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New environmentally friendly low-pressure refrigerants mini-channel

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Abstract Nowadays, in addition to the thermodynamic properties of refrigerants, their impact on the environment is of high significance. Hence, it is important to use refrigerants with the lowest possible values of ozone depletion potential and global warming potential indices in refrigeration, organic Rankine cycle (ORC), air conditioning, and heat pump systems. Natural refrigerants are the most environmentally friendly; unfortunately, they have less favourable thermodynamic properties. Currently, low-pressure refrigerants from the FC (fluorocarbons, fluorine liquids) and HFE (hydrofluoroether) groups are increasingly used. This paper presents the most important properties and applications of selected refrigerants from these groups and also reviews the literature on their use.

Keywords: Refrigerants; Global warming potential; Ozone depletion potential; Fluorinert liquid; Hydrofluoroether

Nomenclature

c_p – specific heat
D – diameter
G – mass flux density
GWP – global warming potential

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d_h – hydraulic diameter
L – length of the channel
m_c, m_r – mass flux of coolant and refrigerant
ODP – ozone depletion potential
q – flux density
t – temperature
t_s – saturation temperature
x – coordinate along the channel

Greek symbols

α – heat transfer coefficient
η – kinematic viscosity
μ – dynamic viscosity
λ – heat conductivity
σ – surface tension
ρ – density
φ – void fraction

Subscripts

l – liquid phase
v – vapor phase

Acronyms

CFC – chlorofluorocarbon
FC – fluorocarbon
HCFC – hydrochlorofluorocarbon
HFE – hydrofluoroether
ORC – organic Rankine cycle
PFC – perfluorocarbons

1 Introduction

The current state of the environment causes increasing pressure on all industries to minimize the harmful effects of human activities. This includes the refrigeration, air conditioning, and heat pump industries in the broadest sense. The primary indicators describing the environmental impact of a refrigerant are ozone depletion potential (ODP) and global warming potential (GWP). ODP is a measure of the destructive effect of a substance on the ozone layer. This index was referred to as Freon R11, for which ODP = 1. ODP values for individual substances are published in the Montreal Protocol (Annex E of PN–EN 378-1). The GWP index, on the other hand, is the greenhouse effect potential, i.e., it compares how much heat is retained by a certain mass of a gas in relation to the amount of heat retained by the same mass of carbon dioxide (CO_2).

As of 2022 year, the GWP index for refrigerants used in new refrigeration/air conditioning systems should be below 150, except for first-stage refrigeration circuits in cascade systems, where it can be up to 1500. Accordingly, work is underway on substances that meet these requirements and are suitable for refrigeration applications. Research is also carried out on the use of low-pressure substances from the fluorocarbons (FCs) and hydrofluoroethers (HFEs) groups sold by 3M Company for this purpose. These are primarily degreasing, foaming, or fire-extinguishing substances with relatively good thermal properties. Some of them are already used in the electronics industry. Table 1 shows the most important properties of substances from the HFE group (liquids sold commercially by the 3M Company as Novec-engineered fluid), and Table 2 shows those of substances from the FC group.

Table 1: Thermodynamic properties of hydrofluoroether group substances at atmospheric pressure and 20°C [1].

Property	Unit	Novec 7000	Novec 7100	Novec 7200	Novec 7300	Novec 7500	Novec 7600	Novec 649
Boiling point	°C	34	61	76	98	128	131	49
Molar mass	g/mol	200	250	264	350	414	346	316
Critical temperature	°C	165	195	210	243	261	260	169
Critical pressure	MPa	2.48	2.23	2,01	1.88	1.55	1.67	1.88
Evaporation heat	kJ/kg	142	112	119	102	89	116	88
Liquid density	kg/m^3	1400	1510	1420	1660	1614	1540	1600
Kinematic viscosity coefficient	mm^2/s	0.32	0.38	0.41	0.71	0.77	1.1	0.4
Specific heat	J/(kgK)	1300	1183	1220	1140	1128	1319	1103
Heat conductivity	W/(mK)	0.075	0.069	0.068	0.063	0.065	0.071	0.059
Surface tension	mN/m	12.4	13.6	13.6	15	16.2	17.7	10,8
GWP		420	297	59	210	100	700	1

Table 2: Thermodynamic properties of FC group substances (fluorinert liquids) at atmospheric pressure and 20°C [1].

Property	Unit	FC-3284	FC-72	FC-84	FC-770	FC-3283	FC-40	FC-43
Boiling point	°C	50	56	80	95	128	155	174
Molar mass	g/mol	299	338	388	399	521	650	670
Critical temperature	°C	161	176	202	238	235	270	294
Critical pressure	MPa	1.94	1.83	1.75	2.47	1.22	1.18	1.13
Evaporation heat	kJ/kg	105	88	90	86	78	68	70
Liquid density	kg/m^3	1710	1680	1730	1793	1820	1850	1860
Kinematic viscosity coefficient	mm^2/s	0.42	0.38	0.53	0.79	0.75	1.8	2.5
Specific heat	J/(kgK)	1100	1100	1100	1038	1100	1100	1100
Heat conductivity	W/(mK)	0.062	0.057	0.060	0.063	0.066	0.065	0.065
Surface tension	mN/m	13	10	12	15	15	16	16

2 Properties of low-pressure refrigerants

HFE and FC group technical fluids are substances that can be used in heat transfer issues with an emphasis on cooling. This is related to their thermal properties. Since there is insufficient information on the thermophysical properties of HFE group refrigerants, many chemists investigate them in relation to the saturation temperature. Muñoz-Rujas *et al.* [2] conducted a study of the thermophysical properties of the HFE7200 refrigerant in the temperature range of 20–60°C. Zheng *et al.* [3] conducted similar studies in the temperature range of –27.53–80.46°C for the HFE7200 and HFE7500 refrigerants. Table 3 shows a comparison of the thermal properties of HFE7000, HFE7100, water, and R134a refrigerant.

Raush *et al.* [5] carried out tests of density, liquid kinematic viscosity coefficient, and surface tension of HFEs, depending on the saturation temperature. They performed density tests for different saturation temperatures using a vibrating densimeter with a measurement error of about

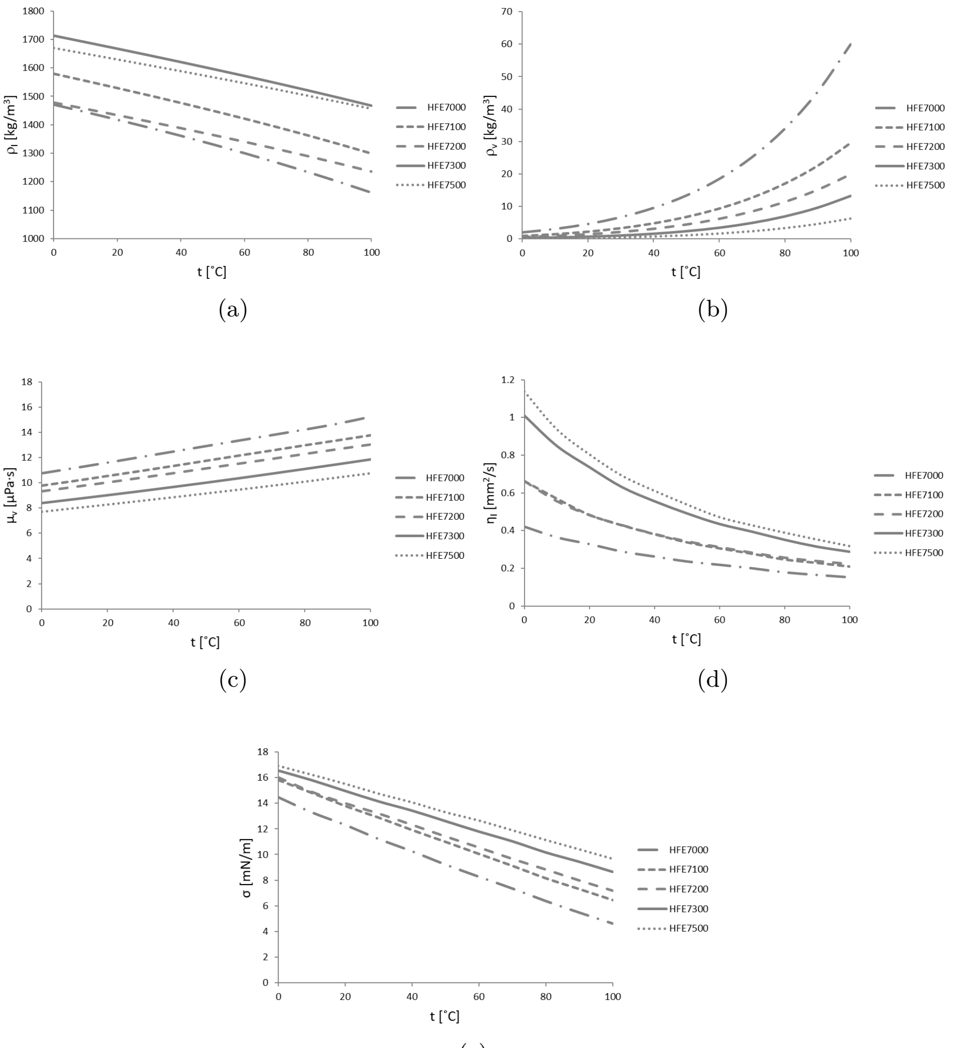
Table 3: Characteristic properties of HFE7100, HFE7000, water, and R134a refrigerants at normal pressure [4].

Property	Refrigerant			
	HFE7100	HFE7000	Water	R134a
Flash-point	–	–	non-flammable	non-flammable
Toxicity	low	low	–	–
ODP	0	0	0	0
GWP	320	530	0	1300
Freezing point, °C	–135	–122.5	0	–96.7
Boiling point, °C	61	34	99.98	–26.074
Critical temperature, °C	195.3	165	373.94	101.06
Critical pressure, MPa	2.23	2.48	22.06	4.0593

0.02%. The liquid-phase kinematic viscosity and surface tension were determined by surface light scattering measurements in the temperature range of 0–100°C with relative measurement uncertainties of 2% and 1.5%, respectively [5]. Figure 1 shows the dependence of the quantities presented in the aforementioned paper on the saturation temperature.

Awareness of the environmental impact of greenhouse gas emissions has led to a search for alternatives to chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and perfluorocarbons (PFCs) refrigerants that will not exhibit undesirable environmental effects. Since HFE fluids have become a good alternative to old refrigerants (including FC group fluids), it is important to understand their thermophysical properties, which describe their suitability for heat transfer, in both single-phase and two-phase processes. Figure 2 shows the specific heat and thermal conductivity of the liquid phase of selected HFE and FC group substances, while Fig. 3 shows the same for the gas phase. As can be seen, the most favourable heat capacity is that of Novec 649, in terms of both liquid and gas phases, while the lowest heat capacity is that of FC72.

In terms of thermal conductivity, the HFE7100 refrigerant shows the most favourable properties, and FC72 has the lowest ones. As can be seen, in addition to environmental aspects, HFE group refrigerants have an advantage over FC group refrigerants in terms of thermal properties. Novec 649 (fluorinated ketone, $C_2F_5C(O)CF(CF_3)_2$) is currently being considered an environmentally friendly alternative for cooling electronics due to its high



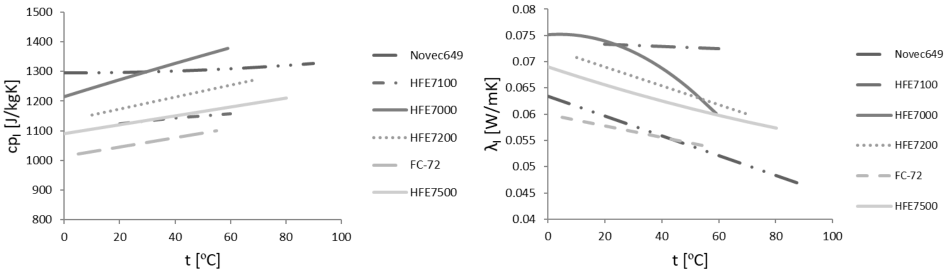
(a) (b)

(c) (d)

(e)

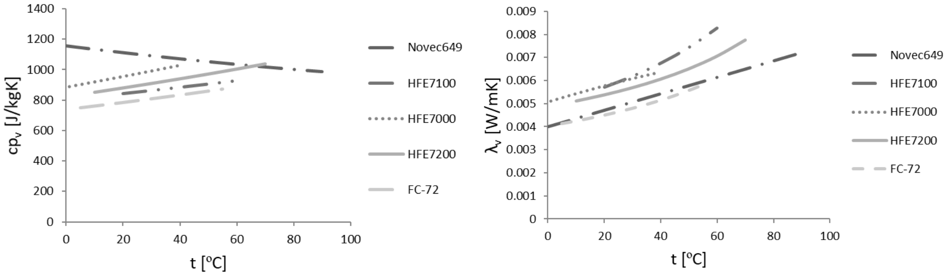
Figure 1: Properties of hydrofluoroether group fluids studied by Rausch *et al.* [5].

dielectric strength and low GWP. It exhibits very low toxicity with long-term stability. Forrest *et al.* [12] conducted a study of this refrigerant boiling in volume in order to cool a nickel resistance wire at a saturation temperature of 49°C. The heat transfer coefficient for Novec 649 is higher than for FC72 under the same conditions. Thus, Novec 649 is considered an alternative to FC72 refrigerant for immersion cooling of electronics.



(a) (b)

Figure 2: Thermal properties of the liquid phase of selected hydrofluoroether and FC fluids [1, 6–11].



(a) (b)

Figure 3: Thermal properties of the gas phase of selected hydrofluoroether and FC fluids [1, 6–11].

3 Application of low-pressure refrigerants in scientific research

In the literature, the use of low-pressure refrigerants in the heat exchange process is increasingly observed, including the use of phase transformations. Bonk *et al.* [13] described an organic Rankine cycle (ORC) microsystem they designed for teaching and research purposes. The goal of this research was to propose a safe and environmentally friendly microscale heat engine.

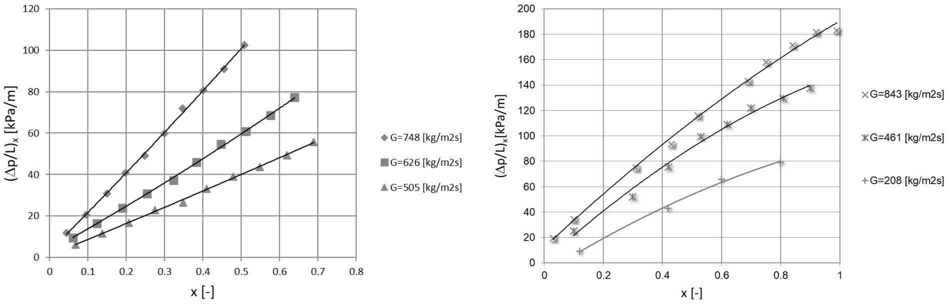
An organic fluid called 3M Novec 649 was used as the working medium in this system. The tested system had an output of 1 kW, and the supply temperature was 140°C. The authors studied the effect of the circuit parameters on its efficiency using the mentioned working medium [13]. Bruder *et al.* [14, 15], on the other hand, conducted a study of the boiling process of this medium in a vertical copper channel. They conducted studies of the temperature distribution on the surface of the channel wall for different flow rates of the medium and performed temperature and heat flux studies using a fibre optic probe and thermocouples. The same authors also presented the results of a study of the boiling process in a 40 mm × 40 mm rectangular channel at a mass flux density of 1000 $\mathrm{kg/m^2s}$ [15]. The study was conducted from single-phase convection to fully developed boiling. Fu and Lin, on the other hand, conducted a study of the effects of mass flow rate, system pressure, and vertical mini-channel diameter on the supercritical heat transfer characteristics of the Novec 649 medium. Experimental results showed that the heat transfer coefficient increases significantly with increasing mass flux, especially for small channel diameters. An increase in mass flux can also result in a smaller decrease in the heat transfer coefficient when the pseudocritical temperature is reached. The heat transfer coefficient decreases sharply when the fluid temperature reaches the pseudocritical temperature and then increases again when the fluid temperature exceeds the pseudocritical temperature. The authors developed an empirical correlation for Novec 649 working fluid to describe the heat transfer

$$\mathrm{Nu} = 3.37 \times 10^3 \mathrm{Re}^{0.47} \mathrm{Pr}^{1.05} \left(\frac{\overline{C}_p}{C_{pw}}\right)^{0.91} \left(\frac{\mathrm{Gr}}{\mathrm{Re}^2}\right)^{-0.36} \left(\frac{D}{L}\right)^{2.16}, \tag{1}$$

where $\overline{C}_p/C_{pw}$ is the dimensionless specific heat capacity (C_{pw} – specific heat in wall temperature), Nu is the Nusselt number, Re is the Reynolds number, Pr is the Prandtl number, and Gr is the Grashof number, D and L denotes the diameter and length, respectively. Equation (1) was developed based on the Jackson method. The deviation of the calculated results according to the correlation from the experimental results is about 20%, and the average absolute error is only 11.4% [16].

Cao *et al.* [17] conducted boiling studies in a volume of HFE7200 medium using nanoparticles. They studied the effect of nanoparticle surface on heat transfer and found that its shape could increase the heat transfer coefficient and critical heat flux by up to 60%. In addition, mathematical modelling was successfully carried out using Zuber's hydrodynamic instability model. Cao *et al.* conducted boiling investigations of a few HFE refrigerants [18,19].

Adebayo *et al.* [20] investigated the use of HFE7000 and HFE7100 refrigerants in cascade systems in combination with $\mathrm{CO_2}$. The use of $\mathrm{CO_2}$ in refrigeration and heat pump systems is also now widely discussed in the literature. Mikielewicz and Andrzejczyk [21–23] conducted condensation studies of HFE7000 and HFE7100 refrigerants in mini-channels. They focused on issues of flow resistance in the condensation process in a pipe channel with an internal diameter of 2.3 mm. They studied the effects of heat flux, fluid flow rate, vapour quality, and saturation temperature on flow resistance. The experimental results were compared with correlations of other authors, and the best fit of the results with the model of Fronk and Garimelli [24] was found [25]. Bohdal and Sikora [26–29] conducted similar studies of the condensation process of Novec 649, HFE7000, and HFE7100 working fluids in single tubular mini-channels with diameters in the range of 2.0–0.5 mm. In addition to heat transfer and flow resistance studies, the authors conducted a flow structure study [27]. Figure 4 shows a comparison of the results of the two teams. Figure 5 shows an example of the results of flow structures during the condensation of the HFE7000 refrigerant in a mini-channel pipe with an internal diameter of 0.8 mm. Al-Zaidi *et al.* [30] also studied the flow structures formed during the condensation of the HFE7100 refrigerant; however, they used multiports made of rectangular mini-channels with hydraulic diameter $d_h = 0.57$ mm, saturation temperature $t_s = 60°\text{C}$, and mass flux density $G = 48-126$ kg/m^{2}s.



(a) (b)

Figure 4: Dependence of flow resistance in the condensation process of HFE7000 refrigerant in a mini-channel according to: a) Mikielewicz, Andrzejczyk [21] for $d_h = 2.3$ mm and $t_s = 52°\text{C}$; b) Sikora, Bohdal and Formela [27] for $d_h = 2.0$ mm and $t_s = 46°\text{C}$.

Pastuszko *et al.* [4] conducted a study on the effect of surface micro-development on heat transfer. They investigated the boiling process of water, ethanol, Novec 649, and FC72 at atmospheric pressure to select such parameters of the developed surface to obtain the highest possible heat transfer coefficient. Three types of structural surfaces were used: smooth micro-ribs with a height of 1.0 mm (designated MF), reinforced surfaces made by sintering micro-rib tips with perforated copper foil (MF+F), and structural

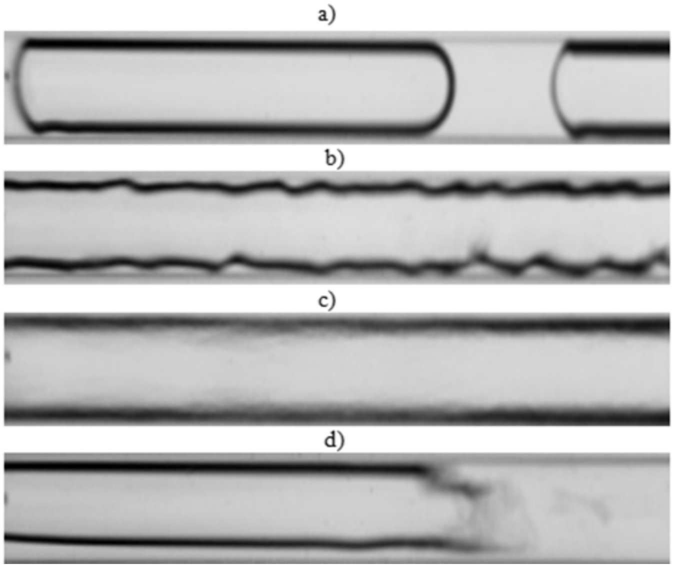


Figure 5: Results of flow structures obtained by Sikora [31] during condensation of HFE7000 refrigerant in a pipe mini-channel with an inner diameter d_h = 0.8 mm: a) plug structure $G = 197$ kg/m^{2}s, $x = 0.004$, $\varphi = 0.44$, $t_s = 31$°C; b) annular-wave structure $G = 369$ kg/m^{2}s, $x = 0.012$, $\varphi = 0.69$, $t_s = 32.5$°C; c) annular structure $G = 491$ kg/m^{2}s, $x = 0.032$, $\varphi = 0.82$, $t_s = 41$°C; d) slug structure $G = 639$ kg/m^{2}s, $x = 0.003$, $\varphi = 0.34$, $t_s = 29$°C.

surfaces formed by sintering braided copper wire mesh with micro-rib tips (MF+M). They reported a simplified semi-analytical model to determine the total heat flux for the studied surfaces.

Piasecka *et al.* [32] conducted extensive research on the boiling process of refrigerants with low ODPs and GWPs. They presented the results of a study of the heat transfer process during subcooled boiling in a multiport constructed of three or five mini-channels 1 mm high. FC72 fluid was used in the study. The mini-channel was lined with a thin film, the temperature of which on the outer surface was measured by infrared thermography. Temperature distributions obtained from the finite elements method (FEM) calculations performed by ADINA software [33] were presented. Sample boiling curves indicating nucleation hysteresis were presented and discussed. Another paper focused on the study of heat transfer during the boiling process in the flow of FC72, HFE649, HFE7000, and HFE7100 fluids in a single 1.7-mm-high mini-channel, oriented vertically or horizontally [34]. Infrared thermography was used to measure the temperature. Observations of flow structures were also made. The results were presented as the change in the heat transfer coefficient along the length of the channel (Fig. 6) and as boiling curves. These authors compared their results with the results of calculations according to the correlations of various authors, and the best match was obtained for the correlation of Mikielewicz [35]. For saturated boiling, their own correlation was proposed

$$\mathrm{Nu} = 4.19\mathrm{We}^{-4.12}\mathrm{Pr}^{0.74}\mathrm{Bo}^{-2.16}, \tag{2}$$

where We is the Weber number and Bo is the Bond number.

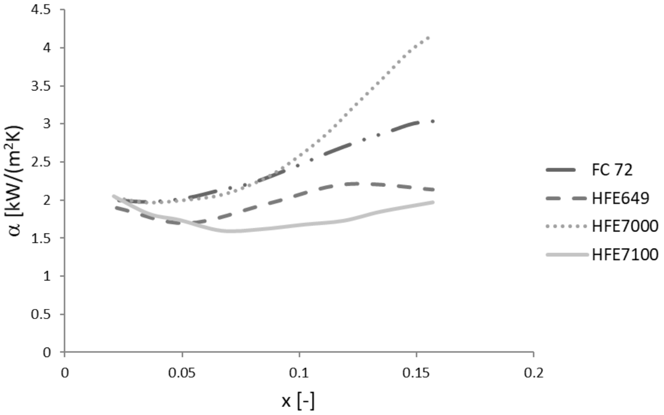


Figure 6: Change in the heat transfer coefficient along the mini-channel during the boiling process of the studied refrigerants at a heat input flux density of $q = 65$ kW/m^2 [32].

Piasecka and Strąk [34, 36, 37] presented the results of similar tests carried out in a single rectangular channel of 180 mm in length and a bundle of five parallel mini-channels of 32 mm in length. The effects of the slope angle of the channels and the porosity of the heating surface on the boiling process were analyzed, and the results of heat transfer during refrigerant flow in rectangular mini-channels under stationary conditions were presented. The influence of selected parameters on the boiling process was discussed, including thermal flow parameters, dimensions, and orientation of the channels. The highest values of the heat transfer coefficient were obtained for channel angles of 0 and 270°. The boiling process of refrigerant from the HFE and FC groups is quite extensively reported in the literature. Cao *et al.* [18] dealt with the process of heat transfer intensification during boiling of HFE7200 and Novec 649.

In order to intensify heat transfer, nanoparticles were used to coat the heat transfer surface. This treatment improved the value of the heat transfer coefficient during boiling of the HFE7200 medium by 190%. At the same time, visualization studies of vapour bubble formation were carried out to determine the diameter and velocity of bubbles detached from the heat transfer surface [18, 19]. A study of the boiling process of HFE refrigerants was also published in the work of Eraghubi *et al.* [38].

Boiling and condensation are of great importance in the cooling process because some of the HFE and FC group refrigerants are nonconductive and can be used to cool electronic components. Since such components are small in size, there is a trend toward the miniaturization of heat exchangers while intensifying heat transfer. Kruzel, Bohdal and Dutkowski [39] presented the results of a study of the condensation process of HFE7000 and HFE7100 refrigerants in a shell-and-tube heat exchanger built with 4- to 6-mm-diameter channels and a shell with an inner diameter of 30 mm. The condensation process took place on the surface of the tube bundle, and water was used as the cooling medium. The authors conducted thermal flow tests under the following conditions: $G = 20-700$ kg/m^{2}s, $q = 3000-60000$ W/m^2, $t_s = 40-80$°C. The same authors conducted tests using HFE7000 refrigerant and a mixture of water and phase-change microcapsules in a shell-and-tube heat exchanger. They showed that, particularly around the phase transition temperature of the phase-change material, there is a sharp increase in the heat transfer coefficient on the side of the mixture of water and microcapsules. This is due to an increase in the heat capacity of this mixture. This results in an increase in the heat exchanger's thermal efficiency in this range of operating parameters. The tests were carried out under the following conditions: mass flux of refrigerant $m_r = 0.0014$–0.0015 kg/s, mass flux coolant $m_c = 0.014-0.016$ kg/s, refrigerant saturation temperature $t_s = 55-60$°C, inlet coolant temperature $t_{cin} = 20-32$°C, and heat flux density $q = 7000-7450$ W/m^2. The average increase in the heat transfer coefficient was 13% [40]. Woodoc *et al.* [41], on the other hand, investigated the use of the HFE7000 refrigerant in an 800-μm-thick silicon mini-heat exchanger (MECH-X). The exchanger was used to cool electronic components, which were heated to 90°C. What is more, Andrzejczyk and Muszyński [23] conducted studies on the influence of refrigerant properties and geometry on the performance of two-phase closed thermosiphon (TPCT). The tests were carried out on HFE7100 refrigerant as well as water, R134a, SES36 and ethanol. The presented constructions of thermosyphons were to be used to recover heat from industrial wastewater, which is of great importance in terms of the energy economy.

4 Conclusions

This article presented a review of available information on new working fluids with low GWP and ODP values. As discussed earlier, refrigerants from the HFE group can be successfully used in a wide range of thermal transformations. They can successfully replace refrigerants from the FC group, which are less environmentally friendly but have similar application ranges. The Novec 649 refrigerant has both a higher heat capacity and thermal conductivity (at least to some extent) than the FC72 refrigerant. Other refrigerants in the HFE group also show better thermal properties than the FC72 refrigerant. Thus, these substances can be used in a wide range of thermal processes as follows:

- for both single-phase and two-phase cooling electronics, also by immersion,
- in ORC systems and other high-temperature refrigeration systems, and
- in cascade heat pumps and refrigeration systems.

In order to intensify heat transfer, HFE group refrigerants can also be used in combination with phase-change materials. Novec 649 and HFE7200 fluids have the lowest environmental impact due to their low GWP, so they are most often preferred over less environmentally friendly refrigerants with similar operating parameters. HFE7500 and HFE7600 refrigerants have saturation temperatures at normal pressure above 100°C, which limits their use in phase transformation (boiling or condensing).

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