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Assessing the applicability of new refrigerants in marine cooling systems

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ABSTRACT

The article assesses the applicability of new refrigerants, being possible substitution for Freon 22, in marine refrigeration and air-conditioning systems. A collection of technical data on the physical properties of the new refrigerants is presented. Suggestions are made about certain energetic and ecological profits which can be gained when using energetically efficient refrigerants with low GWP values. The results of the TEWI comparison analysis for selected refrigerants are also included.

Keywords: TEWI, ODP, GWP, heat pump, air conditioning, cooling installations, refrigerant, R22 substitute, energetic efficiency, R41, R152a, R218, R227ea, RC318, R600a, R290, R1270

INTRODUCTION

The applicability of the refrigerants R41, R152a, R218, R227ea, RC318, R600a, R290, and R1270 in cooling installations was analysed based on the assessment of the use of these substances in the heat pump cycle, for devices operating in the heating mode. The medium used in the reference heat pump installation was R22, due to its favourable thermodynamic properties, along with low energy consumption of the devices filled with this medium. Indeed, many substances which are used as substitutes for Freon 22 reveal higher energy consumption and GWP. The main criterion used for assessing the applicability of the substances, referred to as refrigerants – refrigerating media, is their influence on the environment. The Carnot cycle is considered here the reference for real cycles realised using the media being homogeneous substances, such as Freon R22 and its substitutes.

ECOLOGICAL CRITERIA FOR THE SELECTION OF REFRIGERANTS

Present tendencies in manufacturing of the cooling devices and installations are closely connected with the use of new effective refrigerants. These refrigerants should also meet the requirements concerning atmosphere protection [4]. Ecological problems with the use of older refrigerants have led to the situation in which the chemical industry offers a large and still growing number of new substances, with a guaranty of their favourable thermal, flow and ecological characteristics. Unfortunately, we cannot be sure that no unexpected and unfavourable phenomena will be observed in the future, some time after these substances start being practically used [4]. In the Annex to the standard PN-EN 378 [3] the majority of the new refrigerants are taken into account, including criteria of the assessment of their influence on the environment.

We all are aware that the Earth's atmosphere should be protected. It was particularly evident for the signatories of the "Montreal Protocol" of 1987, as a consequence of the increasing area of holes in the ozone layer in previous years. Consequently, the signatories agreed on substantial reduction of the emission of CFCs until 2000. Poland signed and ratified the Montreal Protocol in 1990, and in 1996 the Act No. 176 was adopted according to which Republic of Poland signs the London and Copenhagen Annex to the Montreal Protocol. Initially, the negative effect of the halogen derivative compounds to the Earth's atmosphere was described by two coefficients. The first is the Ozone Depletion Potential, ODP, which characterizes the effect of a substance on the intensity of ozone decomposition, while the second is the newly introduced GWP (Global Warming Potential) factor, calculated in the relation to CO_2 for which it is equal to 1 (Tab. 1). The carbon dioxide reveals a relatively low potential for creating the greenhouse effect, but its amounts emitted to the atmosphere are so huge that they contribute in about 50% to this effect. On the other hand, despite their small volumetric proportions in the atmosphere, vestigial gases, such as methane and halogen derivative compounds of CFC and HFC type, contribute in nearly 20% to the creation of this phenomenon [4]. Unfortunately for many Freon 12 and Freon 22 substitutes, which are expected to be safe for the ozone layer, reveal high GWP values, close to those revealed by the withdrawn Freons. The GWP value is estimated for the time of 100 years, as the stability of the existence of the given substance in the atmosphere is to be taken into account.

The sole information about GWP of the refrigerants turned out insufficient, as it did not take into account differences in the amount of driving energy consumed by the devices working with different substances. That is why the new factor includes the total level of CO_2 "emission" taking also into account refrigerant losses and the energy used for driving the device. The energy consumed for driving the cooling devices leads to the emission of CO_2, the amount of which depends on the energy source. For instance, the combustion of different fuels generates different volumes of CO_2. Also when the energy is generated without combustion, we will obtain different values

Tab. 1. *ODP and GWP factors describing ecological threat of selected refrigerants to the environment [3]*

Item	Name of substance	Refrigerant	Chemical formula	ODP value (R11 = 1)	GWP value ($C0_2$ = 1, 100-years period)
1	Chlorodifluoromethane	R22	CHF_2Cl	0.06	1700
2	Fluoromethane	R41	CHF_3	0.00	97
3	1,1-difluroethane	R152a	$C_2H_4F_2$	0.00	140
4	1,1,1,2,3,3,3-Heptafluoropropane	R227ea	C_3HF_7	0.00	2900
5	Octofluoropropane	R218	C_3F_8	0.00	7000
6	Octofluorocyclobutane	RC318	C_4F_8	0.00	8700
7	2-metylopropane	R600a	C_4H_{10}	0.00	3
8	Propane	R290	C_3H_8	0.00	3
9	Propylene	R1270	C_3H_6	0.00	3

Tab. 2. *Physicochemical properties of selected refrigerants [7]*

Item	Refrigerant	R22	R41	R152a	R218	R227ea	RC318	R600a	R290	R1270
1	Molecular weight [g/mol]	86.468	34.033	66.051	188.02	170.03	200.03	58.122	44.096	42.08
2	Freezing point [°C]	-157.42	-143.33	-118.59	-160.15	-126.8	-39.8	-159.59	-187.67	-185.2
3	Boiling point [°C]	-40.81	-78.123	-24.023	-36.83	-16.45	-5.975	-11.67	-42.09	-47.69
4	Density of liquid (25°C) [kg/m^3]	1190.7	574.26	899.47	1325.7	1388.9	1498.3	549.86	492.08	504.47
5	Density of vapour (25°C. 1.013bar) [kg/m^3]	3.5859	1.4027	2.7583	7.8513	7.1423	8.4270	2.4396	1.8314	1.7443
6	Critical temperature [°C]	96.145	44.13	113.26	71.95	101.65	115.23	134.67	96.675	92.42
7	Critical pressure [MPa]	4.99	5.897	4.5168	2.671	2.926	2.7775	3.64	4.2471	4.6646
8	Critical density [kg/m^3]	523.84	316.51	368	627.98	573	619.97	224.35	218.5	223.39
9	Heat of vaporisation (1.013bar) [kJ/kg]	233.75	488.82	329.92	105.20	131.42	116.75	365.95	425.83	439.16
10	Thermal conductivity of liquid (25°C) [mW/mK]	83.479	115.25	97.975	44.753	59.402	65.136	88.998	93.621	110.70
11	Thermal conductivity of vapour (1.013bar) [mW/mK]	7.0475	10.120	9.4093	8.1634	10.415	10.212	13.208	11.570	10.576
12	Specific heat of liquid (25°C) [kJ/kgK]	C_p = 1.2568 C_v = 0.69086	C_p = 3.7343 C_v = 1.2560	C_p = 1.8 C_v = 1.1379	C_p = 1.16910 C_v = 0.79750	C_p = 1.1748 C_v = 0.82591	C_p = 1.1135 C_v = 0.80403	C_p = 2.4502 C_v = 1.7007	C_p = 2.7367 C_v = 1.6667	C_p = 2.6701 C_v = 1.5521
13	Specific heat of vapour (1.013bar) [kJ/kgK]	C_p = 0.60629 C_v = 0.49043	C_p = 1.1865 C_v = 0.85355	C_p = 0.97657 C_v = 0.81640	C_p = 0.70620 C_v = 0.64870	C_p = 0.76641 C_v = 0.70035	C_p = 0.74488 C_v = 0.69390	C_p = 1.5583 C_v = 1.3817	C_p = 1.4610 C_v = 1.2333	C_p = 1.3210 C_v = 1.0904
14	Viscosity of liquid (25°C) [μPa s]	164.39	77.997	163.16	166.92	239.46	362.88	150.16	96.948	94.479
15	Viscosity of vapour (1.013bar) [μPa s]	9.6967	7.0552	9.4093	9.7823	9.9046	10.230	6.5810	6.3092	6.3554
16	Cp/Cv (vapour) [25°C. 1.013bar]	1.1847	1.2927	1.1549	1.0655	1.0150	1.0642	1.1053	1.1359	1.1569

of the factor describing the volume of the produced carbon dioxide [kg CO_2/1kWh]. Its assumed values are the following: burned coal z = 1.12; fuel oil z = 0.94; natural gas z = 0.57; wind, water and nuclear power plants z = 0.00. For Poland it is assumed that z ~ 0.7 – 0.8 [4].

Analysing different solutions and refrigerants used for instance in marine cooling installations we can assess the TEWI (Total Equivalent Warming Impact) factor for them and select those revealing its lowest values.

Cooling installations and/or heat pumps contribute to the creation of the greenhouse effect, mostly in an indirect way via CO_2 emission connected with the production of the energy used by their driving systems. Since this energy is most frequently generated in Europe in electric power plants in which mineral fuel is burned, each kilowatt hour of the electric power is connected with the approximate emission of 0.4 ÷ 1.2 kg of CO_2 to the atmosphere, depending on a country.

In this way, the consumption of the driving energy by the cooling system contributes to the creation of the greenhouse effect during the entire time of system operation. Consequently, we should attempt not only to use substances revealing low GWP, which reduces part connected with the emission, but also tend to obtain the highest possible thermodynamic efficiency. An important feature of the present pro-ecological solutions is the use of highly effective compressors, fans, pumps, or other subsystems of the cooling systems or heat pumps.

For simplicity purposes, it was assumed in the present analysis that the installations are identically filled with the medium and the level of leakage is in constant proportion to the installation filling. In practice, leakage flows of the refrigerant are different for different devices and substances, and the risk of their appearance is especially high in cooling installations which are spread over a large area.

A high worldwide effort is made to reduce the emission of greenhouse gases, as a result of which some legal regulations were adopted. Since 2007, on the EU territory the Directive [6] on some fluorinated greenhouse gases is in force, which imposes severe limits to be complied with in the cooling and air conditioning engineering. (Directive no 842/2006 of May 17, 2006, Polish text published in the EU Official Journal No. L161/ of June 14, 2006).

The Total Equivalent Warming Impact (TEWI) factor is calculated from the formula [3]:

$$\mathrm{TEWI} = \mathrm{GWP} \cdot L \cdot n + \mathrm{GWP} \cdot m \cdot (1-f) + n \cdot E \cdot z$$

where:

GWP - Global Warming Potential, in relation to CO_2 [-]
L - amount of the substance emitted to the atmosphere [kg/year]
n - device's operating time [years]
m - amount of the refrigerant in the installation [kg]
f - dimensionless number assessing the recovery ratio [-]
E - energy consumed by the device in one year ($E = t_R\ N$), [kWh]
z - CO_2 emission divided by the scaling energy unit [kgCO_2/kWh]
N - heat pump driving power [kW]
t_R - annual time of operation [h].

Sample TEWI calculation for a heat pump

For comparison purposes, the TEWI factor for the heat pump installation was calculated taking into account the following refrigerants: R22, R41, R152a, R218, R227ea, RC318, R600a, R290, and R1270. The operating parameters and technical data of the installation were the following: mass of refrigerant in the installation m = 5kg, annual emission of the substance L = 1kg, operating time of the installation n = 15 years, annual time of operation t_R = 6000 h, medium recovery ratio f = 0.5, heating power of the heat pump Q_{pc} = 25kW, z = 0.94 kg CO_2/kWh. The assumed identical filling of the installation and similar emission in case of each refrigerant are some simplification of the real situation.

The calculations of a single-stage cycle with SLHE (suction-liquid line heat exchanger) were performed based on the assumptions collected in Tab. 3. The analysed refrigeration cycle is shown in Fig. 1.

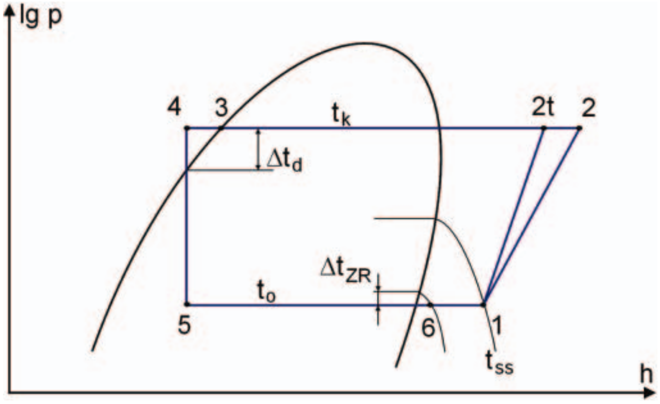

Fig. 1. *Single-stage cycle with SLHE in the lgp-h diagram: t_o – evaporation temperature, t_k – condensation temperature, Δt_{ZR} – superheating of vapour in the evaporator, Δt_d – extra cooling of liquid in extra cooler, t_{ss} - temperature of vapour at compressor's suction side*

Tab. 3. *Initial calculation data*

Data of calculation	
Evaporation temperature t_o [°C]	2
Condensation temperature t_k [°C]	40
Superheating of vapour in the evaporator Δt_{ZR} [K]	4
Sub-cooling of liquid in the SLHE Δt_d [K]	Resulting from SLHE efficiency 0.80
Temperature of vapour at compressor suction side t_{ss} [°C]	20
SLHE efficiency η_{WR} [-]	0.8
Isentropic efficiency of compression η_{iz} [-]	0.85
Compressor's mechanical efficiency η_m [-]	0.9

Tab. 4 collects the results of the TEWI calculations for the following refrigerants: R41, R152a, R218, R227ea, RC318, R600a, R290, R1270 and R22.

Fig. 2 shows the relative TEWI factor calculated for the refrigerants: R41, R152a, R218, R-227ea, RC318, R600a, R290 and R1270, taking R22 (100%) as the reference. After assuming identical conditions for: the heating power, filling of the installation with the medium, the scale of leakage, and the operating time, the calculations have led to nearly 21% reduction of the TEWI factor for **R600a** compared to R22. The second favourable refrigerant was R152a, which revealed the TEWI factor lower by 19% than R22. Similar TEWI results were also obtained for the refrigerants R290 and R1270, for which TEWI decrease amounted to 18 and 17%, respectively.

Tab. 4. Results of heat pump cycle and TEWI calculations for refrigerants: R41, R152a, R218, R227ea, RC318, R600a, R290, R1270 and R22

Refrigerant	q_k [kJ/kg]	m [kg/s]	N [kW]	COP	GWP*L*n	GWP*m*(1-f)	n*E*z	TEWI [kgCO_2]
R41*	319.9	0.078	5.67	4.41	1 455	242.5	479 414	**481 112**
R152a	319.0	0.078	4.32	5.78	2 100	350	365 774	**368 224**
R218	83.7	0.299	4.60	5.44	105 000	17 500	389 140	**511 640**
R227ea	121.7	0.205	4.32	5.79	43 500	7 250	365 434	**416 184**
RC318**	111.7	0.224	4.29	5.82	130 500	21 750	363 136	**515 386**
R22	211.6	0.118	4.46	5.60	25 500	4 250	377 465	**407 215**
R600a	364.98	0.0685	4.22	5.93	45	7.5	356 777	**356 829**
R290	381.89	0.0655	4.39	5.69	45	7.5	371 752	**371 805**
R1270	385.3	0.065	4.46	5.60	45	7.5	377 643	**377 696**

* - not mentioned in the list in prPN-EN 378, ** - missing safety group in Table E1 in prPN-EN 378 -1

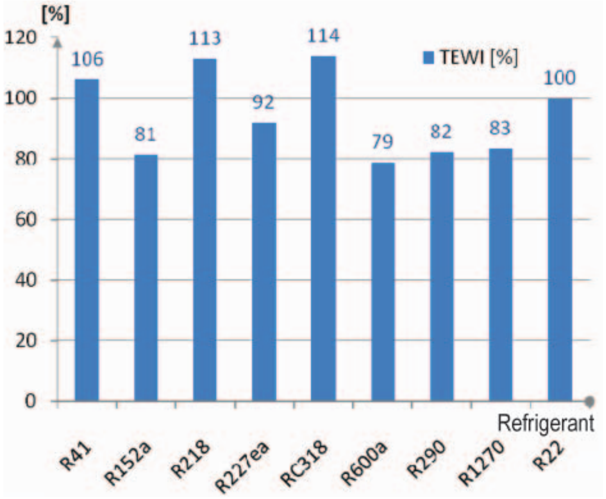

Fig. 2. *Total heat pump TEWI factor for refrigerants: R41, R152a, R218, R-227ea, RC318, R600a, R290, R1270 and R22*

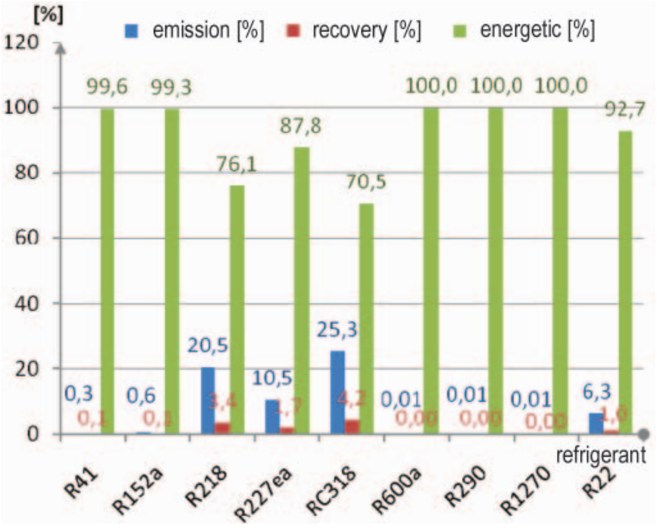

Fig. 3. *TEWI components for R41, R152a, R218, R-227ea, RC318, R600a, R290, R1270 and R22*

The last favourable result in this group was the refrigerant R227ea which revealed lower TEWI by 8%. The remaining refrigerants have higher TEWI values: R41 by 6%, R218 by 13%, and RC318 by 14 % with respect to the referential TEWI factor of R22.

Fig. 3 shows that the proportion of the energetic component in the TEWI factor amounts to 100% for R600a, R290 and R1270, 99.6% for R41, and 99.3 % for R-152a. In those cases the emission and recovery components do not exist or are negligibly small, below 1% of the total TEWI value. For the remaining refrigerants the emission component and the recovery component contribute to a much larger extent: 29.5 % for RC318, 23,9 % for R218, and 12.2% for R227ea.

COMBUSTIBILITY OF REFRIGERANTS

It has been known [2] that the refrigerants R218 and R-227ea are not combustible under the atmospheric pressure and in temperatures not exceeding 80°C (except R152a). However, the tests [5] have also proved that even R22 becomes combustible at the pressure exceeding 5,15 bar and in regular ambient temperature when it mixes with the air to the concentration equal to or higher than 65 per cent. Consequently, these substances should be used in the way protecting against the creation of air mixtures, during leakage examination, for instance. In general, we should not accept conditions for possible creation of such high-concentration mixtures at pressures exceeding the atmospheric pressure.

The refrigerants R600a, R290 and R1270 belong to the group of media revealing increased combustibility (the lower combustibility limit is lower than 3.5% of the volumetric concentration in air). Moreover, R152a is a combustible medium, which was proved in relevant tests. At lower temperatures, higher pressure is required for the refrigerant to become combustible. That is why these refrigerants should not be mixed with air to examine the leakage flows. The problem of combustibility of the refrigerants and the resultant demand for relevant protection of the installation is an important, but fully realisable issue. It is also noteworthy that R717 (NH_3) is in common use in land cold stores, and even in marine refrigeration plants, despite their health threat and combustibility in certain mixtures with air.

Below given is the classification of the refrigerants R41, R152a, R218, R-227ea, RC318, R600a, R290 and R1270 with the reference to the safety groups of these substances according to prPN-EN 378-1 [3]

Tab. 5. *Classification of selected refrigerants by safety group (Annex E to prPN-EN 378-1)*

Refrigerant	Safety group (PN-EN-378)	Fluid group according to PED	Practical concentration limit[1] (kg/m^3)	ATEL/ODL[2] (kg/m^3)	Combustibility LFL[3] (kg/m^3)	Self-ignition temperature (°C)
R41	4	4	4	4	4	4
R152a	A2	1	0.026	0.14	0.13	455
R218	A1	2	0.44	0.44	-	-
R227ea	A1	2	0.49	0.49	-	-
RC318	4	2	0.81	0.81	-	-
R600a	A3	1	0.0086	0.06	0.043	460
R290	A3	1	0.008	0.09	0.038	470
R1270	A3	1	0.008	0.10	0.040	455

1 - lower combustibility limit,
2 - acute toxicity exposure limit ATEL or oxygen defect limit ODL,
3 - lower combustibility limit ,
4 - missing data (according to PN-EN 378, the standard does not refer to substances without attributed safety group)

CONCLUSIONS

The obtained results reveal that differences up to 35% can be obtained when calculating the TEWI factor for a heat pump with different media used by it. Therefore this factor can be considered an applicable and relatively simple criterion for assessing the performance of refrigerators or heat pumps. The refrigerants which occupy top ranks in this analysis are: **R600a, R152a, R290, R1270 and R227ea**; the results of their comparison are better than those obtained for R22. According to [1], R152a is a long-term substitute for R12 and R22; while R600a is a long-term substitute for R12, and R290 and R1270 are long-term substitutes for R22 and R502.

1. Unfortunately, despite their good properties for air conditioning, wider use of R600a, R152a, R290, and R1270 is limited because of their high combustibility (R152a - group A2, remaining – group A3). These media have a very low TEWI factor, which suggests that they are likely to be used in individual design solutions.
   The problem of protection against the danger resulting from their high combustibility can be solved in many cases using relatively simple design means without excessive rise of costs. In this case controlling the filling of the installation is necessary (it should be done following the regulations of the standard PN-EN 378-1 Annex C, C3). When the device is situated in the open area, it does not create serious threat. R717 (NH_3) is used in land cold stores and marine refrigeration plants.
2. The use of R227ea is also a correct choice, as its TEWI factor is relatively low. However, high value of the GWP factor, equalling 2900, may result, in the future, in prohibition of the use of this medium [6].
3. Refrigerants R41, R218, RC318 are less favourable taking into account the TEWI values. They also have low value of the cycle performance, COP. Another disadvantage of R41 is very low critical temperature, equalling to 44.5°C. Moreover, there are no data on the safety group (the medium is not classified in the standard worked out in 2009!), which may suggest that no company submitted it for classification, or there are no relevant tests to allow this medium to be used. The data are also missing on the safety group for RC318.
4. R218 and RC318 reveal high TEWI factors, they are also the substances with high GWP factor ($GWP_{R218} = 7000$, $GWP_{RC318} = 8700$), which practically eliminates them from wider use.

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