Chapter 52
The Impact of Refrigerants on the Efficiency of Automotive Air-Conditioning System

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Abstract Over 95% of new cars in the EU have air conditioning which significantly contributes the global warming by emitted flue gases, and of refrigerants with a high global warming potential (GWP). The paper analyzes automotive conditioning systems in terms of energy efficiency. Currently, in these systems the most popular refrigerants are R134a (GWP = 1430) and R1234yf (GWP = 4). There are some controversies related to the impact of R1234yf on human health, especially during road collision and depletion of the system. The tendency in automotive air-conditioning systems is to shift from refrigerants that were safe for man but not to the environment, on ones that are pro-ecological but can be dangerous to human health and life. The article also presents an overview of the most popular synthetic refrigerants used in automotive air conditioning over several decades in Europa, like R12, R134a, and currently used in the new systems—R1234yf. Due to the environmental impact of refrigerants, the EU imposes tougher requirements for these substances. European Commission Directive 2006/40/EC provides that from January 1, 2017, only refrigerants with GWP lower than 150 may be used in air-conditioning system of new cars. This requirement is now met by synthetic refrigerant R1234yf and natural one R744 (carbon dioxide). The environmentally friendly (GWP = 1) and not posing a threat to humans, R744 seems to be a future-proof alternative to refrigerant R134a.

52.1 Introduction

Substantial automotive air conditioning can be already seen in the solutions from 1930, when first special water coolers were installed in vehicles. They allowed the water to evaporate, which in turns allowed to lower the air temperature in passenger compartments. These devices were mounted outside the vehicle and cold air was forced inside through the open window [1]. Currently, over 95% of new cars in the EU have air conditioning which significantly contributes the global warming by

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emitted flue gases, and of refrigerants with a high global warming potential (GWP). Mobile air conditioning (MACs) has three separate impacts on global warming: (1) the effects of refrigerant inadvertently released to the atmosphere from collisions; (2) the efficiency of the cooling equipment due to the carbon emission from burning fuel to power the system; (3) the carbon emission from burning the fuel to transport the system [10]. The environmental warming impact of refrigerants is being studied by many scientists, including [4, 5, 10] and others. To reduce emission of fluorinated greenhouse gases from mobile air-conditioning systems, the European Directive on MACs introduces a gradual ban on these gases in passenger cars [7].

Some of the used refrigerants may have bad influence on human health. Exposure of vehicle occupants can occur when refrigerant enters passenger compartments due to sudden leaks in air-conditioning systems, leaks caused by collisions, or leaks following services [12]. The largest number of exposures of vehicle occupants is reported for leaks caused by accidents, and the second one for leaks following services [12].

A MACs in its construction is not so different from usual refrigeration system, which can be found even in domestic refrigerators or heat pumps. The only differences between them are in the way the compressor is driven, and most importantly, flexible rubber connections instead of fixed ones, which results from changing operating conditions. A mobile air-conditioning system is exposed to large vibrations which result from engine operation and vehicle movement. In both cases, the compressor in a closed compressor circuit compresses the refrigerant, which gives heat to the environment and takes it from the car cabin or, in the case of a refrigerator, from its interior. The thermodynamic transformations of the refrigerant are exactly the same. They are designed to take away or deliver heat to passenger compartments. The refrigerant itself is a low-boiling substance, which means its boils at a temperature much lower than 0 °C.

52.2 Refrigerants Used in MACs

Refrigerants are evaluated in many aspects. Among others, they are classified because of: (1) origin (natural/synthetic refrigerants); (2) composition (homogeneous/multi-component refrigerants). There is also introduced systematics of these substances in terms of their chemical composition includes: CFC—chlorofluorocarbon; HCFC—hydrochlorofluorocarbon; HFC—hydrofluorocarbon; HFO—hydrofluoroolefin; HFE—hydrofluoroether; FC—fluorocarbon; HC—hydrocarbon. One of the most important divisions of refrigerants is the division due to their flammability and toxicity [9]. These substances are called controlled ones due to that their emission causes the breakdown of ozone in the stratosphere and contribute to the greenhouse effect incensement. In order to assess refrigerants in this respect, environmental indicators were introduced [6, 9]: ODP—ozone depletion potential, GWP—global warming potential, and TEWI—total equivalent warming impact. The impact of the operation of automotive air-conditioning systems on global warming, based on the analysis of the TEWI index can be found, among others, in [14]. The TEWI index determining the relative importance of the direct and indirect effects is used to assess the effect of air-conditioning system on global warming throughout its operation as the GWP function [9].

The first synthetic refrigerant used in automotive air conditioning was refrigerant R12 [6]. In late 1973, Rowland and Molina put forward a thesis on the effect of CFC compounds emission on the ozone depletion [2]. Subsequently, pursuant to the Montreal Protocol (1987) concerning, inter alia, actions to protect the ozone layer, it was decided to remove refrigerant R12 from automotive refrigeration systems. For this reason, since 1994, refrigerant R134a has been used as R12 alternative. Nowadays, refrigerants used in MACs must strictly have ODP index equal 0. Additionally from the beginning of 2017 only refrigerants with GWP lower than 150 may be used in air-conditioning system of new cars [7]. For this reason, the refrigerant R134a due to its very high GWP equal 1430 has to be replaced. One of the alternative refrigerants is R1234yf. It belongs to HFO group, has no impact on the ozone layer, and is characterized by a low GWP index. Table 52.1 compares the refrigerants most commonly used in MACs over the last several decades.

As is clear from the research works [13, 15, 19] on the refrigerant R1234yf, it is environmentally friendly but can be dangerous for people's health and life. Such a situation may occur especially during leakage of this substance due to unsealing of the air-conditioning system [12]. During the frontal collision of the car, the heat exchanger (condenser/evaporator) located in the front of the car is most exposed to damage. The R1234yf gas vapors may be exposed to hot surfaces or an open flame. The side-effect of the decomposition of R1234yf under the influence of heat is the release of hydrogen fluoride, which in combination with water, e.g., fire extinguishing water, forms hydrofluoric acid. Hydrogen fluoride irritates the respiratory system, has a sharp smell, easily penetrates into the body without feeling pain, also through the skin, leading to the death of a human, unless it is subjected to immediate rescue. Penetrating from the engine compartment through the ventilation system into the interior of the car, it easily digests elements made of plastic and even glass [11].

52.3 Research Method—Thermodynamic Calculations of Cooling Circuits for Synthetic and Natural Refrigerants

The most popular refrigerant used in mobile air-conditioning systems is still R134a. It has been replaced the withdrawn from use and production of R12 refrigerant due to R12 significant impact on the ozone layer and contributing to the greenhouse effect. Currently, refrigerant R134a is withdrawn from car air conditioning. Alternative refrigerants that meet the index GWP index <150 [7] and there are technical reasons to use them in a car air-conditioning system include:

Table 52.1 Selected properties of refrigerants used in MACs [3, 8]

Properties	R12 (ISCEON 12)	R123a (Suva 134a)	R1234yf (Opteon yf)
Chemical formula	CCl_2F_2	$C_2H_2F_4$	$C_3H_2F_4$
Molar mass, g/mol	120.91	102.03	114
Boiling point (1.013 bar), °C	−29.75	−26.10	−29.4
Critical temperature, °C	111.97	101.1	95
Critical pressure, bar	41.4	40.6	34
Stream pressure (25 °C), bar	6.5	6.6	6.7
Critical density, kg/m^3	565	511.9	478.01
Specific heat of liquid (25 °C), kJ/kg/K	1.00	1.44	1.39
Specific heat of stream (25 °C), kJ/kg/K	0.606	0.85	0.91
ODP index, –	1	0	0
GWP index, –	10,200	1430	4
Temperature of self-ignition, °C	–	>750	405
ATL index (atmospheric life time), years	130	16	0.03
Concentration of explosion limit in the air, %	–	–	6.2–12.3
Preferred oil	PAG[a]	PAG[a], POE[b]	PAG[a], POE[b]
Security group	A1	A1	A2L

[a]Poly alkaline glycol
[b]Polyolester

– R1234yf with GWP index equal 4;
– R744 (CO_2) with GWP index equal 1;
– R152a with GWP index equal 142;
– R290 (propane) with GWP index equal 3;
– R600a (isobutene) with GWP index equal 3.

The value of GWP index for the refrigerant R12, according to various estimates, is higher than 10,000, whereas for the refrigerant R123a is equal 1430.

For the thermodynamic analysis of cooling circuits, synthetic refrigerants R12, R134a, R152, and R1234yf were selected. Energy software [16, 18] were used to calculate the energy efficiency of refrigeration systems (MACs). Thermodynamic calculations were carried out for the same operating conditions of the device, assuming the following assumptions:

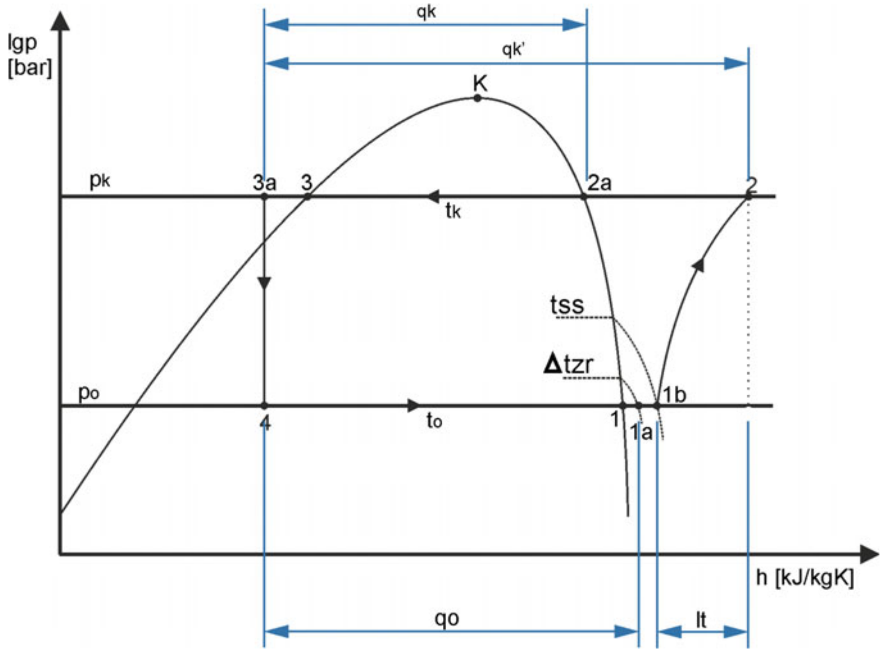

Fig. 52.1 Superheated circulation with sub-cooling in the lgp–h system

- external air temperature, $t_p = 30$ °C;
- air temperature in the vehicle cabin, $t_{\text{kab}} = 20$ °C;
- evaporation temperature of the refrigerant, $t_o = 10$ °C;
- condensing temperature of the refrigerant, $t_k = 40$ °C;
- overheating on the expansion vale, $\Delta\text{tzr} = 5$ K;
- isentropic efficiency of the compressor, $\eta_{\text{is}} = 0.7$;
- suction temperature of the compressor, $t_{\text{ss}} = 18$ °C;
- cooling capacity, $Q_o = 3$ kW;
- cooling of the liquid medium in the condenser, $t_d = 5$ K.

Figure 52.1 shows the most commonly used circuit in this type of systems, superheated with internal sub-cooling.

The unit cooling capacity determines the relationship:

$$q_o = h_{1a} - h_4 \tag{1}$$

The individual compression work is given as:

$$l_t = h_2 - h_{1b} \tag{2}$$

The unit efficiency of the condenser (the total heat given) describes the formula:

$$q_{kr} = h_2 - h_{3a} \tag{3}$$

The theoretical refrigeration efficiency coefficient of the circulation is given as:

$$COP_{CH} = q_o / l_t = Q_o / N_t \tag{4}$$

Theoretical power of the compressor motor determines the relationship:

$$N_t = \dot{m}\, l_t \tag{5}$$

Mass refrigerant stream describes the formula:

$$\dot{m} = Q_o / q_o \tag{6}$$

Proper heating capacity (condenser power)

$$Q_k = \dot{m}\, q_k \tag{7}$$

Natural refrigerants were also analyzed: R290 and R600a. The calculations were carried out using analogous methodology as in the case of synthetic refrigerants.

52.4 Results and Discussion

Results of calculations in the form of comparison of synthetic refrigerants R12, R134a, R152, and R1234yf in terms of system operation is presented in Table 52.2. As can be seen from the results, refrigerant R152a shows a similar level of energy efficiency and seems to be a good alternative to the withdrawn refrigerant R134a. Both refrigerants are characterized by high energy efficiency, the working pressures in the system are similar. From the point of view of mass flow rate, steam density and, what follows, pressure drops in the flow, it is more beneficial [17].

Results of calculations in the form of comparison of natural refrigerants R290 and R600a in terms of system operation are presented in Table 52.3. The refrigerant R744 (CO_2) works in supercritical circulation, which does not allow for exact comparison of system operation parameters with those working in the area of wet steam. It is worth noting, however, that some experimental works indicate that the installation with CO_2 is more effective than currently used installations with R134a, while these tests are not equivalent due to the different constructions of the analyzed solutions [14].

The obtained results confirm that natural refrigerants as R290 and R600a are an energetically justified alternative to the refrigerant R134a. Both propane and isobutene demonstrate high energy efficiency in the analyzed range of variability of the mobile air-conditioning system operation parameters.

Table 52.2 Comparison of synthetic refrigerants in terms of system operation

Properties	R12	R134a	R1234yf	R152a
q_o, kJ/kg/K	123.5	159.7	134.0	257.2
l_t, kJ/kg/K	21.8	27.8	25.7	43.9
q_{kr}, kJ/kg/K	134.5	170.3	142.1	269.0
$q_{\mathrm{kr}'}$, kJ/kg/K	150.1	190.3	162.7	304.5
$\dot{m}$, kg/s	0.024	0.019	0.022	0.012
N_t, kW	0.53	0.52	0.57	0.52
Q_k, kW	3.27	3.20	3.13	3.23
$\mathrm{COP_{CH}}$, –	5.66	5.77	5.26	5.77

Table 52.3 Comparison of natural refrigerants in terms of system operation

Properties	R290	R600a
q_o, kJ/kg/K	301.2	295.1
l_t, kJ/kg/K	51.3	55.1
q_{kr}, kJ/kg/K	320.4	330.6
$q_{\mathrm{kr}'}$, kJ/kg/K	355.8	354.1
$\dot{m}$, kg/s	0.01	0.01
N_t, kW	0.51	0.55
Q_k, kW	3.19	3.31
$\mathrm{COP_{CH}}$, –	5.88	5.45

The disadvantage of refrigerants from the group of hydrocarbons is their flammability. For this reason, they are classified in the A3 safety group. Refrigeration equipment filled with these substances is subject to explosion-proof regulations, and construction requirements are contained in relevant standards (EN 378, DIN 7003).

52.5 Conclusions

Refrigerants used in automotive air-conditioning systems are classified as controlled substances. This means that their production, distribution, and leakage to the atmosphere should be constantly monitored. As demonstrated by known theoretical analyses and experimental studies, new synthetic factors meet environmental requirements, but in some cases show low energy efficiency. In addition, their impact on human health and life is often neglected. Currently, the EU's tightening requirements force manufacturers to look for refrigerants that, in addition to neutral behavior in relation to the environment, will also be safe in operation.

The European Union aims to minimize the negative impact of cooling, heating, and air-conditioning installations on the natural environment. This is also evident in the case of automotive air-conditioning systems in which from January 2017 only refrigerants with GWP indicators not higher than 150 may be used [7].

The study was focused on properties evaluation of synthetic and natural refrigerants that could be used as alternative refrigerant for R134a one. There were taken under consideration refrigerants: from synthetic group R1234yf and R152a, and from natural group R290 and R600a. All refrigerants were compared to the base ones: R12 and R134a. As the analysis showed, the refrigerant R152a seems to be more favorable in terms of energy efficiency as the refrigerant R134a than R1234yf. Its energy efficiency with the assumption made is higher than R1234yf by about 9%. In relation to the refrigerant R134a, any change in efficiency is noticed, whereas the mass flow of refrigerant allows the selection of a smaller compressor. Unfortunately, the flammability of the refrigerant R152a at least for the moment eliminates it from general use.

Both isobutene (R600a) and propane (R290) show higher efficiency compared to the refrigerant R1234yf, by approx. 3% and by approx. 12%, respectively. Unfortunately, their flammability is also an obstacle here. Initially, it did not meet with the approval of representatives of motor vehicles companies, although it is strongly promoted by the European Union. In addition, many studies confirm its negative impact on human health and life. This objection resulted in a work on alternative refrigerants that meet the EU directives. Such alternative refrigerants include, for example, R744—carbon dioxide. Currently, in the European Union, but not only, cars containing this factor in the air-conditioning system are used. As research has shown, it is completely safe for people's health and life, even when it is leaking. Installations using CO_2 as a refrigerant show a similar COP value with installations using R1234yf, taking into account the same operating parameters. The advantage is that it is not necessary to dispose of the refrigerant R744 when scrapping the vehicle. The disadvantage is undoubtedly higher (about 10 times) system pressure (supercritical circulation). However, it does not cause problems related to process control.

In addition to CO_2, R600a (isobutene) and R290 (propane) are also interesting alternative refrigerants for mobile air-conditioning systems in terms of ecology and price. However, these are flammable substances (belonging to the A3 safety group) and therefore require different installation designs and additional safeguards.

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