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Review

Current Research Trends in the Process of Condensation of Cooling Zeotropic Mixtures in Compact Condensers

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Abstract: This paper is an introduction to the cycle proposed by the authors related to research directions concerning the problems of condensation of zeotropic refrigerant mixtures. For over a hundred years, research has been conducted on the search for new working fluids in the cycles for cooling devices and heat pumps. Initially, the natural refrigerants used were replaced with homogeneous synthetic refrigerants, followed by mixtures of two or more refrigerants. Among the mixtures, there are azeotropic and zeotropic mixtures. In the case of an azeotrope mixture, a liquid solution of two or more chemical compounds is in thermodynamic equilibrium with the saturated vapor resulting from this mixture. The chemical composition of the liquid and vapor is identical. A zeotropic mixture is a liquid-vapor system in which the composition of a liquid mixture (solution) of two or more chemical compounds is always different from that of the saturated vapor generated from this liquid. This is due to the different boiling and condensation temperatures of the individual components of the mixture at the same pressure. There is a so-called temperature glide. The phase transformations of individual components do not run simultaneously, which means that the boiling or condensation phase transition temperature changes during the process being carried out. This raises a number of computational, design, and operational problems for power equipment. Today, however, zeotropic mixtures find an alternative to refrigerants with a high GWP potential. Despite the disadvantage of temperature glide, they also have advantages. These include ecological, energy, and economic indicators. As a result, they are increasingly used in the energy economy. This prompts researchers to conduct further research in the field of a detailed description of the phenomenon of boiling and condensation phase transformations of zeotropic mixtures under temperature glide, searching for new computational relationships, new design solutions, and applications. It is still an insufficiently recognized research problem. Bearing the above in mind, the authors made an attempt to review the state of knowledge in this area. Particular attention was paid to the progress in modeling the condensation phenomenon of zeotropic mixtures for application in compact heat exchangers. Miniaturization of cooling devices creates great application possibilities in this area.

Keywords: temperature glide; zeotropic mixtures; condensation; heat exchangers

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1. Introduction

Starting from the second half of the twentieth century and in the present twenty-first century, a dynamic increase in energy consumption, especially from non-renewable sources, has been observed. The consequences of obtaining energy according to the principles of conventional energy, i.e., by burning fuels, are becoming a very dangerous environmental problem. The products of the combustion process have a negative, destructive effect on the environment and effectively increase the global greenhouse effect. In addition, they directly or indirectly contribute to the degradation of the protective, stratospheric ozone layer. As a result of the dynamic reaction of international bodies, a long-term, wave-like elimination of the causes that influenced the creation of destructive effects began. The international struggle continues to this day, generating new, significant problems at the same time.

From today's perspective, it is undisputed that, to a large extent, the responsibility for causing destructive effects is generally borne by the so-called energetic media, including refrigerants. However, there is no sufficiently proven thesis. On the other hand, it is undeniable that the greatest restrictions primarily affected refrigerants. It happened, in fact, directly after the publication of two very important studies, i.e., an article Moliny et al. [1] in 1974 and the report from the Earth Summit in Rio de Janeiro in 1992 [2]. First, there have been international pressures towards the complete elimination of certain refrigerants or the maximum reduction in their use. There would be much fewer problems later if such interactions were carried out comprehensively, in one step. Their common feature is the double-track and two-stage elimination.

In the first stage, under the provisions of the Montreal Protocol of 1987 [3] and other, further international agreements, it was decided to eliminate halogen derivatives of the CFC and HCFC groups, i.e., those that contained chlorine in their chemical composition, directly involved in chain reactions of ozone depletion (O_3) in the stratospheric layer. Provisions on the elimination of ozone-depleting substances have been implemented into national legislation. Many years of procedures have led to a situation where the refrigerant for which the Ozone Depletion Potential (ODP) value is greater than zero cannot be used at present. In the meantime, however, some so-called at that time, pro-ecological substitutes were used for the phased-out freons, including the refrigerant from the HFC group (hydrofluorocarbons), which was R134a. As a replacement for R12 freon, it was effectively used in small and medium-sized cooling devices, practically until 2012.

With some delay, the second phase began, which involved phasing out those refrigerants that were contributing to the greenhouse effect. The value of the Global Warming Potential (GWP) index, which should be close to zero, was adopted as the basic measure of the destructive impact in this respect. For the refrigerant R134a mentioned above, the destructive factors are: ODP = 0, GWP = 1430 [4]. The inconsistencies in the double-path elimination of some refrigerants consisted of the fact that the refrigerant, approved for wide applications, with the value of the ODP index, was withdrawn in the following years due to the fact that the GWP value was exceeded. Applicable provisions in relation to the so-called fluorinated gases [5,6]—with a high GWP value—allow predicting the cut-off time of their withdrawal.

This has already brought some additional chaos again in the design phase of cooling machines and devices. It should be emphasized here that this problem does not only concern refrigeration devices, but also other devices in which the refrigerants are the so-called working media mentioned. Among these types of devices are air-conditioning devices, heat pumps, ORC (Organic Rankine Cycle) systems, heat recovery systems, and other devices used, for example, in distributed energy, including those cooperating with renewable energy sources.

As can be seen from the above, the problem of the correct choice of a refrigerant in the above-mentioned energy systems becomes very serious. The selection of the working medium currently requires a systemic approach, especially in terms of striving for increased energy efficiency requirements [7]. Obtaining high efficiency of energy conversion in the above-mentioned devices makes it necessary to use optimization methods in the design and operation of their individual elements.

For many years, research has been carried out in many global and national centers on the selection of appropriate refrigerants that would meet the ecological and technical requirements in refrigeration systems, heat pumps, ORC systems, etc.

In the meantime, criteria preferences are used in the selection of working refrigerants. If in the "freon era", the basic criterion was the appropriate thermodynamic properties of the medium (on which the efficiency of the cycles depends), currently the first is the ecological criterion, and then the following criteria: work safety, flammability and explosion-resistance, thermodynamics and others [8,9]. It can be concluded that so far there is no clear answer to the question of which of the refrigerants will be recommended in the coming years and in the longer term. This answer is particularly difficult in relation to the use of homogeneous, single-component refrigerants (pure refrigerant). The limits of the current choice of homogeneous refrigerants are actually in the area of natural refrigerants (i.e., NH_3, CO_2, propane, butane, etc.), while among synthetic refrigerants are HFO refrigerants (including R1234yf—for refrigeration devices and R1234ze (Z)—for heat pumps), for which the GWP index = 0–4. The limitations regarding the selection of single-component refrigerantss have been and are a sufficient reason for a detailed analysis presented in many publications [10,11]. They highlight the use of mixtures (solutions) of two-component and multi-component refrigerants. The behavior of such mixtures, especially during phase transitions (including boiling and condensation), is significantly different from homogeneous refrigerants. The method was developed on the basis of a heat transfer model by Cavallini et al. [12] for pure liquids by including additional heat transfer resistances during the condensation of zeotropic mixtures. The heat transfer resistances were modified from the Bell and Ghaly [13] method by taking into account the effect of interfacial roughness and nonequilibrium phenomena, following the approach by Del Col et al. [14]. The model requires low computational effort. The predicted results by the model showed a good agreement with experimental results covering various mixtures and a wide range of working conditions.

A wide range of problems with mixtures of refrigerants also extend to the phase transitions of boiling and condensation in the flow. Limiting ourselves to selected issues within the transformation of condensation, it should be emphasized that the authors of the works [15–17] published recently highlighted the very important problems of condensation of refrigerant mixtures, especially zeotropic mixtures. The rightness of addressing this subject was confirmed by the dynamic increase in the publications of various authors [18,19]. Therefore, it is necessary to present the global trends in scientific research conducted in global centers. There are new directions of research. Deng et al. [20] developed a simplified model for condensation heat transfer of zeotropic mixtures inside horizontal tubes. Wang et al. [21] investigated condensation heat and mass transfer characteristics of low GWP zeotropic refrigerant mixture R1234yf/R32 inside a horizontal smooth tube. A non-equilibrium film heat and mass transfer model was also developed. The authors obtained a strong agreement with the experimental data. Condensation heat transfer and pressure drop characteristics of zeotropic mixtures of R134a/R245fa in plate heat exchangers was analyzed by Zhang et al. [22]. Authors considered mass transfer resistance on the vapour and the liquid side. Effects of mass flow, vapour quality, thermophysical properties and mass fraction on the heat transfer coefficients were analyzed. The experimental data indicated that condensation of the mixtures is a shear-controlled governed process, similar to pure fluids. Heat transfer degradation of the mixture increased with decreasing condensation temperature and mass flux. Authors obtained a good prediction for the heat transfer results MAD 12.2%. Azzolin at al. [23] investigated condensation of ternary low GWP zeotropic mixtures inside channels. The effects of tube diameter, mass velocity, vapor quality and saturation-to-wall temperature difference were taken into account. A good compliance was obtained for the Friedel [24] and Cavallini et al. [25] models. Due to the fact that the condensation process of zeotropic mixtures is not isothermal, and the continuous changes in the composition of the liquid and vapor phases led to increased pressure drops, the models developed for pure fluids were modified. The solution of Silver [26] and Bell and Ghaly [13] were used. Garimella et al. [27] conducted an experimental investigation of the condensation heat transfer and frictional pressure drop of a zeotropic mixture of R245fa and n-pentane in smooth horizontal tubes. It was found that the heat transfer coefficient increased with increasing mass flux, vapour quality, and decreasing saturation temperature. The pressure gradient increased along with increasing mass flux, vapour quality, and decreasing saturation temperature. Bell and Ghaly [13] and Price and Bell [28]'s methods underestimated the decrease in the heat transfer coefficients. Here the Milkie et al. [27] correlation was used for the underlying pure fluid model. Authors obtained a 35% MAD with Thome [29] correlation using the Price and Bell approach. It was found that the Lewis approach outlined by Webb [30] was not applicable in the above conditions. Song et al. [31] experimentally investigated condensation two-phase flow patterns for zeotropic mixtures of tetrafluoromethane/ethane in a horizontal smooth tube. Experimental and analytical investigation on flow condensation heat transfer of zeotropic mixtures of tetrafluoromethane/ethane was studied by Song et al. [32]. Authors analyzed and discussed the effects of concentration, mass flux, saturation pressure and vapor quality. Sixteen well known models were combined with the enhancement factor proposed by authors and compared with the heat transfer data of R14/R170 mixtures. Predictive abilities most of correlations were improved. The smallest MARD was found for Akers and Rosson correlation [33] (14%), than Shah et al. [34] (20%), Cavallini and Zecchin [35] (21%), Dorao and Fernandino [36] and Huang et al. [37] (24%). A new prediction model with the MARD of 13.91% was developed and presented by authors. Song et al. [38] experimentally and analytically investigated flow condensation pressure drop characteristics of zeotropic mixtures of tetrafluoromethane/ethane. The effects of concentration, mass flux, saturation pressure, heat flux and vapor quality were analyzed and discussed. Authors developed flow pattern-based pressure drop correlation with a MARD of 8.63% for own experimental data and 14.20% for the data presented in [27,39–43]. Best agreement was found for the Kim and Mudawar model [43]. Xu et al. [44] studied heat transfer performance of a pulsating heat pipe with zeotropic immiscible binary mixtures. A zeotropic immiscible working fluid was proposed in this study, taking into account its difficult start and easy dry-out with large heat flux. Authors used a mixture of HFE-7100 and deionized water as a working fluid. The ratio was 50:50. It was found that along with the increase in the proportion of the HFE-7100, the complete distribution of long vapour plugs in the channel gradually decreased, the oscillation frequency of the working fluid increased, and the plug flow achieved a stable one-way pulsation cycle. Authors also analyzed the inclination angle on the heat transfer characteristics. Gravity had an important effect on pulsating heat pipe operation under low heating power. Liquid mass transfer characteristics of zeotropic mixtures of R134a and R245fa during flow boiling in a rectangular channel was investigated by Qi et al. [45]. Flow boiling composition variations and heat transfer characteristics of R134a/R245fa zeotropic mixtures were analyzed. Authors conducted this research in rectangular channels. They developed a correlation for prediction of R134a mass fraction differences in the liquid during stratified bubbly flow of these zeotropic mixtures. The MAE was 11.1%. Mazumder et al. [46] studied the in-tube condensation heat transfer of zeotropic R32/R1234ze(E) mixture refrigerants. The study aimed at the search for replacement of R410A refrigerant. A low-GWP zeotropic mixture of R32 and R1234ze (E) was proposed. It was found that the heat transfer coefficients of pure refrigerants were higher than that of the R32/R1234ze(E) zeotropic mixture for a given set of operating conditions. The difference was less significant when the condensation process was near x = 1. The authors proposed a prediction model that was verified experimentally with the data presented in the literature. The highest agreement was found with the data from Macdonald [47] 10.4%, Zhang [19,48] 13.2%, Wang [49,50] 16% and Jin [51]. Cavallini et al. [52] studied the behavior of water/zeotropic mixture in a tube condenser. Authors tested a high temperature glide R-125/236ea mixture. The experimental results were compared with the method of Colburn and Drew [53] with good agreement. Zhang et al. [54] investigated condensation heat transfer characteristics of zeotropic refrigerant mixture R407C on single, three-row petal-shaped finned tubes and helically baffled condenser. It was found that the condensation heat transfer coefficient of R407C on the petal-shaped finned tube increased with increasing wall subcooling. Authors presented a correlation for the determination of the condensation HTCs of a helically baffled condenser. Venkatarathnam [55] studied the influence of mixture composition on the formation of pinch points in condensers and evaporators for zeotropic refrigerant mixtures. It was found that multi-component fluids are preferred than wide boiling binary fluids, taking into account the point of view of glide matching and pinch points. In papers [56,57], the authors presented the reasons for drop in shell-and-tube condenser performance when replacing R22 with zeotropic mixtures. It was stated that the mixing level in the condensate layer is a factor influential enough to explain the decrease in condenser performance when replacing R22 with R407C, also the mass transfer resistance in the liquid phase may be the reason for the drop in condenser performance. Zhang et al. [58] suggested the use of R441A refrigerant, which is a wet zeotropic mixture, as a suitable working fluid in subcritical ORC using a single screw expander without considering the isentropic efficiency of the expander. Numerous experimental studies have been carried out on the use of zeotropic mixtures in organic Rankine cycles. Experimental investigation of the effect of a recuperative heat exchanger and throttles opening on a CO_2/isobutane autocascade was conducted by Sobieraj [59]. Weith et al. [60] analyzed two different modes of operation: pure electric power and CHP generation. The siloxanes hexamethyldisiloxane (MM) and octamethyltrisiloxane (MDM) were chosen as working fluids. The authors used mixtures of these components. A thermodynamic analysis was conducted and the Kandlikar model was used to describe the experimental data. Results showed an increase in heat transfer areas of 0.9% and 14%, respectively, compared to MM. The author proved the possibility of utilizing a natural refrigerant carbon dioxide along with isobutane as a working binary pair for further development of environmental-friendly refrigeration systems. Heberle and Brüggemann [61] presented a thermo-economic analysis of zeotropic mixtures and pure working fluids in ORC for waste heat recovery. Cost-efficient design parameters for the temperature difference at the pinch point were identified for pure working fluids and mixtures. Low minimum temperature differences in the evaporator and high values in the condenser were suitable for a cost-efficient organic Rankine cycle system. The economic parameters showed a high sensitivity regarding the isentropic efficiency of the turbine. Collings and Yu [62] investigated the application of the ORC cycle to small scale units based on positive-displacement expanders with fixed expansion ratios. The dynamic cycle showed an increase in specific power and better heat source utilization by increasing expander inlet superheat as the working fluid composition, allowing for the same electricity level to be generated from a smaller flow rate of thermal fluid. Tian et al. [63] compared energy, exergy, and economic (3E) parameters of an organic Rankine cycle using zeotropic mixtures based on marine engine waste heat and LNG cold energy. The effects of mass fraction and the difference in temperature of pinch point (PPTD) on output work, energy efficiency, exergy efficiency, and levelized energy cost (LEC), payback period (PBP), and total cost were investigated. The maximum energy and exergy efficiencies are 22.09% and 23.28%, respectively. It was found that the beneficial effects of zeotropic mixture to the PTORC net power output was limited. Llopis et al. [64] provided evaluation of zeotropic refrigerants in a dedicate d mechanical subcooling system in a CO_2 cycle. Authors proved that the use of zeotropic blends in the subcooler allows to reduce the irreversibilities in this heat exchanger. Sohrabi et al. [65] presented a thermodynamic optimization and comparative economic analysis of four organic Rankine cycle configurations with a zeotropic mixture. Presented data showed that the use of a Pentane and Hexane led to a increase in the power and energy and exergy efficiencies. The dual-pressure ORC with a recuperator has the highest generated power among all cycles, which was 16.2% more than the generated power in the simple Organic Rankine Cycle in its optimum mole fraction. As expected, the RD-ORC also has the highest value of the energy and exergy efficiencies, equal to 16.9 and 34.4%, respectively. Zhi et al. [66] conducted analysis and optimization for waste heat recovery with an improved transcritical-subcritical parallel organic Rankine cycle based on zeotropic mixtures. The system proposed by the Authors has better performance than other organic Rankine cycle systems, and based on zeotropic mixture R600a and R601a (0.5/0.5) shows a higher net power that achieves an improvement of 8.04% than the original system.

Among the large number of issues that are the basis of the large-scale analyzes of the condensation transformation of refrigerant mixtures currently carried out, the following can be mentioned:

- the mechanism of generating the phenomenon of temperature glide,

- evaluation of the selection of mixtures of refrigerants, in relation to the operation of the condenser and evaporator as well as other elements of the system,
- application of ORCs into small-scale systems,
- the problem of non-linear dependence of mixture properties on the temperature in the condensation and boiling process,
- the use of optimization methods based on the "pinch point" method in relation to the assessment of the efficiency of the condensation process in the condenser based on matching the temperature distribution profiles of the factors that perform heat exchange (glide matching),
- modeling of heat transfer processes and flow resistance during condensation of zeotropic mixtures in conventional channels and mini channels; progress in the development of heat and mass transport modeling during condensation, mixing of refrigerants,
- influence of the temperature glide on the selection of the comparative cycle realized in compressor cooling systems and heat pumps,
- operational aspects of refrigeration equipment working with mixtures of refrigerants.

The range of problems presented above does not exhaust their number in the research field but is intended to indicate that these issues are interesting and practical. In this paper, as one of the proposed from the series of studies on selected problems of condensation of cooling zeotropic mixtures, attention was paid to the following issues: the mechanism and interpretation of the temperature glide of mixtures, the possibility of using the Carnot cycle in relation to this type of mixtures, and the influence of some parameters on the efficiency of the Lorenz reference cycle in relation to the compressor cycle heat pump. Other selected topics will be presented in the following sections.

2. Characteristics of the Condensation Process of the Mixed Zeotropic Refrigerants

In the area of designing heat exchangers, which are components of steam, compression refrigeration devices, efforts are made to minimize the heat exchange surface and flow resistance in evaporators and condensers. One of the methods allowing for obtainment of optimal solutions is the rational use of phase changes of refrigerants (especially evaporation and boiling), during which relatively high (compared to single-phase changes) values of the heat transfer coefficient are obtained. During phase transitions of refrigerants, a new phase is formed at the interface (e.g., a transition from vapor to liquid phase occurs during condensation). For both boiling and condensation, the conversion of one phase into another requires that the basic criteria for this type of transition are met. For the mentioned phase transitions, the first criterion is the existence of a temperature gradient on the surface (heated during boiling, or cooled in the case of condensation), and the second criterion is the presence of the seeds of the new phase [67]. The given conditions for the initiation and development of phase transformations apply to both single-component, homogeneous refrigerants, and their mixtures. In paper [9] it was indicated that solutions (usually defined—despite formal differences—with mixtures) that do not comply with Raoult's law qualify as real solutions. According to [68,69] they are divided into two groups, where the first group includes mixtures that behave during phase changes similar to homogeneous refrigerants, which are referred to as azeotropic or near-azeotropic mixtures. For azeotropic mixtures, there are extreme points (states) on the phase equilibrium curves, in which the compositions of the liquid and vapor phases are the same [9]. If there are no extreme states on the phase equilibrium curves, then the mixture qualifies as zeotropic. During the phase transitions, the zeotropic mixture behaves quite differently from the homogeneous medium. The following presents, on the basis of the condensation transformation, a comparison of the mechanisms of its implementation for homogeneous and zeotropic refrigerants.

Figure 1 shows the isobaric condensation process of a homogeneous refrigerant in the coordinates T–s.

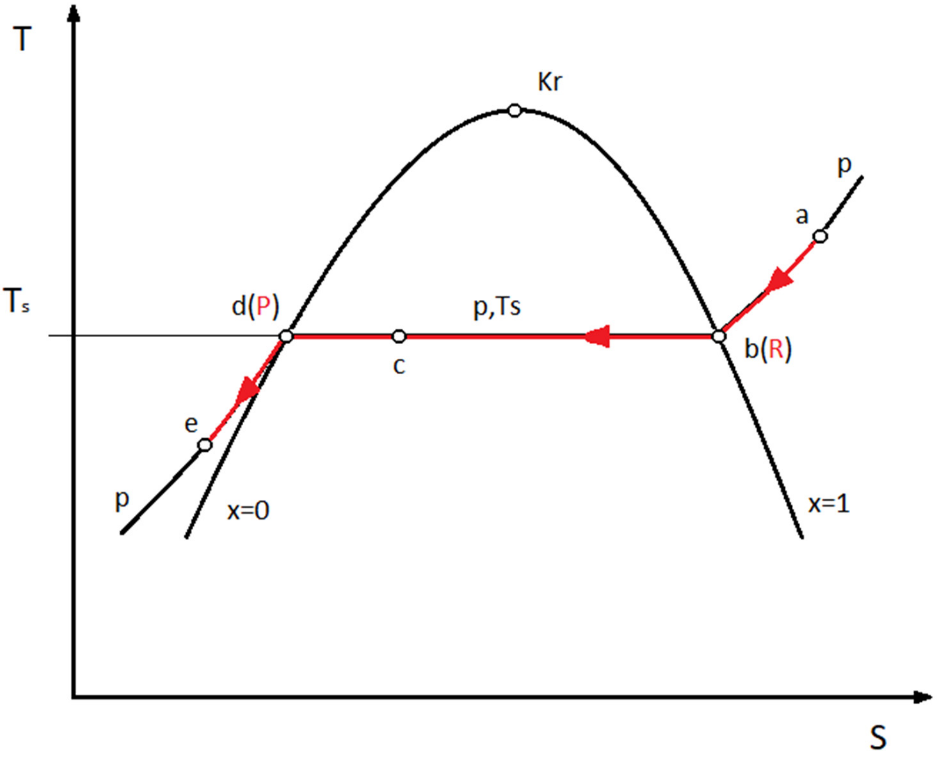

Figure 1. Interpretation of the isobaric-isothermal condensation process of a homogeneous, single-component refrigerant on the graph in the coordinates T–s.

A homogeneous, single-component refrigerant with a state of a (superheated steam) is subject to isobaric cooling (heat removal by an intermediate coolant). The transformation of a → b is an isobaric one-phase transformation until it reaches the state

b (with vapor quality x = 1). The b state is called the R (b = R) dew point—which means that this state is the starting point for an isobaric—isothermal phase transition.

b → d, during which the actual condensation process takes place, associated with the reduction of the vapor dryness degree x, lasting to the state d, called the bubble point P (d = P). While in state b the refrigerant appears as dry saturated vapor (x = 1), in state d it is a saturated liquid (x = 0). Further, isobaric heat reception in the transformation d → e leads to the state of a supercooled liquid (state e) and is a single-phase transformation. If on the path b → d (i.e., R → P) the process runs under equilibrium conditions at saturation pressure p, then the value of the saturation temperature Ts (Ts = const in this transformation) is a clearly defined pressure function, i.e., Ts = f (p). It can be simplified to assume that for azeo- or near-azeotrotropic mixtures the processes described above will be similar.

In order to demonstrate the differences in the phase transformation of the mixture condensation, a zeotropic binary mixture (composed of two components) of the ammonia-water type (NH_3/H_2O) at a saturation pressure p = 15 bar (Figure 2) was taken into account. The choice of a representative NH_3–H_2O zeotropic mixture is not accidental. The author of [69] is one of the few who conducted experimental tests of this type of mixture, for the full range of concentration, thus obtaining very high temperature glide values reaching zakresu $\Delta T_G = 78 \div 93$K, which was also confirmed in [47,70]. The course of the phase equilibrium curves for the mixture NH_3–H_2O, shown in Figure 2, has been reconstructed on the basis of information provided in the works [71].

The state of the zeotropic mixture, like a single-component, homogeneous refrigerant, may be in the areas of superheated steam, two-phase or overcooled liquid. Figure 2 presents a graphic interpretation of the isobaric transformation of cooling the zeotropic mixture, the initial state of which lies in the area of superheated steam (similar to the homogeneous refrigerant in Figure 1). On the method of isobaric transformation a → b, the superheat is collected up to the b state lying on the dew point line—dew point R. $\xi(b')$ corresponding to the state b′ lying on the bubble curve. Saturated dry vapor in state b is in equilibrium with the resulting liquid phase in state b′. Further heat dissipation, after reaching state b, causes entry into a two-phase region—state c—lying in this region, and is shown for example.

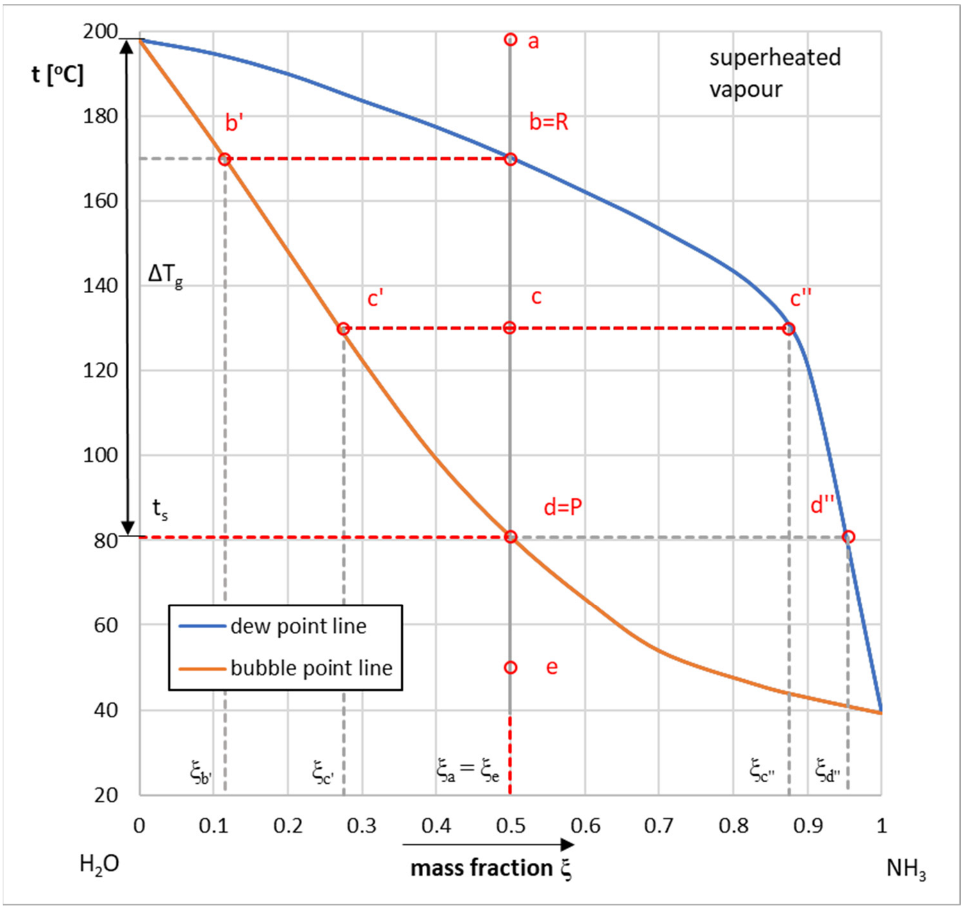

Figure 2. Interpretation of the isobaric condensation transformation of a binary azeotropic mixture of NH_3–H_2O type at saturation pressure p = 15 bar [71].

During the b $\rightarrow$ c transformation carried out in the conditions of isobaric heat reception, the quantitative increase in the liquid phase takes place, at the expense of the loss of the vapor phase. In state c, there is a saturated wet vapor of the mixture (similar to the case of a homogeneous medium—Figure 1) consisting of phases of various concentrations, i.e., the liquid phase with the state c′ and the vapor phase with the state c″, with concentrations, respectively, $\xi(c')$oraz $\xi(c'')$. The final state of the zeotropic mixture in the biphasic region is the d state, which corresponds to the point P on the bubble curve. Conducting the process of isobaric heat collection on the way from state P makes it possible to obtain the liquid phase of a supercooled mixture with state e of a mixture with a concentration of $\xi(e) = \xi(a)$, equal to the value in the initial state a.

The consequence of the above classic description of the condensation mechanism of the zeotropic mixture is the fact that in the isobaric process, the saturation temperature drops in the two-phase transformation from the dew point temperature t_R to the bubble state temperature t_P. It also means that the condensation of the zeotropic mixture is an isobaric-non-isothermal transformation. In the process of the phase transformation of the boiling of the same zeotropic mixture (from state e to a), the nature of changes in parameters will be similar. The difference between the dew point temperature t_R and the bubble point t_P is marked in Figure 2 with the symbol $\Delta T_G = t_R - t_P$ and is called the temperature glide. It should be emphasized that the temperature drop in the isobaric condensation process of the zeotropic mixture is not directly related to the temperature drop caused by the flow resistance of the condensing mixture in the condenser pipes.

If you compare the isobaric condensation processes shown in Figure 1, for a homogeneous refrigerant, and in Figure 2, for a zeotropic mixture, there are very clear quantitative and qualitative differences. For a homogeneous medium, the condensation process is a typical isobaric-isothermal transformation, and the characteristic states of the dew point R and the bubble point P are unequivocally defined by the constant value of the saturation temperature $T_s = T_R = T_P = f$ (p), which depends on the type of refrigerant and saturation pressure p. In the case of a zeotropic mixture, this transformation is isobaric-non-isothermal and is carried out with the temperature slide ΔT_G. The value of the condensation temperature of the mixture depends to a large extent on the composition of the mixture—concentration, i.e., $T = T(p,\xi)$. This is, of course, a significant problem in the adoption of the design condensing (or boiling) temperature in the heat exchanger calculations. According to [72] it is recommended to initially take as the design condensation temperature of the zeotropic mixture—the temperature at the dew point R on the inlet to the condenser, and the temperature of the bubbles P on the outlet from the evaporator—as the evaporating temperature.

For many years, studies have been published in which attempts are made to explain the mechanisms of phase transformations of zeotropic mixtures. The authors' work [9] presents some aspects of this problem in relation to condensation in minichannels. However, the dynamic development of multidirectional research was conducted in recent years, has significantly expanded the current state of knowledge in many world centers. Based on the analysis of selected publications, some key issues were presented.

The authors of the work [68] drew attention to the fact that the thermodynamic and thermophysical properties of the zeotropic mixture sometimes differ significantly from the properties of its components, both in the vapor and liquid phases. In this respect, it is necessary to explain three problems, i.e., phenomena occurring during phase transitions, the formation of temperature glide and the causes and effects of changing the properties of the mixture.

The problem of the formation of the temperature glide plays a very important role. If the temperature glide ΔTG is a complete change in the saturation temperature during the phase change occurring under constant pressure conditions, its formation undoubtedly depends on the volatility of the components of the zeotropic mixture, resulting from the different values of the normal boiling point of the components at the same pressure.

The author of the work [73] presented the already classic version of the causes of the temperature glide. In the case of a two-phase boiling transformation, when the zeotropic mixture has reached its bubble point, the component with the lowest boiling point is activated first (in relation to the others). It evaporates with the remaining components saturated and their normal boiling point higher. After reaching the R dew state, the temperature rises at the end of the evaporation process. In practice, this means an increase in the saturation temperature of the mixture in the discharge section of the evaporator, in relation to the feed temperature. In the two-phase condensation process, the less volatile component of the mixture is first processed (Figure 2), reducing the temperature at the same time, until reaching the point of bubbles in the whole mass of the mixture [74].

The bubble point temperature t_P and the dew point t_R depend on the value of the saturation pressure. Figure 3 presents a graph of the dependence of the temperature t_R and t_P on the saturation pressure, for example for the zeotropic mixture R407F (R32/R125/134a) [27].

As a consequence of different values of the dew point temperature and bubbles for p = const, there is a temperature glide $\Delta T_G = f$ (p). Figure 4 illustrates the dependence of the temperature glide on the saturation pressure for a few selected zeotropic mixtures.

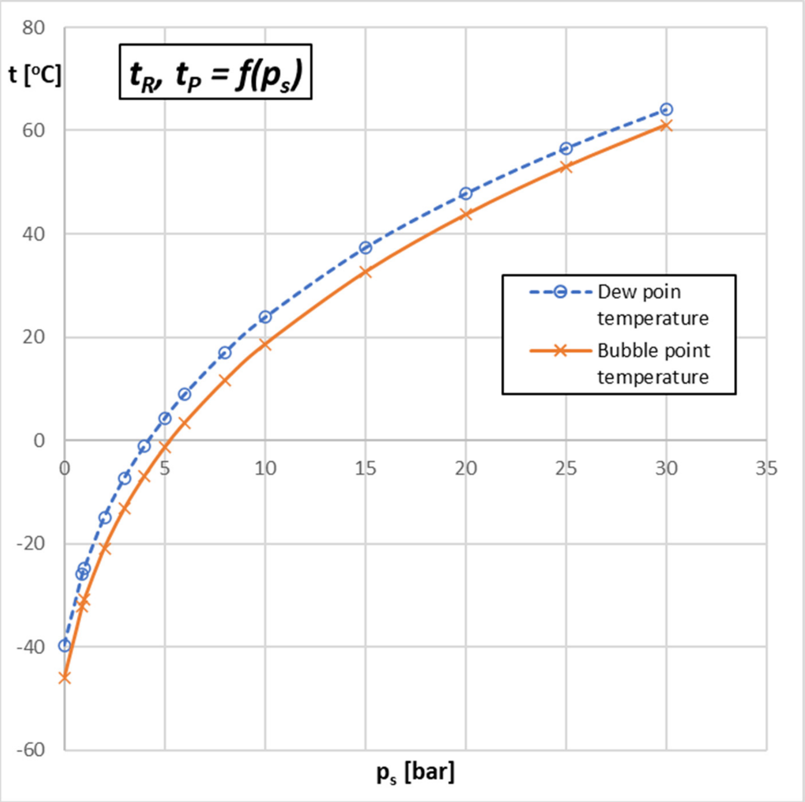

Figure 3. Dependence of the dew point temperature t_R and bubble point t_P on the saturation pressure p for the zeotropic mixture R407F [75].

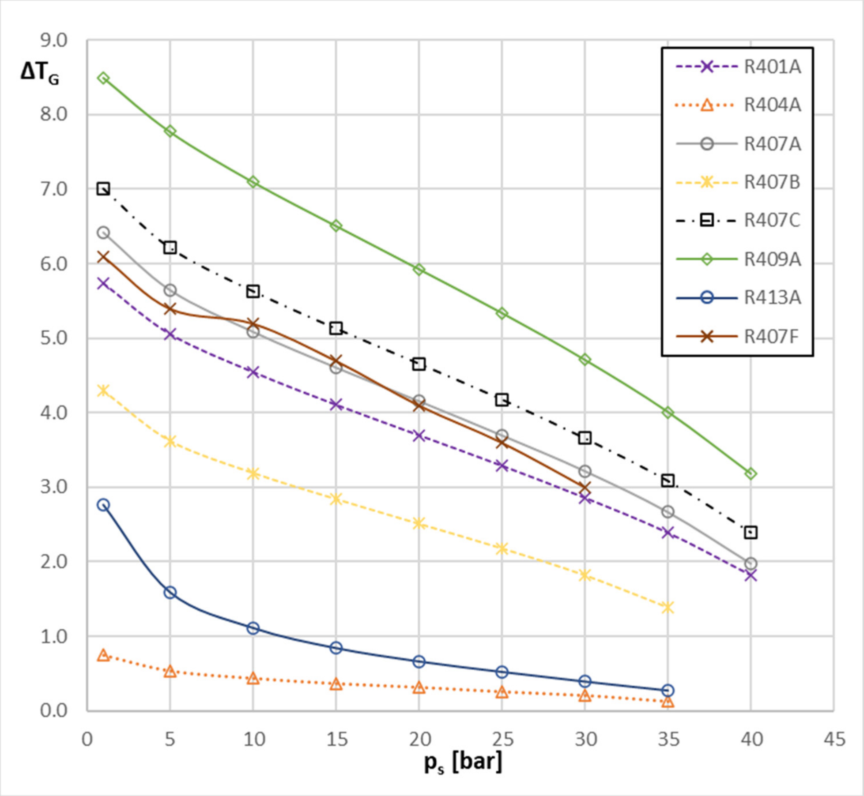

Figure 4. Dependence of the temperature glide ΔTG on the saturation pressure p for zeotropic mixtures: R401A, R404A, R407A, R407B, R407C, R409A, R413A [76].

The charts shown in Figure 4 were prepared on the basis of the data compiled in [76] taken from the study [29]. From the course of the dependence $\Delta T_G = f(p)$ for the R407C zeotropic mixture, it follows that the plot of this dependence is close to a linear one. Using this special property of the R407C mixture, the authors [76] proposed interesting calculation procedures for determining the parameters of wet saturated steam R407C at the inlet to the evaporator.

In addition to zeotropic mixtures, the components of which are synthetic refrigerants, it is necessary to take into account those consisting of natural refrigerants such as: ammonia, carbon dioxide, propane, butane, isobutane, propylene, as well as HFO refrigerants, e.g., R1234yf. For example, the authors of [77] presented the properties of zeotropic mixtures of propane/isobutane type intended for use in low-temperature heat pipes. The results of experimental studies [77] are interesting, in particular the dependence of the temperature slip (called by the authors [77] non-isothermal phase transformation) on the composition of the propane/butane mixture (50/50 wt.%) Under evaporation conditions at a constant saturation pressure p = 3 bar shown in Figure 5.

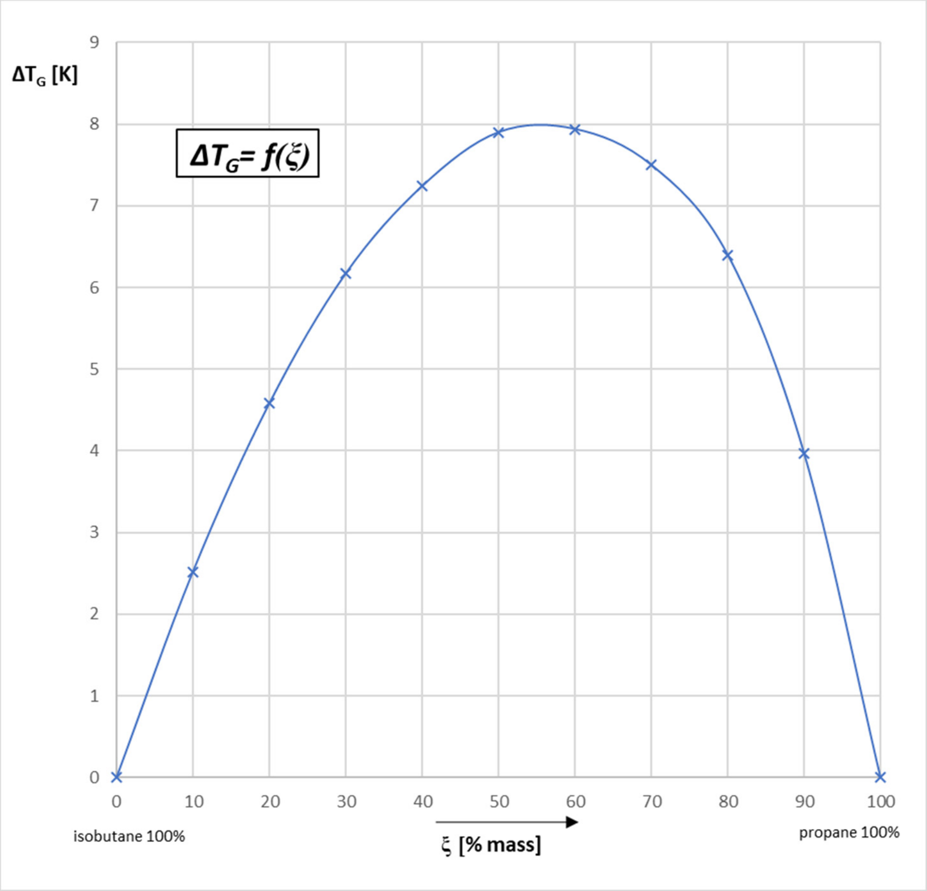

Figure 5. Temperature slip ΔTG in the isobaric process (p = 3 bar) of the evaporation of the zeotropic mixture propane/isobutane (50/50 wt.%) Acc. To [77].

The above description of the condensation mechanism of the zeotropic mixture, the result of which is a temperature glide, can be significantly extended if the results of theoretical, analytical and empirical studies are taken into account. Their discussion is beyond the scope of this study, some of them are of a fundamental nature. Already in the work [78] it was indicated that the mechanism of this process should be treated as coupled phenomena of heat and mass transport. A very large number of parameters makes it practically impossible to achieve an unambiguous description. In the generally understood model of condensation, the method of summing heat and mass transport resistances can be used, the author [78] enumerates, inter alia, the following resistances: diffusion in the vapor phase, penetration of non-heterogeneous heat flux, interfacial surface resistance, thermal resistance of the condensate layer, heat transfer resistance in the layer liquid, etc. Of course, not all of the resistances mentioned have the same effect on the efficiency of heat transfer in the exchangers. Many studies indicate that in the conditions of non-isothermal phase transformation of the zeotropic mixture condensation, the efficiency of this process is significantly influenced by the thermal resistance associated with the discharge of sensible heat in the vapor phase and the diffusion resistance associated with the continuous change in the concentration of both phases, resulting in complex mass transport. Due to the considerable complexity of the condensation mechanism, there are various methods of its modeling. The authors [79] list four groups of the most commonly used types of models, in particular:

- based on the analysis of behavior equations,
- non-equilibrium taking into account the theory of the boundary layer,
- balance,
- empirical.

In most cases, model considerations are limited to binary zeotropic mixtures, although work is also carried out on multicomponent mixtures [80].

In conclusion, it should be stated that the temperature glide that occurs during the condensation and boiling of zeotropic mixtures is an undesirable phenomenon and a disadvantage of these mixtures. It was stated explicitly in [81] that, for this reason, zeotropic mixtures are not suitable for direct application in installations. As a result of this disadvantage, there is the additional problem of selecting a suitable reference circuit for zeotropic mixtures. In addition to the temperature glide, a disadvantage of mixtures of this type is the non-linear equilibrium phase shift in the two-phase region. Yet, not only can these disadvantages be eliminated, but they can sometimes have energetically beneficial effects.

3. Conclusions

This paper presents the directions of research conducted for many years and concerning the energy efficiency of boiling and condensation phase transformations. The present state of knowledge about the mixtures mentioned, which are already used as alternative replacements for the withdrawn refrigerants—mainly fluorinated gases, was indicated. Based on the collected and analyzed bibliography on this subject, the current research trends in the process of condensation of cooling zeotropic mixtures in compact condensers were indicated.

1. There is a constant need to conduct pro-ecological research in the scope of limiting the harmful influence of working refrigerants on the natural environment.
2. In recent years, many of the existing refrigerants have been replaced with new refrigerants with low GWP and ODP values. In many cases, single-component refrigerants have been replaced by mixtures, including azeotropic and zeotropic mixtures.
3. Zeotropic mixtures are an alternative to refrigerants with a high GWP potential. Despite the disadvantage of temperature glide, they have their advantages, including the expected ecological, energy, and economic indicators.
4. The conducted research has shown that the behavior of zeotropic mixtures, especially during phase transformations (including boiling and condensation), differs significantly from homogeneous refrigerants.
5. Many researchers have developed models for the condensation of refrigerants in the form of zeotropic mixtures. They take into account additional heat transfer resistance resulting from the occurrence of the temperature slip resulting from time delays in the implementation of phase transformations of individual components of the mixture. The influence of the mass flux, steam quality, thermophysical properties, and mass fraction on the heat transfer coefficients was analyzed.
6. Due to the fact that the condensation process of zeotropic mixtures is not isothermal and the continuous changes in the composition of the liquid and vapor phases lead to

increased pressure drops, models are often developed for homogeneous fluids which are then modified.

7. There is a clear lack of models for the condensation of refrigerants in the form of zeotropic mixtures that separately describe the condensation phase transformation of individual components of the mixture with the simultaneous impact of this process on the condensation of other components and vice versa.
8. In numerous publications, the authors present the results of their experimental research for various zeotropic mixtures, including those consisting of natural and synthetic refrigerants. Depending on the type of mixed refrigerants, the temperature glide may vary from a few to several dozen degrees Celsius. This causes greater or lesser deviations in the heat exchange process and pressure drops in relation to the condensation of one-component media. There is a need to improve these models in order to precisely indicate the size and direction of these deviations in relation to homogeneous fluids.
9. The results of experimental studies show that the shear effect occurs at the interface of the individual components of the zeotropic mixture, which increases the flow resistance. Further explanation and a more precise description of this effect will show its evident influence on the mechanism of heat, momentum and mass exchange in the process of condensation of heterogeneous factors.
10. The review of the state of the art in the field of condensation of zeotropic mixtures shows that there is a need for further research in the field of:
    - searching for new zeotropic mixtures with improved physicochemical properties. This will allow to improve the efficiency of the condensation process by increasing the value of the heat transfer coefficient and reducing the flow resistance;
    - better understanding of the mechanism of generating the phenomenon of temperature glide, thanks to which it will be possible to more precisely predict the consequences of this phenomenon and enable the prevention of its side effects;
    - improving the modeling of heat transfer processes and flow resistance in conventional channels and minichannels, which will improve the process of designing and constructing highly efficient heat exchangers in the form of conventional and compact condensers;
    - evaluation of the impact of temperature glide on the operation of compressor cooling systems and heat pumps, which will contribute to improving efficiency and increasing the level of stability of operation in operating conditions.

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