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Critical evaluation of R134a, R1234yf and R744 in passenger car cooling systems

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Abstract

The Montreal Protocol on ozone-depleting substances and the Kyoto Protocol to the United Nations Framework Convention on Climate Change are affecting the refrigeration industry. Both documents have banned the use of substances responsible for ozone depletion and global warming. The automotive industry must keep up with these changes. The design of cooling systems in cars must meet the requirements of new refrigerants.

In addition, changing the production profile of large car companies towards electric and hybrid cars increases this need. This development has a significant impact on the solutions installed in passenger vehicles. The paper presents a critical assessment of R134a, R1234yf, and R744 in passenger car heat pump systems. The possibility of their use in common air conditioning systems with motor drive and in the heat pump of an electric vehicle was presented. The calculation algorithm of the heat pump system has been developed, showing the influence of the physical properties of refrigerants on efficiency during the process of the designed heat pump system. The impact of using new refrigerants in the car production process has been analyzed and commented on. The influence of thermodynamic and ecological properties of refrigerants on the process of designing a heat pump system using a calculation model was described. Types of heat pump in electric cars and a calculation model were presented.

Keywords: R134a, R1234yf, R744, Heat pump, Car, Air-conditioning

1 Introduction

The automotive sector (AS) is an important sector for the European Union (EU) economy, employing more than 8 million people. The electric vehicle is an increasingly important component of the global car fleet [1] The global stock of electric passenger cars reached 3.1 million in 2017, an increase of 57% on the previous year, and BEVs account for two-thirds of the world's electric car fleet according to an IEA report of 2018 [2]. The automotive sector is currently in the middle of a transformation, caused mainly by environmental issues. The electrification of vehicles has become a key trend in the AS, driven by clean energy and climate-change concerns such as support zero-emission vehicles and carbon taxes – intended to reduce greenhouse gasses emissions. One important element of this transformation is air conditioning (AC) systems in electric cars (ECs).

On September 16, 1987, in Montreal, over 160 countries signed a protocol to counteract the degeneration of the ozone layer. The key point of the document was to reduce or totally eliminate refrigerants, which significantly affect the destruction of the ozone layer and increase global warming.

International agreements have significantly affected the automotive industry. The refrigerants used have been subject to restrictions and actions have been initiated to obtain solutions compliant with the regulations. The EU has also introduced F-Gas regulation [3], monitoring and limiting the automotive use of refrigerants.

The car industry over the years has moved away from AC systems using chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HFCFs) and has started introducing hydrofluorocarbons (HFCs). AC systems have been adapted to 1,1,1,2-tetrafluoroethane R-134a after dichlorodifluoromethane R-12. In accordance with the current legal regulations related to the influence of AC refrigerants on the environment the R-134a refrigerant from the CFC group was replaced by the R-134a refrigerant belonging to the HFC group. Subsequent legal regulations, caused by the negative influence of refrigerants on global warming, imposed restrictions on the use of R-134a in AC devices in motor vehicles, mainly due to the high value of the GWP (Global Warming Potential) index.

As a consequence of these restrictions, natural refrigerants seem to be the best solution in the refrigeration industry [4]. The changes and regulations affecting AC systems are driving the development of systems with refrigerants that have a negligible impact on the environment. One alternative to R-134a is R-1234yf belonging to the HFO (hydrofluoroolefin) group. This refrigerant is the subject of numerous studies. According to Gaurav and Raj Kumar [5] the refrigerant mix-

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ture R-134a/R-1234yf/R-1234ze (40%/22%/38%) is only one replacement option for R-134a. This result shows that the interchangeability of R-134a with R-1234yf mixture is possible without any changes in the design of the system. R-1234yf is characterized by a low GWP of 4. This value is 350 times lower than for R-134a. An additional feature of R-1234yf is that the decomposition time of R-1234yf is 11 days. This is a huge advantage over R-134a, whose decomposition time is 13 years [6] Due to this difference AC systems designed for R-134a must be redesigned before the new refrigerant can be used.

Another refrigerant commonly used is carbon dioxide. Carbon dioxide was one of the first refrigerants used in AC. Alexander Twining proposed the use of it in a British patent in 1850 [7]. Due to the appearance of AC refrigerants from CFC and HCFC groups carbon dioxide was used less frequently. Due to their specificity and thermodynamic properties, carbon dioxide was replaced with substances from the CFC and HCFC groups.

In ECs the AC system, which is the most energy demanding auxiliary component, plays a significant role in providing comfort during driving and energy utilization. The paper presents a critical evaluation of R134a, R1234yf. and R744 in cooling systems of passenger cars. The possibility of using them in common AC systems in a car with the motor drive and in the heat pump of the electric vehicle is presented. The influence of use of the new refrigerant in the vehicle industry was analyzed and commented. The thermodynamics and ecological aspects were analyzed.

Table 1: Properties of refrigerants

	R134a	R1234yf	R744	Unit
Formula	CH2FCF3	CF3CF = CH2	CO2	
Chemical Abstracts Service number	811-97-2	754-12-1	124-38-9	
Molecular mass	102	114	44	g·mol -1
ODP	0	0	0	
GWP100	1300a	<1a	1	
Safety classification	A1	A2L	A1	
Critical temperature c	374.21	367.85	304.1	K
Critical pressure c	4.06	3.38	7.37	MPa
Density of liquid	1206 (at 25oCd)	1091.91 (at 0oCd)	1101 (at -37oCd)	kg m-3
Density of saturated stem	8.288 (at 15oCd)	37.92 (at 25oCd)	1.997 (at 0oCd)	kg m-3

2 Description of the refrigerants

Table 1 shows the functional parameters of refrigerants.

[a] IPCC (The Intergovernmental Panel on Climate Change) 5th report, chapter 8 [8]

[b] ANSI/ASHRAE standard 34-2013 (A-non-toxic, 1- non-flammable, 2L- mildly flammable 3 – flammable) [9]

[c] REFPROP (REFerence fluid PROPerties) 9.1 [10]

[d] Calm and Hourahan 2011[11]

R134a was introduced as a substitute for R12 due to its lower ecological harmfulness. Because of the restrictions related to refrigeration systems in 2017, the use of R12 was banned in new AC car systems. This restriction precludes the use of R134a in future AC systems in electric cars too. The gas is stable under normal conditions and does not have flammable properties. It has a higher density than atmospheric oxygen, which means it has the possibility of displacing it in closed areas. It is perceptible in the air by its ether smell and inhalation may result in nausea and dizziness. The factor was used by most companies producing vehicles and competition between manufacturers led to widespread use of the systems in light of their efficiency and weight. The service infrastructure during this period has gained knowledge and experience regarding the systems, which reduces the time of diagnostics and service. New designs of AC systems for R134a factor in vehicles until 2017 reduced all system defects previously encountered. Through competition, the systems have been improved and developed over the years. Many companies supplying elements for AC systems have developed production methods which reduce the failure of the system. The refrigerant self-ignites at 405°C, resulting in harmful hydrogen fluoride. It has an ether fragrance and a low GWP index. Typical methods for producing HFO-1234yf start with 1,2,3,3,3-pentafluoropropene. Hydrogenation of this alkene gives 1,2,3,3,3-pentafluoropropane, which upon heating with an Al-based catalyst undergoes dehydrofluorination [8] In the early 20th century, carbon dioxide was a popular solution in AC systems. After 1940 it was supplanted by synthetic substances. The solution with dry ice was used in other types of devices that keep the temperature low. Due to the low temperature of the critical point, circulation of the refrigerant is supercritical. The first commercial devices with an overcurrent circuit appeared on the market only in 1999, and commercial refrigeration appliances only in 2003 [12] Carbon dioxide has a very low critical temperature, which distinguishes it from the other factors. R744 is characterized by high pressure in the installation from 30 to 130 bar. Such high-pressure forces duly selected wires and increase the sensitivity of the system to unsealing. R744 uses gas coolers that can be used in a heat pump, it is a good alternative to electric vehicles in which the temperature of the battery is often under the control of the AC system. The system forces the gas radiator to be used in a heat pump; carbon dioxide is an odorless gas that does not show flammable properties. R744 is a natural refrigerant with a low potential of creating a greenhouse effect. Carbon dioxide can be obtained by distillation from air, but the method is inefficient. Industrially, carbon dioxide is predominantly an unrecovered waste product, produced by several methods which may be practiced at various scales [13].

3 Comparison of operating parameters of refrigerants

Reasor et al. (Reasor et al. 2010) [14] carried out thermodynamic simulations using various types of refrigerants. The studies carried out included R134a and R1234yf. Indicating that R1234yf has a 40% higher pressure drop in the exchanger than R134a, the authors conclude that R-1234yf may not be as good a replacement for R-134a as is generally assumed. In 2013 Kwang-Li [15] performed tests to determine and compare the heat transfer coefficient in the evaporation process for natural refrigerants and R-1234yf. This experiment showed that of all refrigerants CO2 showed the best heat transfer coefficient. Brown et al. [16] performed simulations in 2002 that compare R134a and R744. They showed that R744 has worse operating parameters in similar conditions. Mota-Babiloni et al. [17] in 2015 conducted an experiment comparing R1234yf and R134a. The test result showed that the internal exchanger clearly improves the efficiency of the system with R1234yf. This is proof of the unquestionably better performance of R134a in a traditional AC system without an internal heat exchanger. At the same time, the values of GWP for the synthetics clearly indicate that natural R744 can be a substitute that meets all restrictions regarding the use of refrigerants. The comparison was made to illustrate the environmental impact of the refrigerants and the differences in performance used in system design.

4 Environmental impact

Policy targeting the negative impact of refrigerants on the environment also sets time periods for the withdrawal of some of these substances. This derives directly from EU law and forms part of a sustainable development policy [18]. In accordance with Regulation (EC) No. 1005/2009 of the European Parliament and of the Council of 16th of September 2009 on substances that deplete ozone, production of coarse HCFC agents will cease in 2020. The limitations on refrigerants are related to indicators determining the impact on the natural environment. ODP Ozone Depletion Potential for R-11 factor for which ODP is 1. Refrigerants and their impact on the environment are determined in accordance with the ODP and GWP indicators. According to the values in Figure 1, the values for all discussed factors are at level 0. Global Warming Potential is the main determinant of changes introduced on the market of refrigerants; R1234yf and R744 have a similar value and currently both meet requirements. As reported [19], it appears that the intermediates used in the preparation of R1234yf are substances from the HCFC group of hydrofluorocarbons, which are controlled substances that have a negative effect on the ozone layer. Substances from the HCFC group are subject to restrictions. Also affecting the legitimacy of choice of the AC refrigerant are substances formed during the decomposition reaction. R1234yf after entering the atmosphere forms trifluoroacetic acid, which is an organic carboxylic acid about 10,000 times more potent than acetic acid. The ISO817 standard indicates two classes of toxicity of refrigerants: low-toxicity and high toxicity. The classes are expressed in the occupational Exposure Limit OEL indicator. The amount of refrigerant during work related to refrigerant systems is determined according to the parameter. According to the information in Tab.**??**, it is indicated that the OEL for compressed refrigerants meets the conditions for low-toxic gases below 400 ppm. At the same time, due to the harmful acid appearing in certain conditions with R1234yf, SAE international in 2007-2009, together with Audi, BMW, Chrysler, Daimler, Ford, GM, Renault, Jaguar Land Rover, and Toyota carried out research on the combustibility of the refrigerant during operation and accidents. No ignition was found under the test conditions or during an accident at a speed of 70 km / h. The average ignition temperature for R1234yf is 405°C. Is not possible to exclude the occurrence of the said temperature during an accident. R744 is a natural factor that is nontoxic and its increased level in the air is manifested by the disturbance of vital functions. At the same time, the level of carbon dioxide already in low concentrations

Table 2: Environmental properties

Refrigerant	R134a	R1234yf	R744
Combustibility	1	2L	1
Ignition temp	-	405oC	-
Flammability limit	YES	6.2-12.3%	YES
Safety class	A1	A2L	A1
ODP/GWP	0/1400	0/4	0/1

affects the level of comfort and concentration, which is why CO_2 level sensors installed in cars to monitor air quality can also perform an additional warning function after the possible unsealing of an AC system using R744 refrigerant.

5 Industry potential

Air conditioning systems in vehicles can be divided into three categories:

-currently used - available in new vehicles -future solutions

Currently used vehicles have installations for refrigerant R134a and R1234yf and theoretically R744 (Daimler offers a new model with R744). Adapting old AC systems to different refrigerants requires modifications in the basic system by specialists. The automotive industry does not provide that kind of modification, meaning that the AC system is designed for one kind of refrigerant. Companies producing elements of AC systems have guidelines from the manufacturer regarding not only the parameters of the system but also specific requirements for working conditions provided for only one refrigerant. Requirements for AC pipe systems are for example related to resistance to working pressure and the effect of vibrations from the internal combustion engine. In electric vehicles requirements for an AC loop are created to resist the lowest level of vibration but also have higher noise requirements. That creates differences in every type of refrigerant and also the type of vehicle. Currently, the design of AC systems is carried out simultaneously with the design of other systems in vehicles. This solution allows effective use of the working space in vehicles, also limiting the possibility of future changes. From the economical point of view a future solution with one type of refrigerant is the best way to lower the cost of validation. The fact that AC systems with R744 are now available in new vehicles means the technology has completed the validation process and is safe for use. The new AC systems are offered only in high-value vehicles, but this is the first step to implementing this technology in other models. Future solutions for combustion engine vehicles or electric vehicles with one type of refrigerant would reduce the cost of validation.

6 Heat pump systems

Currently, various types of heat pump systems are used. The heat pump used in the Nissan Leaf (Fig. 1.) is a set of three heat exchangers, two expansion valves (I, III), a three-way valve (II), a bypass valve (II), an airflow blocker and an electric AC compressor. During operation on hot days, the internal condenser is bypassed, the heating circuit expansion valve (IV) is bypassed by opening the bypass valve, and the external heat exchanger works in condenser mode.

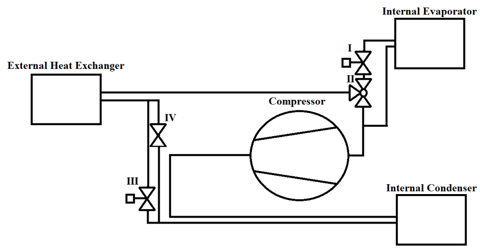

Figure 1: Nissan Leaf heating-cooling system diagram (I III expansion valve, II three-way valve , IV bypass)

During cold days, the airflow through the internal condenser heats the passenger compartment. The expansion valve (I) and internal evaporator are omitted by setting the three-way valve (II). The bypass valve is closed in parallel, which causes the refrigerant to flow through the expansion valve. When the humidity level is increased, it is possible to run the evaporator and the internal condenser at the same time using a three-way valve and a bypass valve.

The solutions used differ from one company to another, the American company Tesla uses a different type of system in its electric vehicles. During cold days, heat is taken from the fluid cycle of electric motors and electronics. This heat can be supplied to the cabin circulation, bypassing the liquid at higher temperatures to the circulation using a three-way valve (II). This allows you to control the temperature of the engines and electronics in the electric car. On hot days, the refrigeration circuit increases its efficiency and exchanges heat with the cabin circuit in the heat exchanger. Mitsubishi Motors Corporation has introduced a system consisting of a refrigeration cycle, en-

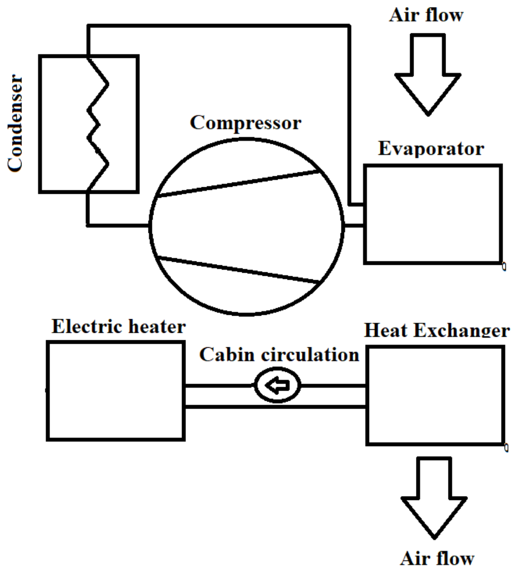

Figure 2: Tesla Model S heating-cooling system diagram (I II three-way valve)

gine cycle, and passenger compartment circuit. During hot days, the heat in the cabin is dissipated in the evaporator. On cold days, an electric heater in the cabin circuit is used.

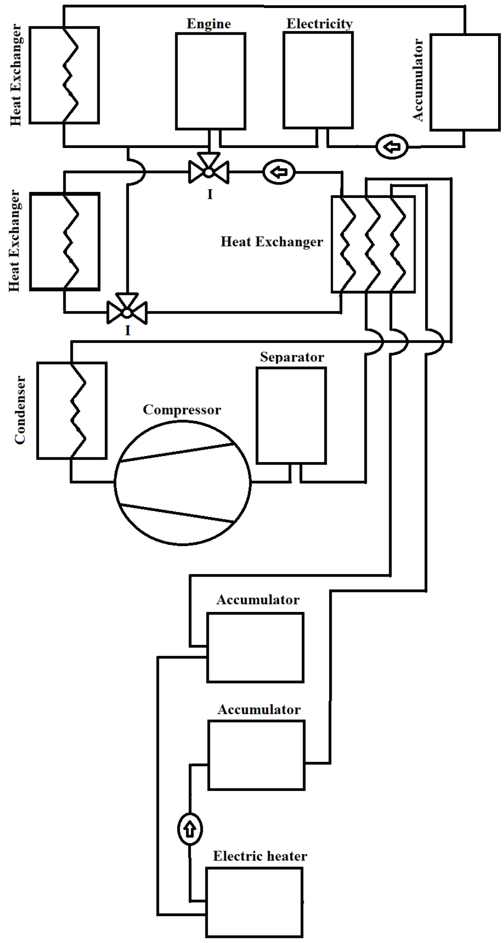

Figure 3: Mitsubishi i-MIEV (I three-way valve)

7 Heat pump calculation methodology

The calculation conditions used when designing the heat pump are in each case matched to the refrigerant, the type of vehicle and the conditions in which it will be operated The methodologies presented below should be interpreted individually by selecting the appropriate parameters. This model was presented for a theoretical circuit consisting of a compressor, evaporator, expansion valve, and condenser. Properly adopted points correspond to:

I. The evaporated refrigerant in the gas phase in front of the compressor

II. The compressed refrigerant in the gas phase with increased pressure at the exit from the compressor

III. The condensed refrigerant in the liquid phase at the outlet of the condenser

IV. Refrigerant before the evaporator

$$h_I = f(X_I T_I)$$

where: h_I - enthalpy in point I[kJ/kg], X_I - degree of dryness of the factor in point I [-], T_I-temperature at a point I [°C]. The equation shows that Enthalpy at the point I. The enthalpy in point II and II is calculated in the same way as in point I

$$h_{II} = h_I + \frac{h_{II_s} - h_I}{\eta_{I_s}}$$

where: h_{II} - enthalpy in point II[kJ/kg], h_{IIs} - enthalpy in point II for isentropic compression [kJ/kg], h_{is} compressor internal efficiency [-].

$$h_{IV} = f(P_I h_{III})$$

where: h_{IV} - enthalpy in point IV[kJ/kg], h_{III} - enthalpy in point III[kJ/kg], P_I -pressure at point I [MPa]. In the next stage, the formulas for calculating the heat stream transferred in each heat exchanger are presented.

$$\dot{Q}_{cz} = \dot{m}_{cz} \times (h_{II} - h_{III})$$

where: $\mathbf{Q_{cz}}$- heat flow transferred in the condenser [kW], $_{cz}$- mass stream of circulating refrigerant[kg/s].

$$\dot{Q}_p = \dot{m}_{cz} \times (h_I - h_{IV})$$

where: $\mathbf{Q_p}$ - heat flow transferred in the evaporator [kW]. The formulae for the evaporator and condenser air streams determined from their mass streams are presented below.

$$\dot{Q}_s = \dot{Q}_{a,cond} = \dot{m}_{a,cond} \times c_{p,a}(T_{aim} - T_{ot})$$

where: $\mathbf{Q_{a,\ cond}}$ - heat flux of the air stream supplied to the condenser [kW], $_{a,\ cond}$ - mass stream supplied to the condenser [kg/s].$c_{p,\ a}$ - specific heat of air [kJ/kgK], T_{aim}- the desired temperature of air supplied to the cabin [°C]. T_I- ambient temperature [°C]. The following parameters are required to calculate the evaporator energy and compressor power.

$$\dot{Q}_p = \dot{Q}_{a,evap} = \dot{m}_{a,evap} \times c_{p,a}(T_{ot} - T_I)$$

where: $Q_{\ a,evap}$ - heat of the air stream supplied to the evaporator [kW], $_{a,evap}$ - mass stream supplied to the evaporator [kg/s].

$$\dot{Q}_{compr} = \dot{m}_{cz} \times (h_{II} - h_I)$$

where: $\mathbf{Q_{compr}}$ - - heat flux of the air stream supplied to the evaporator [kW]. The vehicle's low ambient temperature heating mode is supported by electric heaters that increase the air temperature, minimizing the airflow. When the ambient temperature at a point I is higher, the air supply to the evaporator is blocked and the refrigerant is heated by an electric heater. The heat of the air stream is supplied to the evaporator [kW].

$$\dot{Q}_{heater} = \dot{m}_{a,evap} \times c_{p,a}(T_{min} - T_{ot})$$

where: $\mathbf{Q_{heater}}$ - heat flux of the air stream supplied to the evaporator [kW], T_{min} - minimum required air temperature to the evaporator[°C] Formula for the COP factor during heating mode:

$$COP_{heat} = \frac{\dot{Q}_{a,cond} + \dot{Q}_{heater}}{\dot{Q}_{compr}}$$

The formula for the COP factor during cooling mode:

$$COP_{cooling} = \frac{\dot{Q}_{a,evap}}{\dot{Q}_{compr}}$$

The computational methodology is based on input data. The parameters of refrigerants such as R134a, R1234yf, and R744 are based on reliable materials. Accordingly, the multitude of situations related to temperature, humidity and the speed of movement increases the number of conditions that should be simulated. The algorithm represents the design aspects to be taken into account when selecting the appropriate refrigerant to be used in AC systems due to the system efficiency factor. Differences in the functional parameters of the individual factors significantly affect the COP of the designed system. Electric cars already meet the environmental requirements, which augurs well for their future share in the automotive market. The heat pump system clearly meets the requirements for maintaining air parameters in the passenger compartment. All additional heat pump functions will affect overall performance accountability. A heat pump with an additional system to control the temperature conditions of the battery will have valves and a pump, increasing the weight of the vehicle and using energy. A multitude of solutions will also be associated with an increase in the number of valves and lines filled with medium. All these elements will add to elements that negatively affect the range of the vehicle.

8 Conclusions

Vehicles, regardless of the manufacturer, have solutions that fall into the group of heat pumps. Whatever the type of system, the principle of operation is similar. Due to current regulations, the refrigerant that is widely used at present is R1234yf. A car's heat pump performs many tasks and its operation significantly affects the range of the vehicle. Current systems have an increased level of complexity compared to systems used only for cooling. The presented calculation method has many stages. At the calculation stage, real input data must be available. Due to the mechanical complexity of the systems and various climatic conditions, it is difficult to enter input data correctly into the calculations. In light of the solutions used at present, it is advisable to validate calculations in real conditions under different climatic conditions for the current refrigerant. The validation process should be based on the validation of the calculation assumptions made during the design process and should take into account the impact of the complexity of the system in the overall energy accounting of the system to create appropriate combinations of input parameters for heat pumps designed to work on R744.

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