys. 2. Odwracalne obiegi referencyjne dla chłodzenia przy stałych, niezmiennych poziomach temperatur źródeł ciepła; 1 – 2 – 3 – 4 – 1 cykl Carnota, 1 – 5 – 6 – 4 – 1 obieg z idealną regeneracją

Fig. 2 shows the reversible, Carnot cycle: 1 – 2 – 3 – 4 – 1 and the reversible regenerative cycle: 1 – 5 – 6 – 4 – 1 in the T-s coordinate system. Both types of cycles are car-ried out at constant, unchanging levels temperature of the sources, i.e. upper $T_G = T_k$ = const and lower $T_d = T_o$ = const. In the regenerative circuit, the entropy increase Δs1-5 in the trans-formation 1 → 5 is numerically equal to the decrease in entropy in the transformation 6 → 4, i.e. Δs6-4, so the sum of the entropy increases in the regenerative cycle is zero, so this cycle is equivalent to the classical form of the Carnot cycle.

In a series of papers by the authors [36], an interesting energy and exergy analysis of the Carnot cycle was presented for the cases of its implementation in heat pumps. The analysis mainly includes external causes of irreversibility, with particular em-phasis on the impact of a finite temperature difference in heat exchange at the sources. There is no doubt that the condition of reversible heat transfer is met (dT→0) should be understood in practice as the use of heat exchangers with an infinitely large heat exchange surface. The coefficient of energy efficiency of a heat pump, called the coefficient of thermal efficiency of a pump ε_C (also marked with the symbol COP) operating according to the Carnot cycle, is described by the equation:

$$\varepsilon_{pc,C} = \frac{\dot{Q}_k}{\dot{W}_{ob}} = \frac{T_k}{T_k - T_o}, \qquad (1)$$

where:
Q'_k – heat stream discharged to the upper source (condenser thermal power),
$\dot{W}_{ob} = P_N$ – stream of energy supplied to the cycle (driving power).

From the analysis of the *Carnot* cycle, that the limitations imposed on the circulation are so severe that its practical implementation becomes impossible, but it remains as a model for homogeneous refrigerants.

There are many papers describing attempts to optimize the operation of domestic and indus-trial refrigeration systems and their components. Some of them are typically theoretical works, there are also works based on the results of experimental and computer research. Many model has been widely used for exploring refrigeration systems problems. One of them is the Lorenz cycle where the heat transfer process is isobaric, but no longer isother-mal (so-called "temperature glide"). In zeotropic mixtures, the phase transitions of evapora-tion and condensation are isobaric but not isothermal. Depending on the properties of the mixture, the transformation may take place in the range of several or more degrees, called: temperature glide.

For such cooling cycles, the primary comparative circuit should be a re-versible circuit with a variable source temperature, that is, for example, the Lorenz cycle. The assumptions for the consideration of the Carnot cycle show that the heat capacities of both heat sources are infinitely large, which makes it possible to assume a constant level of their temperature. In addition, there is no thermal resistance between the sources and the refrigerant in the cycle, which means heat exchange at an infinitely small temperature difference, i.e. reversible. The heat efficiency coefficient of the Carnot cycle, described for the heat pump by equation (1), does not depend on the type of refrigerant, but on the temperature value of both sources.

In a reversible cycle, all component transformations are reversible, i.e. in all states of the cycle, the conditions of thermodynamic equilibrium and the resulting thermal and mechani-cal equilibrium are maintained. Maintaining a constant temperature level of heat sources in real conditions is practically impossible, which, with limited thermal capacity, leads to a change in their temperature. To meet the condition of external reversibility of the circuit, the temperature of the refrigerant in thermal contact with the sources changes in the same way as the temperature of the sources. The temperature distribution profiles of the sources and the medium should therefore be parallel. Assuming the possibility of realizing the Carnot cycle in such cases would lead to external irreversibility.

In practice, the implementation of the real cycle, so in the reference cycle, the refrigerant absorbs heat from the lower source and gives the heat to the upper source. The process of heat exchange is mediated by cooling media acting de facto as sources. Air and water are the mediating media in most cases. Therefore, the intermediate medium flows through the heat source exchanger – the evaporator, in which it is cooled, and in the exchanger of the upper source – the condenser is heated.

We assume that the refrigerant in the cycle is an a [37–40] mixture characterized by the so-called "Temperature glide ΔT_G" (i.e. a change in temperature during phase change).

This means that the temperature of the mixture increases in the evaporator and decreases in the condenser. Due to the minimization of the heat exchange surface of the evaporator and condenser, a counter-current flow of heat exchange fluids is required in them (Fig. 3).

Fig. 3 confirms what has already been said, that the Carnot cycle should not be

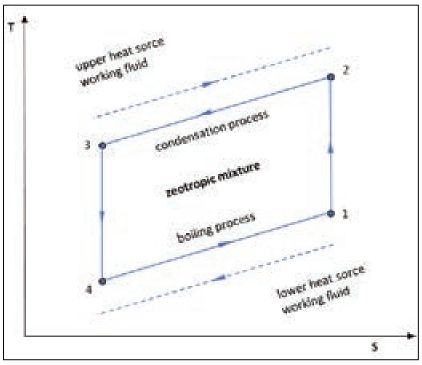
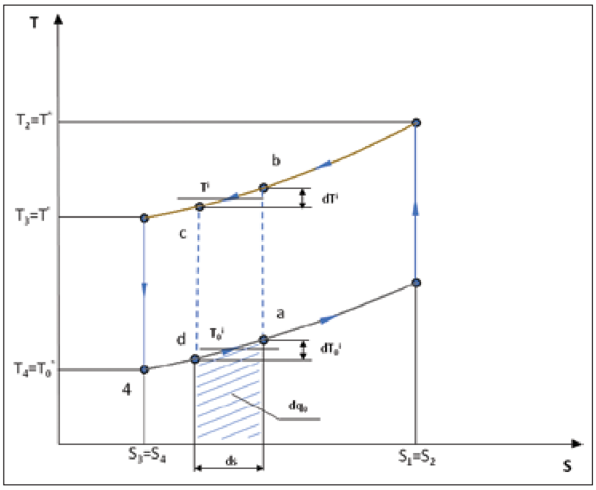


Fig. 3.
The idea of heat exchange in a refrigeration cycle with variable temperature of heat sources
Rys. 3. Koncepcja wymiany ciepła w obiegu chłodniczym przy zmiennej temperaturze źródeł ciepła

used when the temperature of the heat sources changes, so it is necessary to propose a different model adequate to the situation. It remains correct to assume that the new model cycle is to be reversible, and that the non-isothermal phase transitions of boiling in the evaporator and condensing in the condenser represented as reversible transformations. In the model of such a cycle, they were replaced by polytropic transformations, while the compression and expansion transformations were left as isentropic, as in the Carnot cycle. In this way, a model and comparative cycle of Lorenz was proposed, the basis of which was presented by the author [41] in 1894. Despite the passage of so many years, the foundations of the circuit con-struction have not been undermined, while in published works, even in recent years, e.g. [42–45], certain modifications have been introduced. The diagram of the Lorenz cycle is shown in the T – s coordinate system in Fig. 4.

Fig. 4.
Reversible Lorenz reference cycle as a comparison for a compressor heat pump
Rys. 4. Odwracalny obieg wzorcowy Lorenza jako porównanie dla sprężarkowej pompy ciepła



The classic form of the Lorenz cycle analysis in relation to the heat pump is presented below. A reminder of the simplifications used in the construction of the model cycle will highlight the directions and possibilities of its modernization.

The comparative Lorenz cycle presented in Fig. 3.3, in the T – s coordinate system, for the heat pump is carried out by 1 kg of refrigerant. Temperature differences in heat exchange processes at the sources are treated as infinitely small.

The cycle consists of two isentropic transformations (1 → 2 i 3 → 4) and two polytropic transformations (2 → 3 i 4 →1). Lorenz cycle 1 – 2 – 3 – 4 – 1 can be treated as a superposi-tion of infinitely many elementary Carnot cycles a – b – c – d – a, where the following desig-nations were introduced: Ti – mean temperature of the upper source, and T_o^i – average temperature of the lower source. Unit mass refrigeration capacity dqo and the thermal efficiency of the upper source dq of the elementary cycle was determined by the relationship:

$$dq_o = T_o^i \cdot ds, \tag{2}$$

$$dq = T^i \cdot ds., \tag{3}$$

The coefficient of heat efficiency of the elementary Carnot cycle has the form:

$$\varepsilon = \frac{dq}{dq - dq_o} = \frac{T^i \cdot ds}{T^i \cdot ds - T_o^i \cdot ds}, \tag{4}$$

$$\varepsilon = \frac{T^i}{T^i - T_o^i}. \tag{5}$$

For a finite cycle 1 – 2 – 3 – 4 – 1 the pump's coefficient of performance is:

$$\varepsilon = \frac{q}{q - q_o}, \tag{6}$$

where:

$$q = \int_3^2 dq = \bar{T} \cdot (s_2 - s_3), \tag{7}$$

$$q_o = \int_4^1 dq_o = \bar{T}_o \cdot (s_1 - s_4), \tag{8}$$

and hence:

$$\varepsilon = \frac{\int_3^2 dq}{\int_3^2 dq - \int_4^1 dq_o}, \qquad (9)$$

where and $\overline{T}_o$ i $\overline{T}$ denote average equivalent temperatures of the lower and upper sources, respectively. For an elementary Carnot cycle one can write; that:

$$\varepsilon = \frac{dq}{dq - dq_o} = \frac{T^i}{T^i - T_o^i}, \qquad (10)$$

as a result of:

$$\frac{dq}{T^i} = \frac{dq_o}{T_o^i}. \qquad (11)$$

Assuming that the heat dqo is supplied in the elementary cycle during the transformation d → a a from the heat exchange medium at the lower source (e.g. from water or air):

$$dq_o = m_o \cdot c_o \cdot dT_o^i, \qquad (12)$$

while the amount of dq discharged from this circuit to the heat exchange medium at the upper source (e.g. to the condenser cooling water):

$$dq = -m \cdot c \cdot dT^i, \qquad (13)$$

where: m_o, m – the amount of refrigerant at the downstream and upstream, respectively, c_o ,c – specific heat of intermediate media, dT^i_o and dT^i – elementary increases in the temperature of intermediary fluids. The specific heats co and c are assumed to be constant, independent of temperature.

Substituting dependencies (12) and (13) into (11) results:

$$-m \cdot c \cdot \frac{dT^i}{T^i} = m_o \cdot c_o \cdot \frac{dT_o^i}{T_o^i}, \qquad (14)$$

and after integration, the dependence:

$$-m \cdot c \cdot \int_{T_3}^{T_2} \frac{dT^i}{T^i} = m_o \cdot c_o \cdot \int_{T_4}^{T_1} \frac{dT_o^i}{T_o^i}, \qquad (15)$$

which for constant quantities of specific heat can be written in the form:

$$m \cdot c \cdot \ln\frac{T_2}{T_3} = m_o \cdot c_o \cdot \ln\frac{T_1}{T_4}, \qquad (16)$$

where: T_2 and T_3 – the initial and final temperature values of the mediating medium at the upper source, respectively, and T_1 and T_4 – the temperature values of the mediating medium at the lower source.

By introducing in Fig. 3 the following designations of the temperature in the circulation states: $T_1 = T_o'$, $T_4 = T_o''$, $T_3 = T'$, $T_2 = T''$ can be written for the entire Lorenz cycle, i.e.: *1 – 2 – 3 – 4 – 1*, dependencies determining the heat transferred (for example to water) to the upper source:

$$q = m \cdot c \cdot (T'' - T') \qquad (17)$$

and the heat removed from the water at the lower source:

$$q_o = m_o \cdot c_o \cdot (T_o' - T_o''). \qquad (18)$$

Taking into account that from equation (16) it can be determine:

$$\frac{m_o \cdot c_o}{m \cdot c} = \frac{\ln\frac{T_2}{T_3}}{\ln\frac{T_1}{T_4}} = \frac{\ln\frac{T''}{T'}}{\ln\frac{T_o'}{T_o''}}, \qquad (19)$$

and the relationship determining the coefficient of performance of the heat pump according to the Lorenz cycle should be given in the form:

$$\varepsilon = \frac{q}{q - q_o} = \frac{m \cdot c \cdot (T'' - T')}{m \cdot c \cdot (T'' - T') - m \cdot c_o \cdot (T_o' - T_o'')} = \frac{T'' - T'}{(T'' - T') - \frac{m_o \cdot c_o}{m \cdot c} \cdot (T_o' - T_o'')} = \frac{1}{1 - \frac{\ln\frac{T''}{T'}}{\ln\frac{T_o'}{T_o''}} \cdot \frac{T_o' - T_o''}{T'' - T'}}. \qquad (20)$$

If the temperature differences, i.e. and are small, then it can be assumed [46] that:

$$\ln\frac{T''}{T'} = 2 \cdot \frac{T'' - T'}{T'' + T'}, \qquad (21)$$

$$\ln\frac{T_o'}{T_o''} = 2 \cdot \frac{T_o' - T_o''}{T_o' + T_o''}. \qquad (22)$$

Considering (21) i (22) dependence (20) was obtained in the form:

$$\varepsilon = \frac{1}{1 - \frac{\frac{T'' - T'}{T'' + T'}}{\frac{T_o' - T_o''}{T_o' + T_o''}} \cdot \frac{T_o' - T_o''}{T'' - T'}}, \qquad (23)$$

and after transformations:

$$\varepsilon = \frac{1}{1 - \frac{T_o' + T_o''}{T'' + T'}}. \qquad (24)$$

If for the entire Lorenz cycle *1 – 2 – 3 – 4 – 1* the logarithmic mean temperatures of the lower and upper sources are defined in the form:

$$\overline{T}_o = \frac{\int_4^1 T_o^i ds}{s_1 - s_4} = \frac{T_o' - T_o''}{\ln\frac{T_o'}{T_o''}} \cong \frac{T_o' + T_o''}{2}, \qquad (25)$$

$$\overline{T} = \frac{\int_2^3 T^i ds}{s_2 - s_3} = \frac{T'' - T'}{\ln\frac{T''}{T'}} \cong \frac{T'' + T'}{2}, \qquad (26)$$

and hence the coefficient of performance of the heat pump operating according to the Lorenz cycle is:

$$\varepsilon = \frac{1}{1 - \frac{2 \cdot \overline{T}_o}{2 \cdot \overline{T}}} = \frac{1}{1 - \frac{\overline{T}_o}{\overline{T}}} = \frac{\overline{T}}{\overline{T} - \overline{T}_o}. \qquad (27)$$

If the refrigerator would operate according to the Lorenz cycle, then the coefficient of cooling capacity of the cycle ε_{ch} can be written (compared to formula (24) for the heat pump as:

$$\varepsilon_{ch} = \frac{1}{\frac{T'' + T'}{T_o' - T_o''} - 1}, \qquad (28)$$

and after entering the average logarithmic temperature differences according to (25) and (26), the relationship describing the Lorenz cycle cooling capacity coefficient takes the form:

$$\varepsilon_{ch} = \frac{\overline{T}_o}{\overline{T} - \overline{T}_o}. \qquad (29)$$

The relations defining the coefficient of performance of the heat pump ε according to (27) and the coefficient of cooling capacity for the Lorenz cycle are equal to those in the Carnot cycle i.e. $\varepsilon = \varepsilon_C$ and $\varepsilon_{ch} = \varepsilon_{ch,}$ if $T_o = \overline{T}_o$ and $T = \overline{T}$.

Current research trends in the application of the Lorenz cycle

In zeotropic mixtures, the phase transitions of evaporation and condensation are isobaric but not isothermal. Depending on the properties of the mixture, the transformation may take place in the range of several to a dozen or so degrees, called temperature glide. For dry cooling cycles, the basic comparative cycle should be a reversible cycle with variable source temperature, e.g. the Lorenz cycle. For example, the zeotropic refrigerant is R407C, whose temperature glide is 5K (average value over the entire range of applicability). It is a mixture of three homogeneous refrigerants with the following percentages: 23% R32, 25% R125 and 52% R134a. For example, at a condensation pressure of 2 MPa, the condensation temperatures of individual components are: R32 = 31.44 °C, R125 = 39.83 °C, R134a = 67.48 °C. Comparing the component data and the R407C refrigerant characteristics chart, it can be seen that the temperature glide value does not result directly from the difference in phase transformation temperatures of the least and most volatile component. The value of temperature "glide" depends primarily on: the saturation temperature of individual components of the mixture and the share of individual components in the entire mixture. The temperature glide value directly affects the change in temperature of the boiling and condensing process of the refrigerant. During the condensation process it gradually decreases, and during the boiling process it increases. This causes the grinding lines to deviate from the theoretical Carnot cycle and, as a result, reduce the coefficient of performance of this cycle. The studies published by many authors from various world centers are currently focused on problems related to the possibility of approximating the refrigeration thermo-dynamic cycles implemented in real systems to the model Lorenz cycle [1,34]. This cycle is important due to the prospects of significantly expanding the applicability of mixtures of azeotropic refrigerants. The proposals contained in these works are aimed at the application of methods leading to an increase in their energy efficiency. The considerations covered by this study are limited to the scope of heat pumps with azeotropic mixtures. Many interesting scientific threads related to the Lorezno cycle have been studied in scientific works. López et al. [47] presented the thermodynamic efficiency of the Lorenz system. Mittal et al. [48] ana-lysed the probability distribution for the number of cycles between successive regime transitions for the Lorenz model. A new approach to Lorenz cycle (stepped pressure cycle) was presented by Cao et al. [42]. 12.3% and 18.7% COP increase were achieved in the pilot system by applying dual and triple sub cycles, respectively. Kim et al. [49] provided a Numerical analysis of heat transfer characteristics of a novel heat exchanger for Lorenz-Meutzner cycle with zeotropic mixtures. The paper presents computational simulation includes a heat exchanger model developed for predicting the air outlet temperature accurately. The predict-ed results were validated against experimental gliding temperature with different mass fractions of few zeotropic mixture combinations. Based on the geometrical effect of heat exchangers on the LM cycle, a novel design of the heat exchanger was proposed. The design of the heat exchanger indicated the largest air temperature difference, leading to the highest coefficient of performance (system energy efficiency) of the LM cycle compared with the baseline cycle with R600a. Yoon et al. [50] investigated the influence of refrigerant charge, capillary tube length, compressor capacity, and mixture composition on the performance of the LM cycle.

The study [44] fits well into the trends mentioned above. It was found that the implementation of the Lorenz cycle in heat pumps with zeotropic mixtures allows to increase the thermal efficiency coefficient ε of the cycle even by 25 ÷ 30%. They also provide criteria for assessing whether and when such an increase can be achieved. For these reasons, a brief analysis of the authors' work is presented [44].

Figure 5 shows a comparison of the Carnot cycle (a): 1 – 2 – 3 – 4 – 1 and the Lorenz cycle (b):

1L – 2L – 3L – 4L – 1L in the T – s coordinate system. Heat source temperature levels are marked with the symbols: T – upper source temperature and To – lower source temperature. It should be noted that in the Lorenz cycle model, the isentropic compression of the refriger-ant from the same states in the transformation 1 → 2 was preserved.

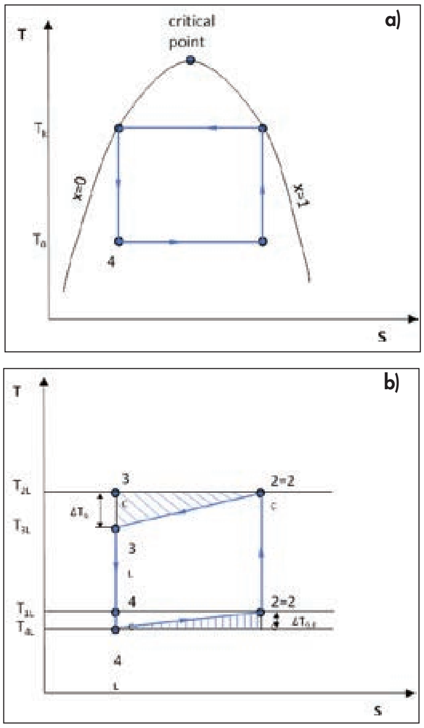


Fig. 5
Comparative interpretation of Carnot (a) and Lorenz cycles (b) in the T – s coordinate system according to the authors' model [44]
Rys. 5. Porównawcza interpretacja obiegów Carnota (a) i Lorenza (b) w układzie współrzędnych T – s według modelu autorskiego [44]

It was assumed that in the model Lorenz cycle, the temperature values of the zeotropic mixture in individual cycle states are known, i.e.: T1, T2, T3 and T4 and the values of the temperature glide at the heat sources, ΔT_G – at the upper source and ΔT_G,o – at the lower source respectively. According to dependencies (25) and (26) it is possible to calculate the logarithmic mean values of the temperature in the Lorenz cycle:

$$\bar{T}_o = \frac{T_1 + T_4}{2} \qquad (30)$$

and

$$\bar{T} = \frac{T_2 + T_3}{2}. \qquad (31)$$

Authors [44] found that taking into account the actual conditions of cycle implementation requires the introduction of the efficiency η_{wym} in accurate calculations. heat exchangers in both Carnot and Lorenz cycles. The value of this efficiency (including the impact of thermal, hydraulic, mechanical losses, etc.) is practically η_{wym} = 0.4 ÷ 0.5. For example, the improved coefficient of thermal performance of the Carnot cycle with the efficiency of the exchangers is:

$$\varepsilon_C = \eta_{wym.} \cdot \frac{T_k}{T_k - T_o}. \qquad (32)$$

In the further analysis of the authors, two quantities marked with symbols θ_0 and θ and defined by dependencies were introduced:

$$\Theta = 2 \cdot \frac{\bar{T}}{T_2} \text{ oraz } \Theta_o = 2 \cdot \frac{\bar{T}_o}{T_1}, \qquad (33)$$

which are supposed to reflect the deviation of the shape of the Lorenz cycle from Carnot.

After taking into account (30) and (31) it was obtained, that:

$$\Theta = \frac{T_2 + T_3}{T_2} \text{ and } \Theta_o = \frac{T_1 + T_4}{T_1}, \qquad (34)$$

and implementing (34) into (27):

$$\varepsilon_L = \frac{\bar{T}}{\bar{T} - \bar{T}_o} = \frac{T_2 + T_3}{(T_2 + T_3) - (T_1 + T_4)} = \frac{T_2}{T_2 - \frac{\Theta_o}{\Theta} \cdot T_1}. \qquad (35)$$

Formula (35) shows that the value of the thermal efficiency coefficient ε_L of a heat pump operating according to the Lorenz cycle is significantly influenced by the value (θ_0/θ). It is in turn related to the values of the temperature glide ΔT_G and ΔT_G,o. Fig. 4 shows the following relationships:

$$T_3 = T_2 - \Delta T_G \text{ and } T_4 = T_1 - \Delta T_{G,o}, \quad (36)$$

and hence:

$$\Theta = \frac{T_2 + T_3}{T_2} =$$

$$= \frac{T_2 + T_2 - \Delta T_G}{T_2} = 2 - \frac{\Delta T_G}{T_2}, \quad (37)$$

$$\Theta_o = \frac{T_1 + T_4}{T_1} =$$

$$= \frac{T_1 + T_1 - \Delta T_{G,o}}{T_1} = 2 - \frac{\Delta T_{GG,o}}{T_1}. \quad (38)$$

The Lorenz cycle is transformed into the Carnot cycle if $\theta_0 = \theta$ it results from the formula (38), while (according to [44]): the use of the Lorenz cycle causes an increase in the value of the coefficient of performance of the heat pump when the condition is met $\theta > \theta_0$. The formulated criterion is of significant importance in the analysis of the selection of the thermodynamic cycle of the heat pump. The authors [44] performed exemplary calculations in which, however, very high values of the temperature glide ΔT_G = 30 K and ΔT_G,o = 20K were assumed.

In practical applications, zeotropic mixtures with lower temperature glide values are used. The usefulness of the methodologies for smaller values was checked. Checking calculations were made for the following parameters of the Lorenz cycle (according to Fig. 4): T1 = 283 K (+10°C), T2 = 333 K (+60°C), T3 = 321 K (48°C), T4 = 275 K (+2°C) , Meaning:

ΔT_G = T2 – T3 = 12 K, ΔT_G,o = T1 – T4 = 8 K. Based on the presented methodology [44], a graph of the relationship $\varepsilon_L/\varepsilon_C$ = f(θ_0/θ) was shown on Fig. 6.

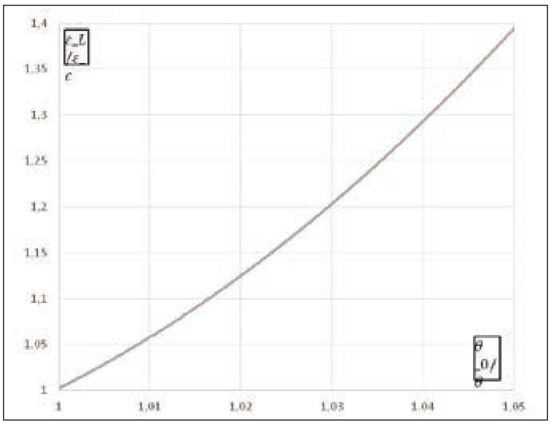
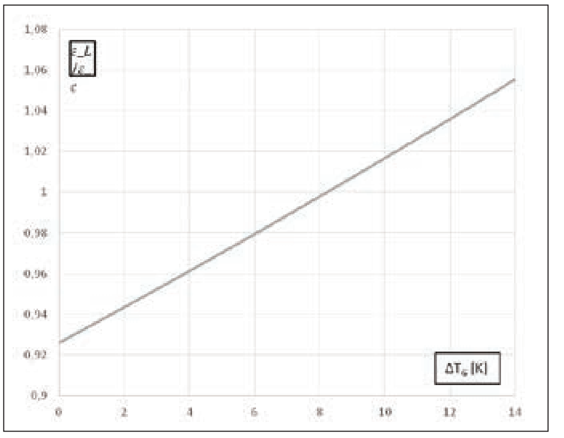


Fig. 6.
Graphical interpretation of the dependency $\varepsilon_L/\varepsilon_C$ = f(θ_0/θ)
Rys. 6. Graficzna interpretacja zależności $\varepsilon_L/\varepsilon_C$ = f(θ_0/θ)

Maintaining the above-mentioned temperature levels: T1, T2 and T4 (T3 temperature value depends on the ΔT_G glide value), calculations were made to determine the influence of the temperature glide at the upper heat source in the Lorenz cycle on the quotient ($\varepsilon_L/\varepsilon_C$) – Fig. 7.

Fig. 7.
Graphical interpretation of the relationship $\varepsilon_L/\varepsilon_C$ = f(ΔT_G), at $\Delta T_{G,o}$ = 8 K
Rys. 7. Graficzna interpretacja zależności $\varepsilon_L/\varepsilon_C$ = f(ΔT_G), at $\Delta T_{G,o}$ = 8 K



The problem of exergy and energy analysis has been discussed many times in relation to zeotropic mixtures in refrigeration cycles. Braimakis and Karellas [52] studied the exergy efficiency improvement potential of dual-phase expansion (trilateral and partial evaporation) Organic Rankine Cycles (ORC) with zeotropic mixtures of R1233zd(E), R1234ze(E) and R1234yf as well as isobutane and propan. Energy, exergy, exergoeconomic, economic, and environmental analyses and multiobjective optimization of a SCMR–ORC system with zeotropic mixtures was investigated by Bu et al. [53]. Sivakumar and Somasundaram [54] presented an exergy and energy analysis of three stage auto refrigerating cascade system using Zeotropic mixture for sustainable development. A detailed analysis of the energy and exergy of zeotropic refrigerants R-455A and R-463A as an alternative to R-744 in automotive air conditioning systems (AAC) was carried out by the author of the paper [55]. Author proposed the use of a blend of CO_2-based zeotropic refrigerants, R-455A (R-744/32/1234yf) and R-463A (R-744/32/125/1234yf/134a), to improve the thermodynamic performance of pure refrigerants CO_2. Author assessed the influence of cooler/condenser pressure, average evaporator temperature, cooler/condenser outlet temperature and refrigerant flow rate on COP and exergy efficiency of cycles. The results showed that under the same operating condition parameters, the cycle COP was improved by 57.6 and 76.5% when using R455A and R463A instead of R744, respectively. The maximum COPs for R744, R455A, and R463A based on optimal cooler/condenser pressure were 3.1, 4.25, and 5.4, respectively. He recommended using a blend of R455A as a refrigerant in modern AAC systems. Savitha et al. [56] prepared a state of the art on the thermodynamic and flammability properties of the low Global Warming Potential refrigerants. Authors also explored scientifically the significant decrease in energy efficiency.

Summary

On the basis of the summary presented above, concerning the directions of searching for effective methods of increasing the efficiency of heat pumps, two model ideal cycles were indicated, i.e. the Carnot and Lorenz cycles. Any attempt to approximate the real cycle implemented in the heat pump to the Carnot cycle – in the case of homogeneous refrigerants or the Lorenz cycle – for systems with variable temperature of heat sources should be considered as indicated. Of course, obtaining maximum effects should be controlled by technical and economic methods [43,45].

At the end of the considerations contained in Part 2, certain aspects should be pointed out that are indirectly, sometimes directly related to the pursuit of the Lorenz cycle.

In compressor cooling devices as well as heat pumps, an increase in efficiency can be achieved by limiting irreversible exergy losses. The sources of these losses in a compressor device are, among others, processes of throttling, compression, and, above all, exergy losses during irreversible heat exchange processes. According to [5] exergy losses in compression and throttling processes may be higher than 30%, and in heat exchangers over 50%. This applies to both homogeneous refrigerants and zeotropic mixtures.

One of the methods limiting exergy losses, and at the same time indirectly approaching the Lorenz cycle, is the stepped pressure cycle method. In the case of heat pumps, for example, sub-division of the circuit can be used [51]. When implementing this method, the ascents can be made in several heat pumps interconnected in the evaporator-condensers of each cascade. The idea of such a cascade connection is shown in Fig. 9.

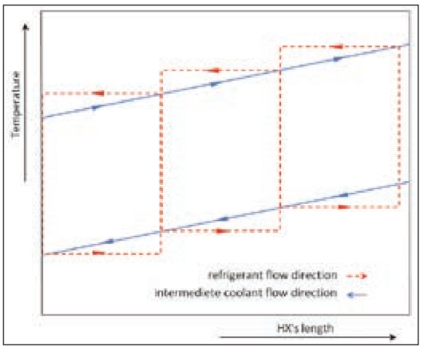


Fig. 9.
The idea of a cascade connection of three heat pumps implementing the Lorenz cycle [44]
Rys. 9. Koncepcja kaskadowego połączenia trzech pomp ciepła realizujących obieg Lorenza [44]

The idea of gradating the pressure in the circuit can be used in systems with variable temperature of heat sources. The efficiency of the system operation can be increased if conditions are created that allow for proper adjustment of the temperature distribution profiles of the refrigerant, e.g. zeotropic mixture, and mediators in heat exchange at the sources. If such adjustment is not possible over the entire heat transfer surface, then perhaps the exchanger should be divided into sections – e.g. into 3 sections, as shown in Fig. 10.

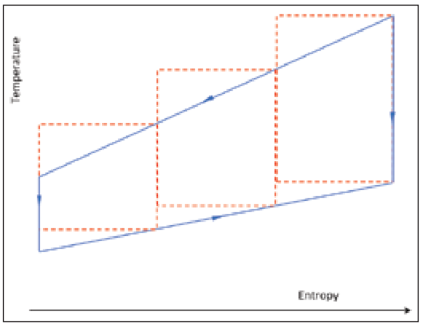


Fig. 10.
The idea of matching the temperature distribution profiles of the refrigerant and the intermediary in a 3-stage heat exchanger system according to [41]
Rys. 10. Koncepcja dopasowania profili rozkładu temperatury czynnika chłodniczego i pośrednika w 3-stopniowym układzie wymiennika ciepła według [41]

Problems related to the matching of temperature profiles, especially in condensers with zeotropic mixtures, will be analyzed in the next parts of the cycle.

Conclusions

1. The need to protect the natural human environment forces the search for new environmentally friendly refrigerants with low values of environmental indicators GP and ODP.

2. Very often, these criteria are met by zeotropic mixtures of refrigerants, which are characterized by the so-called temperature glide, which means that boiling and condensation phase transitions do not occur at constant temperatures. The composition of the zeotropic mixture affects the non-isothermal nature of phase transformations and thus changes the efficiency of the entire cycle due to the discrepancies in relation to the ideal Carnot cycle.

3. This often causes changes in the drive energy consumption by the left-hand drive system and can be a criterion for selecting the mixture composition in terms of the minimum drive energy consumption by the cooling system.

4. In the case of non-isothermal phase transformations, the Carnot cycle (and its modification – the Linde cycle) cannot be treated as model cycles for processes taking place in refrigeration devices and heat pumps.

5. The study shows that in cases with variable temperatures of heat sources, the effective comparative model is the Lorenz cycle.

6. Analyzing the current state of knowledge, criteria for assessing the degree of approximation of the real cycle to the Lorenz cycle were indicated.

7. Attention was drawn to the dynamic progress in the number of publications concerning mixtures of zeotropic refrigerants.

Nomenclature

c	specific heat [J/kg·K]
d	diameter [mm]
w	wall
G	mass flux density [kg/(m^2·s)]

Acronyms

L	length [m]
ṁ	mass flow rate [kg/h]
HX	heat exchanger
HT	heat transfer
q	heat flux density [W/m^2]
Q̇	heat flux [W]
LM	Lorenz – Meutzner cycle
v	velocity [m/s]
x	vapor quality [-]

Index

c	Carnot
ch	cooling
exp	experimental
f	fluid
G	glide
h	hydraulic
i	internal
L	Lorenz
k	critical
ob	refrigeration cycle
0	lower heat source

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