

TECHNICAL UNIVERSITY OF CIVIL ENGINEERING BUCHAREST
FACULTY OF BUILDING SERVICES ENGINEERING
Department of Thermotechnics and Thermal Equipment

DOCTORAL THESIS

SUMMARY

**RESEARCH REGARDING THE CONTRIBUTION OF
REFRIGERATION, AIR CONDITIONING AND HEAT
PUMP SYSTEMS TO GLOBAL WARMING**



PhD Student

Eng. Mioara Vinceriuc

Scientific Coordinator:

Prof. Eng. Grațiela – Maria Țârlea PhD

BUCHAREST

2021

ACKNOWLEDGMENTS

First of all, I would like to thank my scientific coordinator, Prof. Dr. Eng. Grațela Maria Țârlea, for her understanding and pedagogical tact she has shown for more than 15 years, since I first began my studies. Her high academic professionalism, patience, understanding, as well as shared knowledge, constant encouragement and guidance helped me in my successive higher education stages, including all stages in preparation of the doctoral thesis. She provided an important contribution in developing and completing this work.

Under the guidance of Prof. Dr. Eng. Grațela Maria Țârlea, I participated in numerous scientific events both in the home country and abroad, where I presented scientific papers subsequently published in conference volumes (handbooks or workbooks) or in specialized journals.

At this point in the review, I would also like to thank Prof. Dr. Eng. Dragoș Hera, and Prof. Dr. Eng. Ivan Gabriel, as well as the entire teaching staff within the Department of Thermotechnics and Thermal Equipment for expressing their points of view on this subject .

Thanks also to the following professors : Prof. Dr. Eng. Valeriu Damian, Prof. Dr. Eng. Florin Baltaretu. Assoc. Prof. Dr. Eng. Nicolae Iordan, for their dedicated time and availability to discuss my doctoral thesis. Klass Bergl f from the Royal Institute of Technology in Stockholm was also of particular importance in this thesis for the moral support given, the knowledge shared and the very useful advice he gave me.

I thank the general directors Eng. Nicuta Dumitru and Eng. Valeriu Timofan for the valuable engineering solutions and the technical support provided in the conception, design, assembly, commissioning and monitoring of the experimental stand within the Colentina Laboratory of the Technical University of Civil Engineering Bucharest.

I also thank the Romanian General Association of Refrigeration, CLIMALIFE, LINDE, HOVAL companies without which the realization of the experimental stand and obtaining many of the scientific results for this work would not have been possible, as well as to Mr. Constantin Teodor, Mrs. Enik  Beke, for sharing their knowledge with me. Their recommendations were extremely beneficial.

Last but not least, I want to thank colleagues Eng. Ion Zabet, Eng. Valentin Draghici, Stefan Valentin Gagea, Eng. Geol. Dr. Galina Prica and my closest friends, for the support and understanding provided throughout the doctoral thesis. I also thank the late Prof. Emeritus Dr. Eng. Nicolae P. Leon chescu, Dr. Honoris Causa and the late Prof. Emeritus Dr. Eng. Dumitru Teodor Dorin Mateescu, who supported me morally and encouraged me to complete this doctoral thesis. I also want to thank Mrs. Silvia Rusanescu who was by my side and supported me morally throughout the doctoral program.

In closing, it has been an honor to be able to complete my work on this subject: I could not have done it without the support of family and friends. It is with my deepest gratitude that I would like to acknowledge those who have helped me achieve my destiny. In chronological order, my parents: Elena and Dorin Vinceriuc, Daniel Radu, Prof. Math. Georgeta Zamfir, Mihaela Petrescu and again Prof. Dr.Eng. Grațela Maria Țârlea who has been my master's degree coordinator and the scientific coordinator of doctoral studies and doctoral thesis. I hope that the Good Lord will help me to reward them, through my professional results, for the generosity, skill, dedication, and patience with which they have guided me in the subtle process of human and professional education and training, of fulfillment and perfection for the career which is carefully built, with sacrifice and hard work.

Eng. Mioara Vinceriuc

TABLE OF CONTENTS

INTRODUCTION	3
CHAPTER 1. CURRENT STATE OF SCIENTIFIC RESEARCH IN THESIS’ DOMAIN	4
CHAPTER 2. THEORETICAL BASES	5
CHAPTER 3. MATHEMATICAL SIMULATION	7
CHAPTER 4. EXPERIMENTAL RESEARCH AND VALIDATION	15
CHAPTER 5. GENERAL CONCLUSIONS AND PERSONAL CONTRIBUTIONS	22
BIBLIOGRAPHY	25

INTRODUCTION

The content of the doctoral thesis

The study on refrigeration systems in the doctoral thesis was made at the Technical University of Civil Engineering of Bucharest (U.T.C.B) - Colentina Laboratories Complex. The chosen topic is aiming to contribute to the theoretical basis and practical research in terms of development and use of ecological refrigerants (AF). The thesis, entitled "**Research on the contribution of refrigeration systems, air conditioning and heat pumps to global warming**", considers the implementation of EU legislation in the field of refrigeration systems, heat pumps and air conditioning. The ecological refrigerants (AF) proposed in this scientific thesis are chemicals obtained by mixing in different proportions of various current ecological refrigerants with one or more natural or synthetic substances that have zero values of ozone depletion potential (ODP) and low global warming potential (GWP).

This work considers the optimization of the TEWI factor on the domain of application of artificial cold (heat pumps, industrial, air-conditioning).

Results from twelve years of studies in the domain of AF have been published in over 50 articles and papers, featured at conferences, exhibitions and workshops at the national and international level.

❖ Objectives and approaches:

- ❖ **The general objective** → performing scientific research, realised in order to identify new solutions to reduce greenhouse gas emissions

→ performing experimental validations of theoretical approach, for various refrigerants

- ❖ **Primary objective** → the study of refrigeration systems for both an ecological point of view and of energy efficiency

❖ Secondary objectives

→ Realisation of an experimental stand - heat pump designed to determine the performance of the refrigeration systems that can operate with R134a, MV3T, MV3TN in the Atmosphere Protection Laboratory, Colentina Laboratory Complex within the Technical University of Civil Engineering Bucharest.

→ Analysis of the current state of research in the domain of the ecological refrigerants which can be used in refrigeration systems;

→ Creating diagrams and tables with thermodynamic properties of the proposed refrigerant mixtures MVIZ1, MVIZ2, MVIZ3, MV3T and MV3TN;

→ Determining the equations for mixtures state;

→ Development of a new domain of research in the Faculty of Building Services Engineering of UTCB - in the field of refrigerants;

→ Analysis of several variants of refrigeration systems with various refrigeration fluids and proposals of new energy efficient and ecological technical solutions;

→ Use of high-performance simulation programs for the purpose thesis research;

CHAPTER 1. CURRENT STATE OF SCIENTIFIC RESEARCH IN THESIS' DOMAIN

In the last ten years, a lot of research has been done in the field of AF, at international level (see centralizing table), taking into consideration the severe restrictions stipulated by law: Kyoto Protocol, Regulation (EU) 517/2014, Paris Agreement / 2015, Kigali Amendment / 2016 / Montreal Protocol.

	❑ January 1, 2019 the Kigali amendment imposed regulations to reduce the production and usage of hydrofluorocarbons (HFCs), greenhouse gases (temperature increase 0.4°C) ❑ all countries signing the Montreal Protocol agreed to phase out HFCs by more than 80% over the next 30 years (replacing environmentally friendly alternatives). ❑ Kigali amendment (elimination of up to 80 billion tonnes of CO₂ emissions by 2050) ❑ Significant contribution to the objective of the Paris Agreement to limit the increase in global average temperature to a maximum of 2°C
---	---

Centralizing table with the latest research

RESEARCHERS	ARTICLE NAME / REFRIGERATION SYSTEM	STUDIED REFRIGERANTS HFC-134a, HFO-1234yf, MIXTURE ^a
1a	2a	3a
Sofia K. Mylona, Thomas J. Hughes, Amina A. Saeed, Darren Rowland, Juwoon Park, Tomoya Tsuji, Yukio Tanaka, Yoshio Seiki, Eric F. May, 2019 ^a	Thermal conductivity data for refrigerant mixtures containing R1234yf and R1234ze(E) ^a	R1234yf, R-1234ze(E) ^a
Leandro Pereira, Clebson Humia, Ali Khosravi, Rémi Revellin, Jocelyn Bonjour, Luiz Machado, Juan J. Garcia Pabo, 2019 ^a	A study on the fluid refrigerant charge in a two-phase mechanically pumped loop system using R134a and R1234yf ^a	R1234yf, R134a ^a
Giovanni A. Longo, Simone Mancini, Giulio Righetti, Claudio Zilio, 2019 ^a	R1234yf and R1234ze(E) as environmentally friendly replacements of R134a: assessing flow-boiling on an experimental basis ^a	R1234yf, R-1234ze(E), R134a ^a
Saif ZS, Al Chafri, Darren Rowland, Masoumeh Akhfaei, Arash Arami-Niya, Martin Khamphasith, Xiao Xiong, Tomoya Tsuji, Yukio Tanaka, Yoshio Seiki, Eric F. May, Thomas J. Hughes, 2019 ^a	Thermodynamic properties of hydrofluoroolefin (R1234yf and R1234ze(E)) refrigerant mixtures: Density, vapour-liquid equilibrium, and heat capacity data and modelling ^a	R1234yf, R-1234ze(E) ^a
Catherine C. Sampson, Mobolaji Kamson, Matthew G. Hopkins, Paul L. Stanwix, Eric F. May, 2019 ^a	Dielectric permittivity, polarizability and dipole moment of refrigerants R1234ze(E) and R1234yf determined using a microwave re-entrant cavity resonator ^a	R1234yf, R-1234ze(E) ^a
Li Zhaoxua, Liang Kun, Jiang Hanying, 2019 ^a	Thermodynamic analysis of linear compressor using R1234yf ^a	R1234yf, R134a ^a
F. Illán-Gómez, J. R. García-Cascales, 2019 ^a	Experimental comparison of an air-to-water refrigeration system working with R134a and R1234yf ^a	R1234yf, R134a ^a
Zhaohua Li, Kun Liang, Hanying Jiang, 2019 ^a	Experimental study of R1234yf as a drop-in replacement for R134a in an oil-free refrigeration system ^a	R1234yf, R134a ^a
Jaime Sieres, José Manuel Santos, 2018 ^a	Experimental analysis of R1234yf as a drop-in replacement for R134a in a small power refrigerating system ^a	R1234yf, R134a ^a
Gaurav and Raj Kumar, 2018 ^a	Thermo-economic analysis of environmental friendly refrigerant mixtures for replacement of R134a ^a	R1234yf, R134a, R600a, Reco1, Reco2, Reco3 ^a
Gaurav and Raj Kumar, 2018 ^a	Sustainability of Automobile Air-Conditioning System Using Refrigerant R1234yf Instead of R134a ^a	R1234yf, R134a, R744 ^a
Zhaofeng Meng, Hua Zhang, Mingjing Lei, Yanbin Qin, Jinyou Qiu, 2018 ^a	Performance of low GWP R1234yf/R134a mixture as a replacement for R134a in automotive air conditioning systems ^a	R1234yf, R134a ^a
Sergio Bobbo, Giovanni Di Nicola, Claudio Zilio, J. Steven Brown, Laura Fedele, 2018 ^a	Low-GWP halocarbon refrigerants: A review of thermophysical properties ^a	R1234yf, R1234ze ^a
Kamel Sigar Hmouda, Horatiu Pop, Valentin Apostol, Ahmed Qasim Ahmed, 2017 ^a	Refrigerants Retrofit as Alternative for R12 and R134a in Household Refrigerators ^a	R1234yf, R134a, R600a, R290, R12 ^a
Huber, M.L., and M.J. Assael, 2016 ^a	Correlations for the viscosity of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) and trans-1,2,2,2-tetrafluoropropene (R1234ze(E)) ^a	R1234yf ^a

CHAPTER 2. THEORETICAL BASES

2.1. General notions of chemical thermodynamics of ecological refrigerants. Equations of state .

Chemical thermodynamics [3] is the branch of physical chemistry, that studies the chemical and physico-chemical transformations, through methods of general thermodynamics.

2.2 Thermodynamic and thermophysical properties of refrigerants, advantages and disadvantages.

Thermodynamic properties of refrigerant HFC-134a

Thermodynamic properties of refrigerant HFO-1234yf

Thermodynamic properties of refrigerant R404A

2.3 Impact of refrigerants on the environment and on the performance of refrigeration systems.

The acquis communautaire – Montreal Protocol

– Kyoto Protocol

2.3.1. Destruction of the ozone layer

Life on Earth [5,6,17] depends on the existence of a thin shield of "poisonous" gas, placed at the top of the atmosphere: the ozone layer.

The "holes" in the ozone layer. In the early 1970's that the Earth's ozone layer had become thinner due to the damage caused by the emissions of chemicals known as halocarbons, containing chlorides, fluorides, bromine, carbon and hydrogen.

2.3.2. Global warming

The terms "global warming" or "greenhouse effect" are usually used to describe the increase in average temperature of the Earth's surface over time. Under the Kyoto Protocol, the European Union is committed to significantly reducing its greenhouse gas emissions.

Globally, legal regulations have already been developed in an effort to reduce greenhouse gas emissions. In the EU, there is Regulation no. 517/2014 also known as "F-gases" [16].

Total equivalent warming impact (TEWI) [10,16], is a way to assess global warming by combining the direct contribution of refrigerant emissions to the atmosphere with an indirect contribution of carbon dioxide emissions, resulting the need for energy consumption for the refrigeration system.

The calculation relationship for TEWI is presented in detail in standard SR EN 378-1 / 2017 [10] and takes into account the amount of refrigerant in the installation, the amount of expandable refrigerant in the insulation, the amount of CO₂ escaped into the atmosphere to produce the energy unit of the refrigeration system, the energy consumed for operating the refrigeration system during its operation, the efficiency and tightness of the refrigeration system, the production mode of the electric energy of the refrigeration system, the lifetime of the refrigerant.

In conclusion, from an ecological point of view, the refrigerant must be chosen so that according to the regulations of the current legislation, it has zero ODP and GWP low and TEWI as small as possible.

Safety requirements that refrigerants must meet, are provided by standards both at national and international level and refer to: flammability, danger of explosion, toxicity, danger of biological contamination and the effects they may have on the products to be cooled. The location of the refrigeration installation (dwellings, public places, industrial areas) as well as the amount of refrigerant contained in the installation must also be taken into account.

Regarding to economic requirements, the price of the refrigerant must be taken into account, ensuring the lowest possible operating costs and the possibility of production in the country. In any

case, the choice of refrigerant must be made following rigorous technical and economic analysis in order to have the most efficient and ecological installation possible.

2.3.3. TEWI Factor

As mentioned earlier, when choosing a refrigerant or designing a refrigeration unit, air conditioning unit, or heat pump, it is important to evaluate the TEWI factor (the calculation of the effect of global warming during operation). In this way, not all economic aspects are taken into account. But when technological assessment is made and investment decisions are made, in addition to the environmental aspects, the economic aspects become objectively, extremely important. Regarding the refrigeration systems, reducing the impact on the environment often involves high costs. Thus, in many companies, discussions about minimizing environmental issues are often overlooked (as investment costs are crucial).

2.4. The main refrigerants used

Figure 3 shows the strategy for replacing refrigerants in the short, medium and long term. Data on refrigerants definitions, classification, TEWI factor, choice, etc. are found in SR EN 378-1 (Annexes A, B, C, D, E, F, G, ZA, ZB) [10] and REGULATION (EC) NO. 517/2014 F-Gas [16].

SHORT, MEDIUM AND LONG TERM REFRIGERANTS

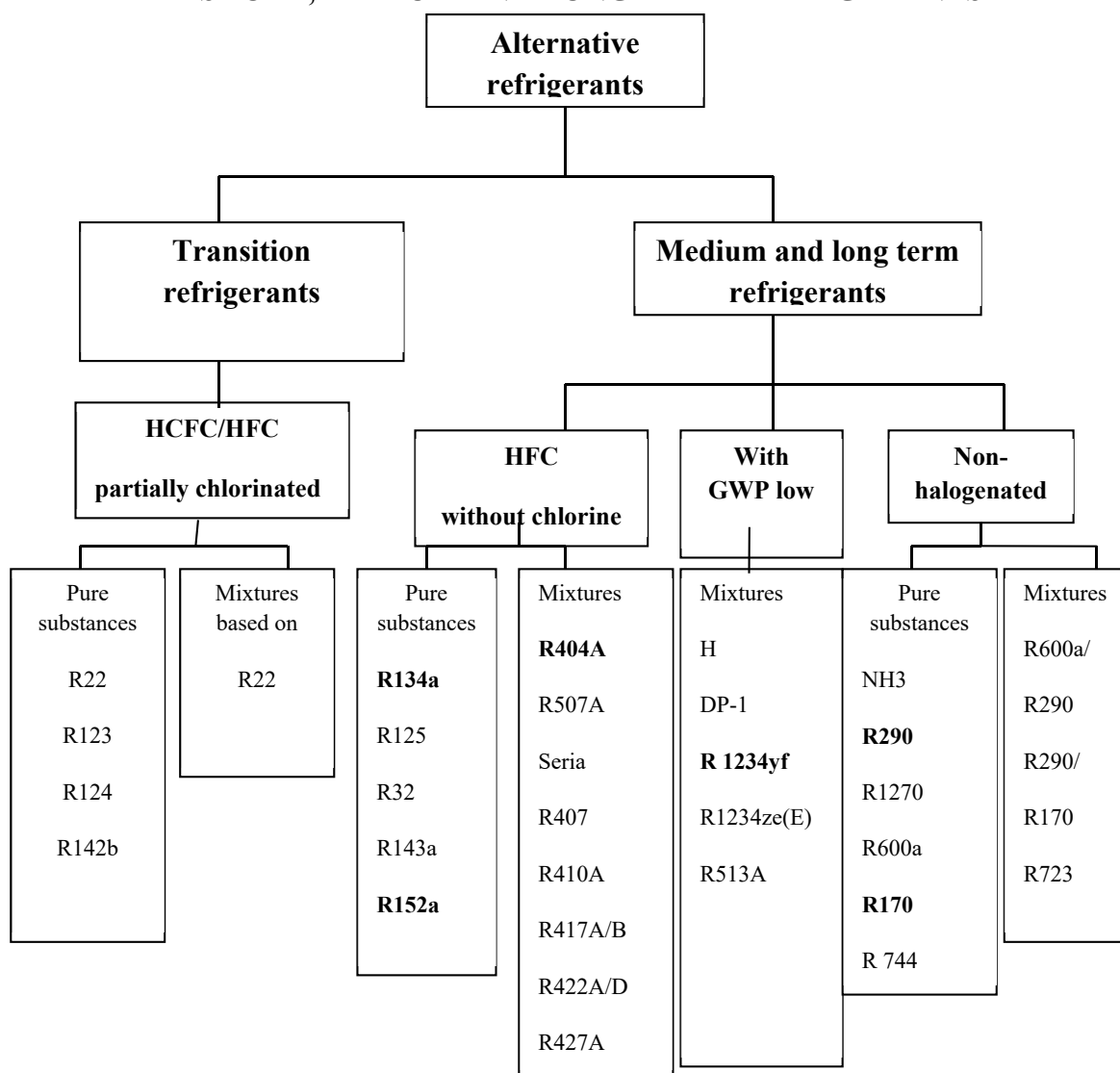


Fig. 3. Classification of refrigerants [8]

CAPITOLUL 3. MATHEMATICAL SIMULATION

3.1. Softwares used for calculation

3.1.1. Overview

Internationally, special calculation softwares are used in the design, research, and implementation stages.

3.1.2. DUPREX versions 3.0

DuPont's DUPREX software [14] is a special version of the KMKreis software that can design a refrigeration cycle considering different refrigerants in different refrigeration systems.

3.1.3. KANSREF versions 1.4

The KANSREF software [13] is applied only for natural refrigerants. This software is applied within the industry, namely in the design of refrigeration and air conditioning systems. Kansref builds the refrigeration cycle and calculates the TEWI factor.

3.1.4. KLEACALC versions 5.0

The KleaCalc software contains several calculation modules that use thermodynamic and thermophysical models of refrigerants.

3.1.5. FORANE versions 3.0

This software is made by ATOFINA for refrigeration and air conditioning. The software introduces the initial parameters of the installation, and the software generates the calculation of the COP performance coefficient.

3.1.6. COOLPACK versions 1.46

The CoolPack is a simulation software that can be used in the design, sizing, analysis and optimization of the refrigeration system.

3.1.7. SOLKANE versions 6

The new SOLKANE software [12] version 6 calculates thermodynamic properties for refrigerants under the SOLKANE brand.

3.1.8. REFUTIL versions 1.1

Refutil version 1.1 uses a variety of refrigerants with four types of refrigeration.

3.1.9. Refprop versions 8.0

The Refprop software reproduces the thermodynamic properties of pure fluids mixed fluids.

Programs of calculation

Duprex

Kansref

KleaCalc

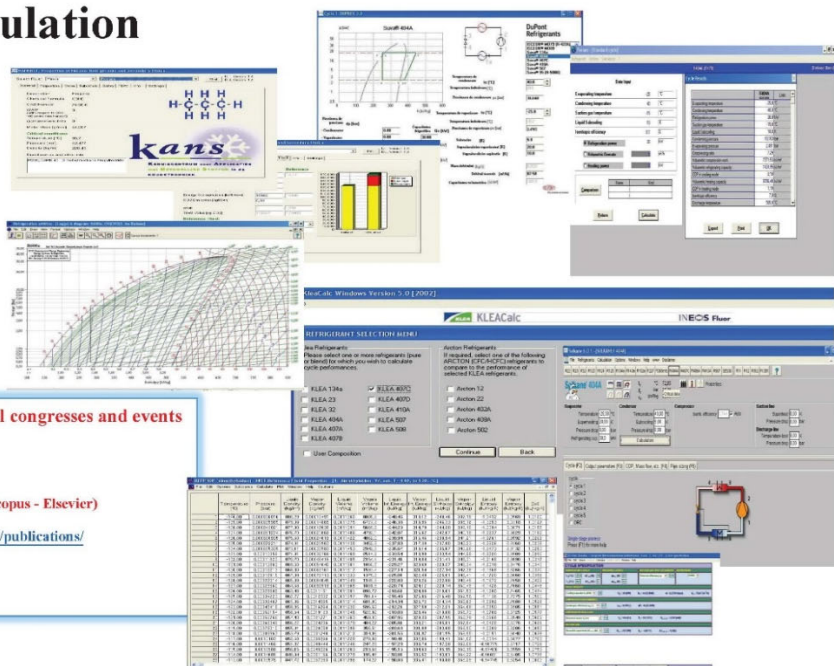
Forane

CoolPack

Solkane

Refutil

Refprop



publications at various national and international congresses and events
13- articles can be found on the site IIFHR

25 – Google Academic (from 2014-present)

8-articles on the site <https://orcid.org/0000-0003-0079-1562> (Scopus - Elsevier)

14 - <https://publons.com/researcher/3110311/vinceriuc-mioara/publications/>

Web of Science ResearcherID [BY-1626-2019](https://orcid.org/0000-0003-0079-1562)

1- <http://www.riss.kr/search>

Personal Contribution: Implementation of a mathematical model - EES (Engineering Equation Solver) –

The results from the simulations performed with the help of the high-performance software EES (Engineering Equation Solver) for the refrigerant R 134a (Fig. 3.1) for the air-water heat pump, are shown below.

Where: T_0 - represents the vaporization temperature; T_c - represents the condensation temperature; P_k - Total compressive strength; l_k - mechanical compression work; Q_m - freon mass flow, P_0 - vaporization pressure, P_c - condensing pressure, Φ_0 - refrigerating power

Simulation results with the EES software for R134a

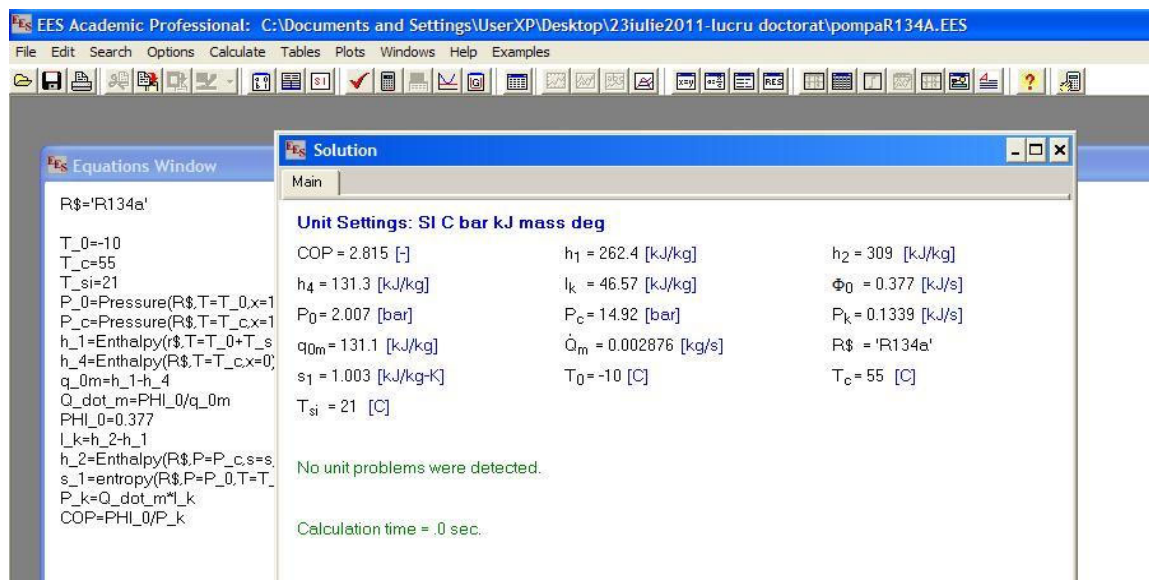


Fig. 3.1. Simulation results with the EES software for R134a

Simulation results with the EES software for R 152a

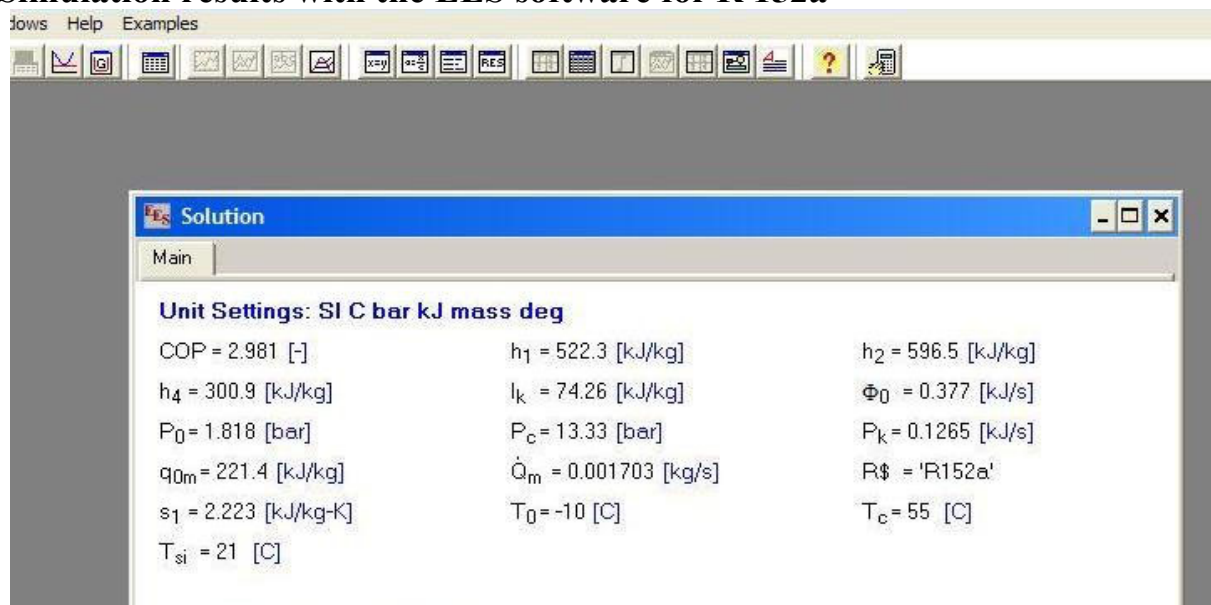


Fig.

3.2. Simulation results with the EES software for R152a

Simulation results with the EES software for R1234yf

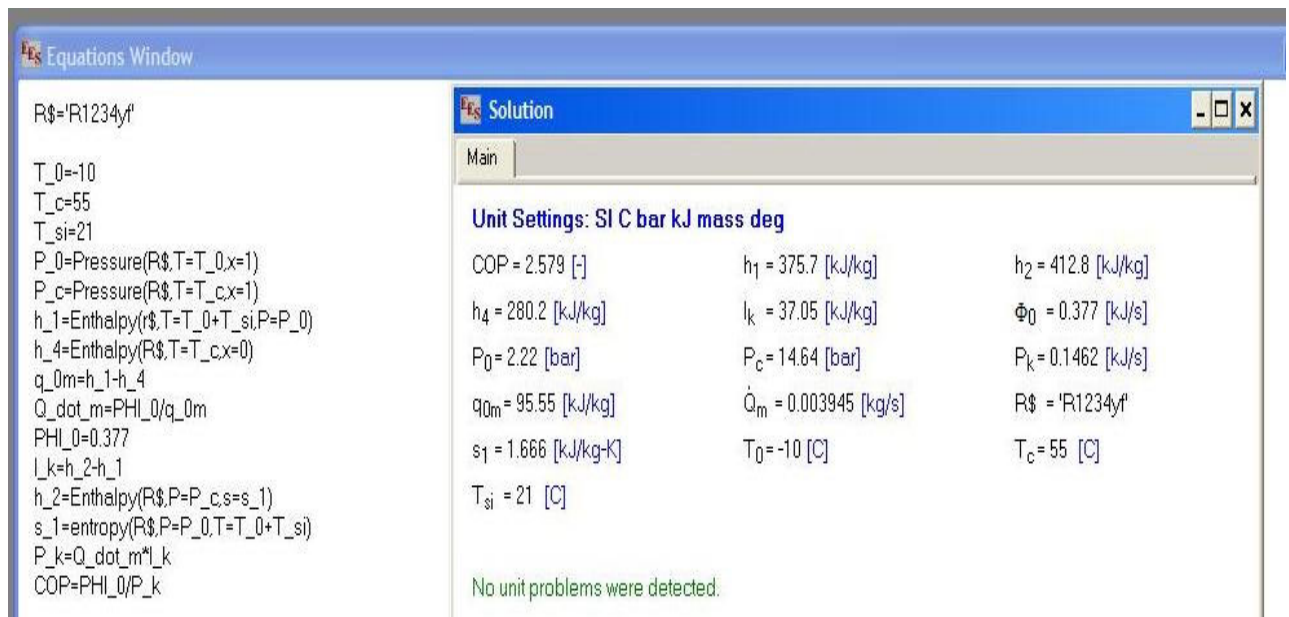


Fig. 3.3. Simulation results with the EES software for R 1234yf

Mathematical modelling flow-chart of thermodynamic processes related to the refrigeration system R 134a, MV3T , MV3TN

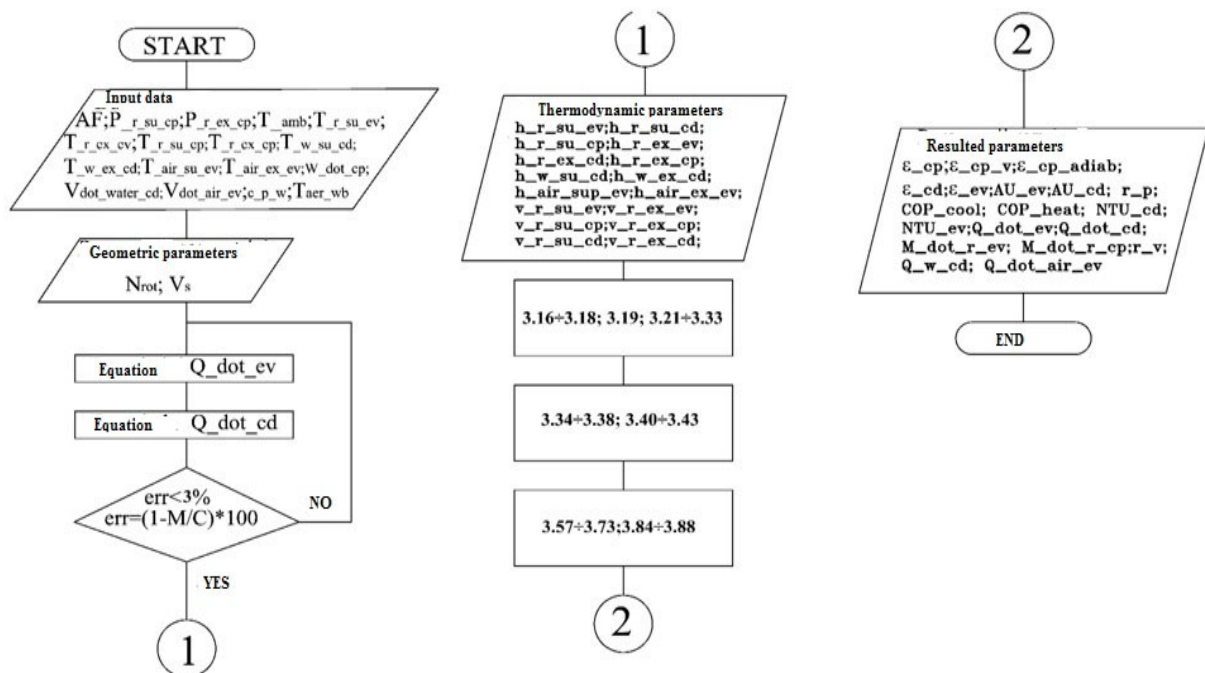


Fig. 3.4 Logical calculation scheme for the mathematical model - personal contribution

Mathematical modelling of thermodynamic processes for the refrigeration systems

Introduced parameters

- evaporating ($P_{r_su_cp}$), condensing pressure ($P_{r_ex_cp}$),
- external air temperature (T_{amb}),
- water temperature inlet and outlet condenser ($T_{w_su_cd}$, $T_{w_ex_cd}$) and temperature inlet and outlet evaporator ($T_{air_su_ev}$, $T_{air_ex_ev}$),
- refrigerant temperature inlet and outlet evaporator ($T_{r_su_ev}$, $T_{r_ex_ev}$),
- refrigerant temperature inlet and outlet compressor ($T_{r_su_cp}$, $T_{r_ex_cp}$),
- electrical input (W_{dot_cp}),
- wet bubble air temperature (T_{aer_wb}) and mass flow for water and condenser ($V_{dot_water_cd}$),
- mass flow air evaporator ($V_{dot_air_ev}$) and water specific heat content (c_{p_w}).

Resulted parameters

- evaporator and compressor refrigerant mass flow ($M_{dot_r_ev}$, $M_{dot_r_cp}$),
- volumetric ratio (ϵ_{cp_v}),
- isentropic ratio (ϵ_{cp}),
- adiabatic ratio (ϵ_{cp_adiab}),
- compression ratio (r_p),
- the global coefficient of heat transfer (condenser- AU_{cd} and evaporator AU_{ev}),
- performance coefficient for cooling (COP_{cool}) and heating (COP_{heat}),
- condenser (ϵ_{cd}) and evaporator ratio (ϵ_{ev}),
- evaporator and condenser number of thermal units (NTU_{ev} , NTU_{cd}),
- cooling power (Q_{dot_ev}),
- condenser thermal power (Q_{dot_cd}),
- compressor volumetric ratio (r_v),
- condenser water thermal power (Q_{w_cd}),
- air cooling thermal power ($Q_{dot_air_ev}$)

Calculation interface related to the mathematical model of thermodynamic processes for the R134a AIR-WATER PC system

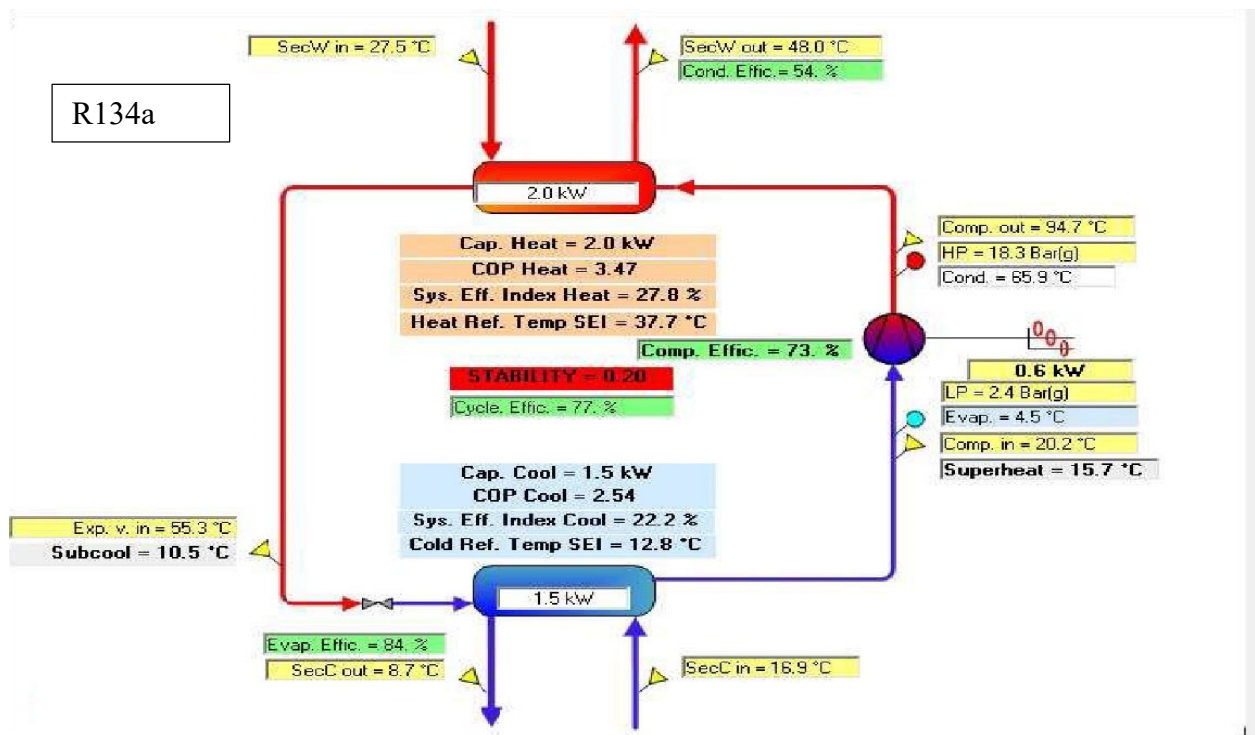


Fig.3.5 Calculation interface to the mathematical model for systems AIR-WATER HP works with R134a refrigerant

Mathematical modelling of the thermodynamic processes related to the refrigeration system operating with the refrigerant MVIZ3 și MVIZ1

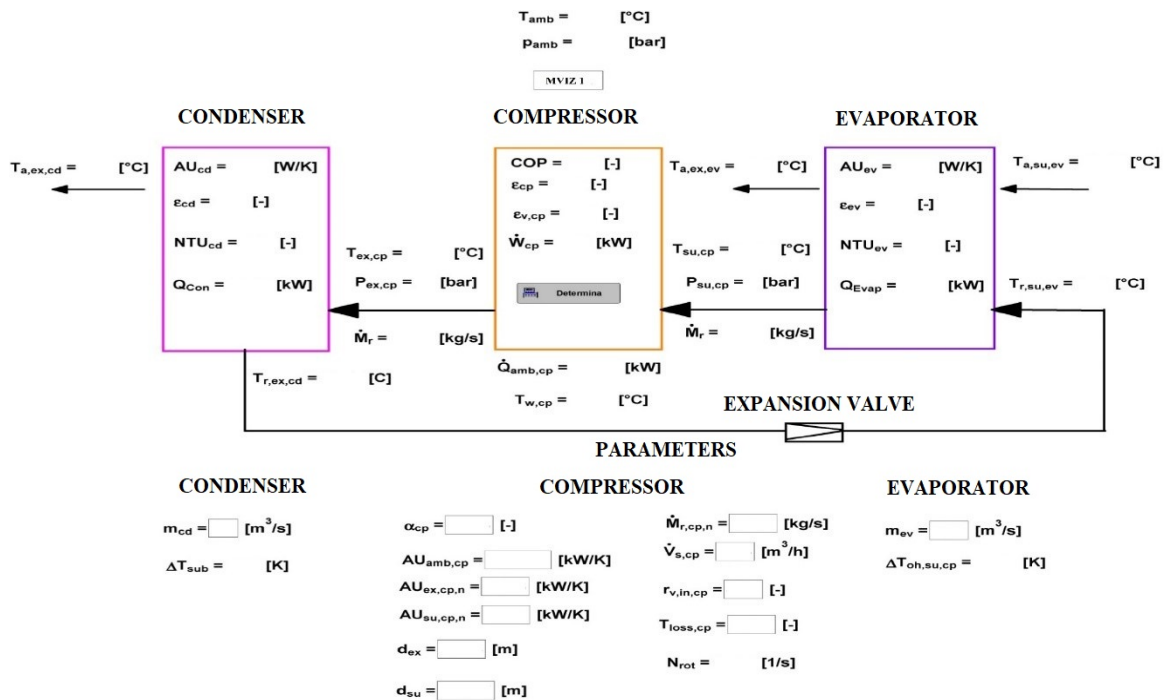


Fig. 3.6 Calculation interface related to the mathematical model MVIZ1 of thermodynamic processes for the refrigeration system with scroll compressors [9]

Simulation of thermodynamic properties of refrigerants for R 134a, R152a, MV3T , MV3TN si HFO 1234yf - experimental model AIR-WATER HP

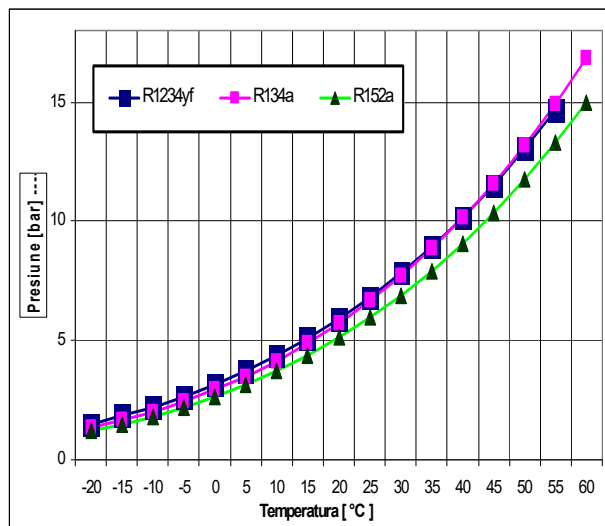


Fig. 3.7 Pressures of the three refrigerants R1234yf, R134a and R152a depending on the temperature

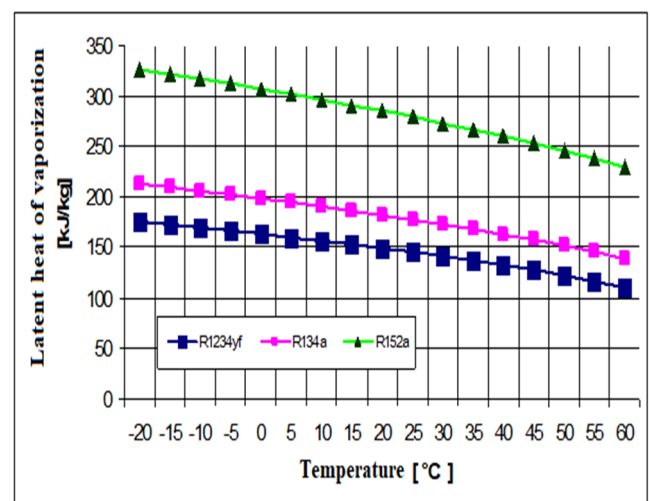


Fig. 3.8 Latent heat of vaporization for refrigerants R1234yf, R134a and R152a depending on the temperature

Simulation of properties of ecological alternatives of refrigerant R404A

The simulations were performed for the experimental model of a refrigeration system with digital scroll compressor.

In addition, a comparative analysis between the refrigerant R404A and two other alternatives (MVIZ1, MVIZ3) was presented in the thesis.

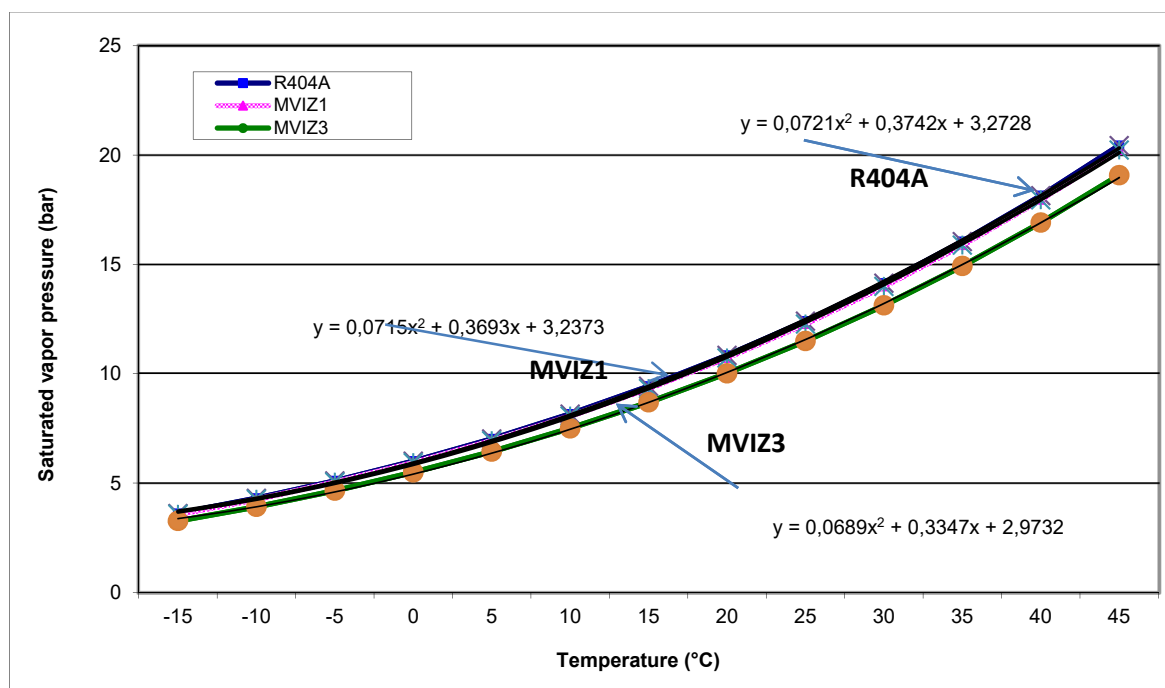


Fig. 3.9 Pressure regime of refrigerants vs.temperature

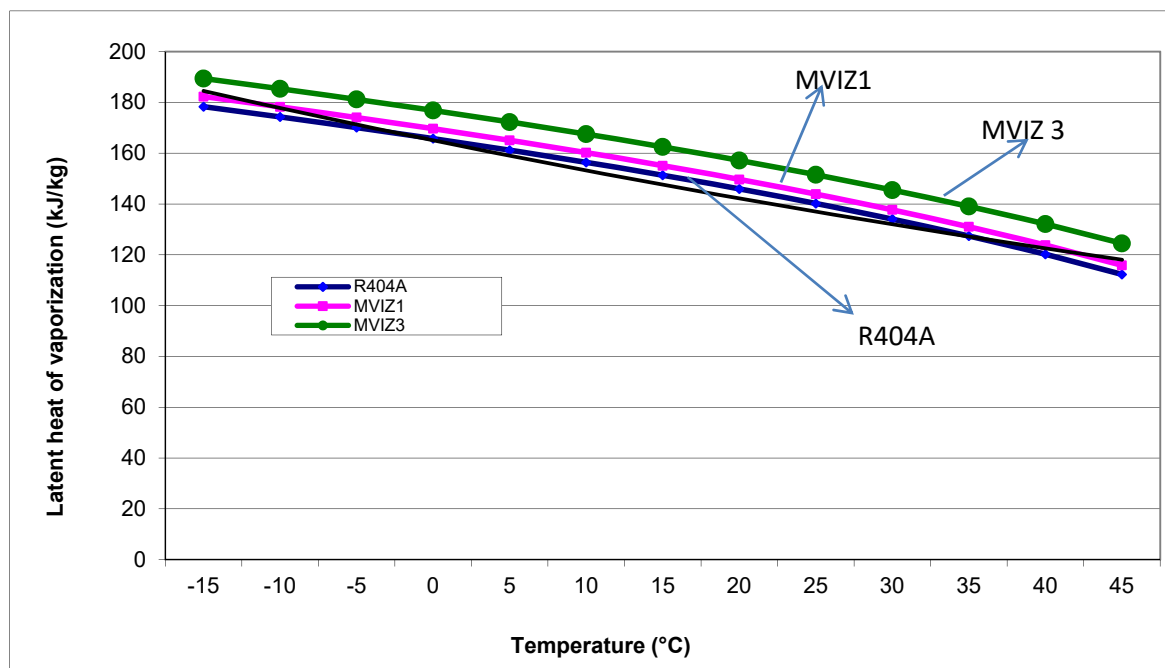


Fig. 3.10 Latent heat of vaporization vs.temperature

Simulation of properties of ecological alternatives for refrigerant R404A

The simulations were made for the experimental model of a refrigeration system with digital scroll compressor.

Comparative analysis between the refrigerant R404A and two other alternatives (MVIZ1, MVIZ3).

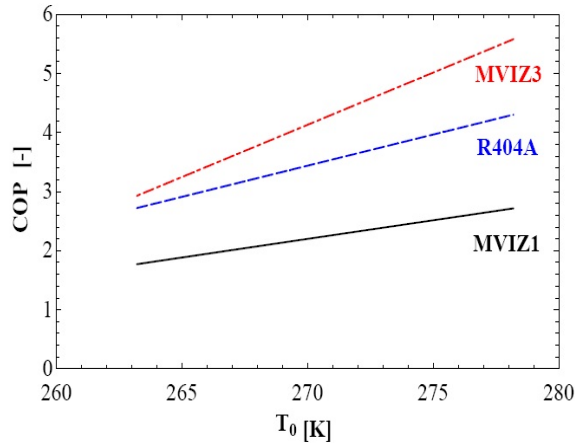


Fig. 3.11 The COP of the installation vs. temperature

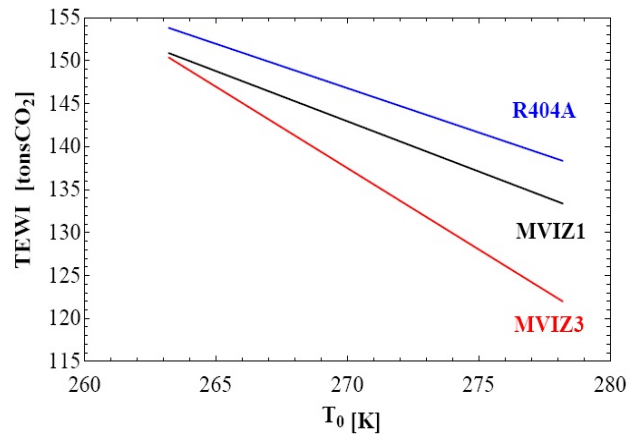


Fig. 3.12 TEWI factor vs. temperature

Simulation of thermodynamic properties of refrigerants R 134a, MV3T, MV3TN and HFO 1234yf

All the experimental model AIR-WATER HP[58] comparative studies are presented for the alternatives MV3T, MV3TN, R1234yf and R134a.

Fig. 3.13 shows that smallest (advantageous) working pressure has MV3TN.

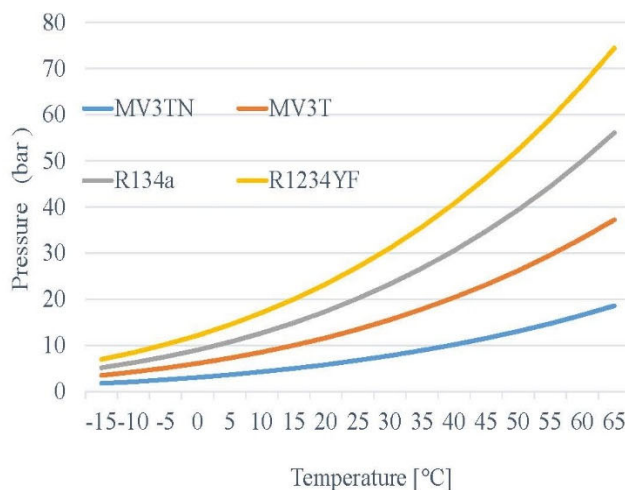


Fig. 3.13 Pressure vs. temperature

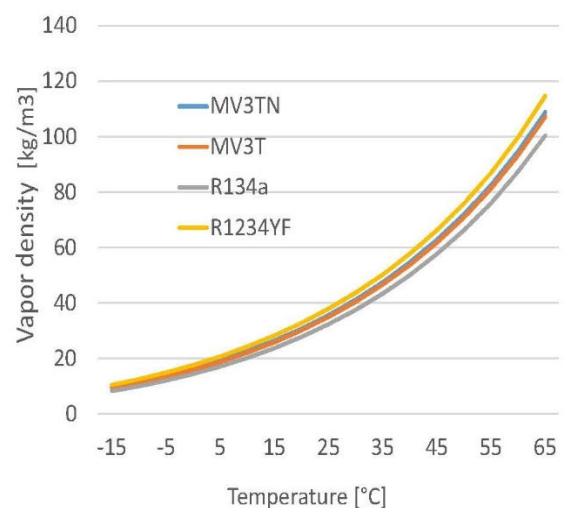


Fig. 3.14 Density vs. temperature

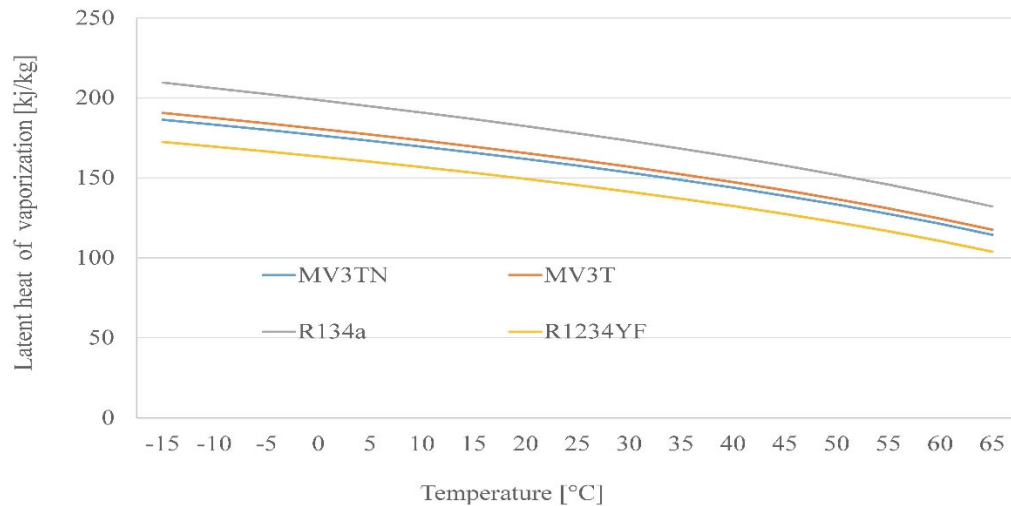


Fig.3.15 Temperature vs. latent heat of vaporization

The MV3T mixture has higher latent heat than the MV3TN being more advantageous.

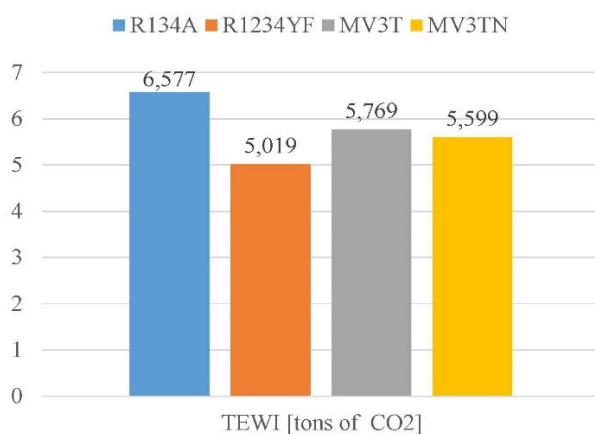


Fig.3.16 TEWI Factor

Refrigerant	R134a	R1234yf	MV3T	MV3TN
GWP [-]	1430	4	717	560
L [kg/s]	0,0624	0,0580	0,0601	0,0596
n [an]	15	15	15	15
m [kg]	0,78	0,725	0,751	0,745
α_{rec} [-]	0,8	0,8	0,8	0,8
E_{annual} [kWh /an]	1153,62	1153,62	1153,62	1153,62
β [kg/kWh of CO2]	0,28985	0,28985	0,28985	0,28985
$GWP \times L \times n$	1338,48	3,48	646,40	500,75
$GWP \times m(1 - \alpha_{rec})$	223,08	0,58	107,73	83,46
$n \times E_{annual} \times \beta$	5015,65	5015,65	5015,65	5015,65
TEWI [kg CO ₂]	6577,21	5019,71	5769,78	5599,86
TEWI [tons of CO ₂]	6,577	5,019	5,769	5,599

The above figures evidence that:

- The lowest (advantageous) working pressure is MV3TN (Fig.3.13);
- Mixtures MV3T and MV3TN have average values (advantageous);
- The mixture MV3T (Fig.3.15) has higher latent heat than MV3TN making it more advantageous;
- From an ecological point of view (Fig.3.16) the MV3TN mixture (GWP = 560) is the most advantageous compared to R134a (GWP = 1430).

CHAPTER 4. EXPERIMENTAL RESEARCH AND VALIDATION

4.1. Experimental air-to-water heat pump model

4.1.1. Overview.

Throughout this doctoral thesis it was followed a development direction of research aiming to obtaining new mixtures of ecological refrigerants that could replace the refrigerants currently used in refrigeration system, that have a zero ODP and GWP as small as possible; the realization of an experimental stand equipped with a refrigeration system with mechanical vapor compression in one step (Fig.4.1 - 4.2) with the possibility of future connection to a solar panel, allowing the use of unconventional energies so that the energy consumption is as low as possible inside the Technical University of Civil Engineering Bucharest (UTCB) - Colentina Laboratory Complex. The air-to-water heat pump (PC) can use three types of energy sources: ambient air, sun and electricity, for domestic hot water production.

Although the air-to-water pump has the lowest COP of all the pumps I refer to, it is, along with the ground-to-water PDC, one of the most common in Europe. The air-water system is a relatively simple system to install and does not require special fitting works (digging, drilling, etc.). The major disadvantage of the system is it cannot operate monovalently at very low temperatures (starting from about -15°C).

They can operate bivalently - parallel monoenergetically by using an electrical resistance which comes into operation at very low temperatures (below -15° C). Due to this, the heating power is limited.

4.1.2. Description of the experimental stand

The air-to-water heat pump (Fig.4.1) used in the doctoral thesis, consists of the following equipments:

- hermetic piston compressor;
- helical tube condenser in the double casing;
- bladed pipe evaporator (Cu/Al);
- thermostatic lamination valve;
- two-stage radial fan;
- double enameled hot water tank with a volume of 270 liters.

The refrigerants proposed the replacement of the refrigerant R134a are MV3TN and MV3T and the domain of application of the air-water heat pump is from +6°C to +35°C. The working pressure is between 6÷12bar and the maximum working temperature is 55°C.

In order to reduce direct emissions there are multiple EU restrictions (MAC Directive - 2006/40/EC) [41] and Regulation (EU) 517/2014 [16].

Consequently, the R134a refrigerant that has been used so far, had to be replaced by another refrigerant which has as low as GWP as possible.

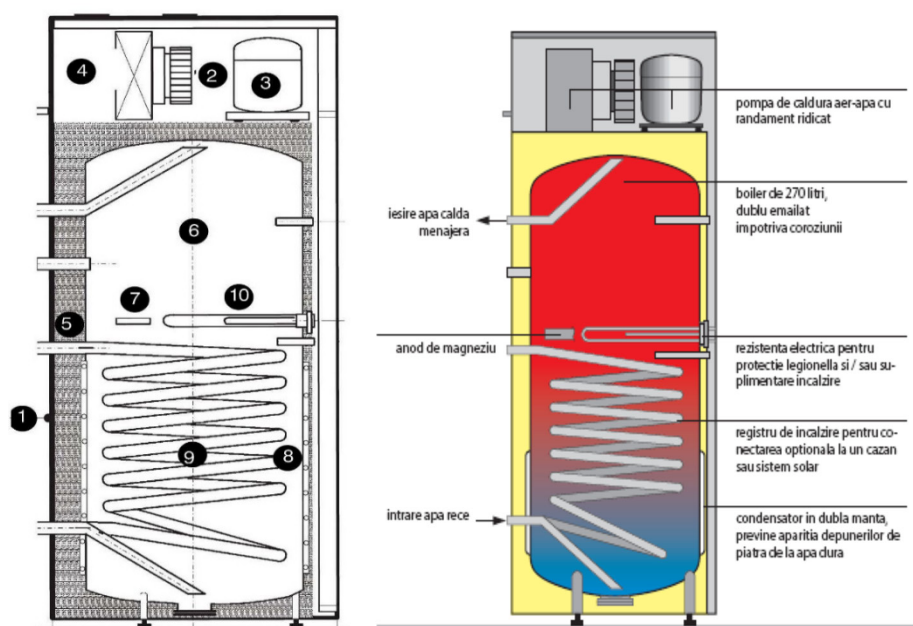


Fig. 4.1 Construction of the air-to-water heat pump

The experimental model analyzed from the technical and constructive point of view has the role of preparing hot water for 13 students throughout the year, regardless of the season, and the residual cold is used to lower the temperature in a teaching laboratory of about 48 sqm .

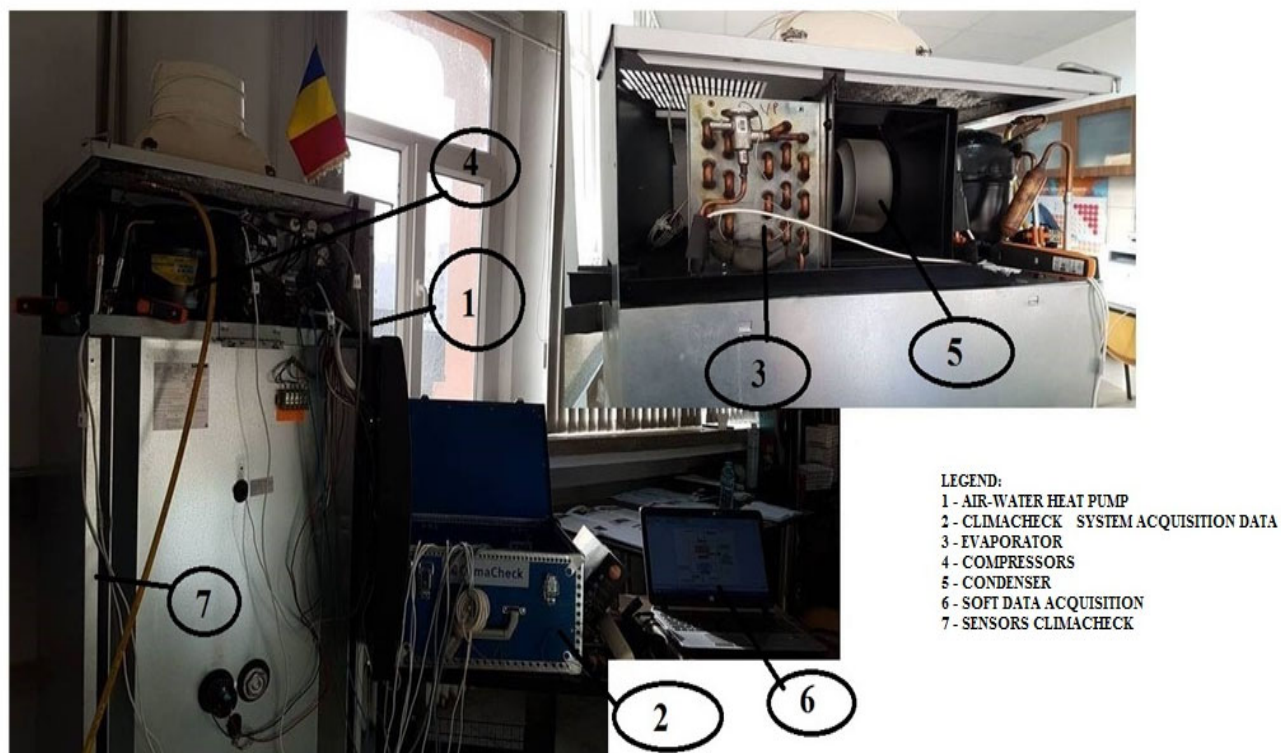


Fig. 4.2 The experimental model of the air-water heat pump

Used measuring equipment



4.3. Analysis and interpretation of experimental data

4.3.1. Case of refrigerant R134a

In the figure 4.3 below is presented the normal decrease of the COP for the operation of the air-water heat pump in cooling and heating regime with the increase of the compression ratio.

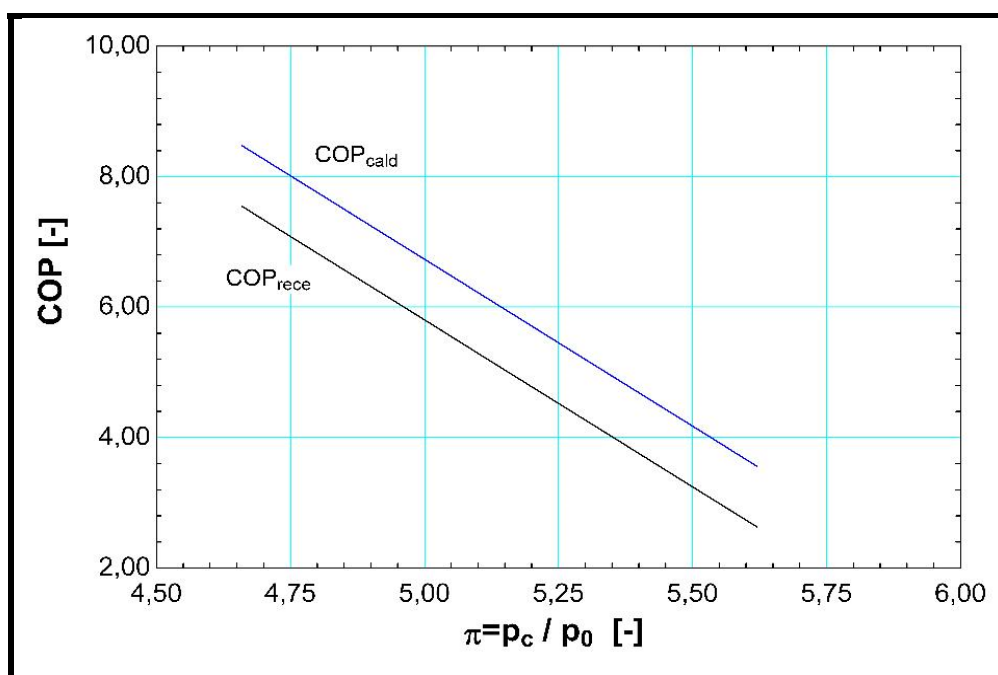


Fig. 4.3 Variation of COP on cooling and heating depending on the compression ratio.

4.3.2 Case of refrigerant MV3T

In the figure 4.4 below is shown the normal decrease of the COP for operation in cooling and heating mode with the increase of the compression ratio depending on the compression ratio.

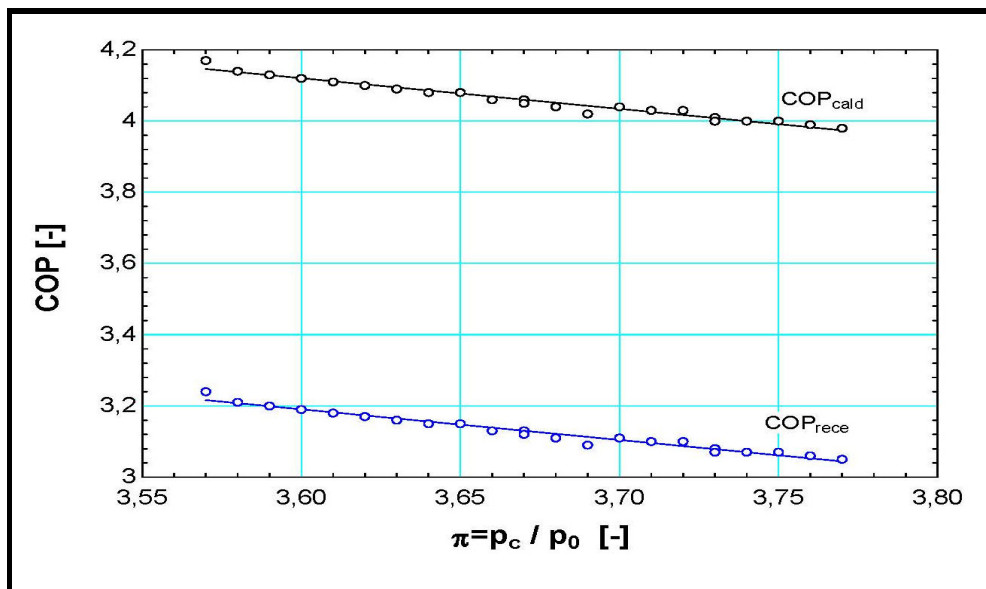


Fig. 4.4 Variation of COP on cooling and heating depending on the compression ratio.

4.3.3 Case of refrigerant MV3TN

In Fig. 4.5 is shown the COP variation on the cooling side depending on the cooling capacity in the vaporization process. There is an increase in the performance coefficient of the PC with the increase of the cooling capacity.

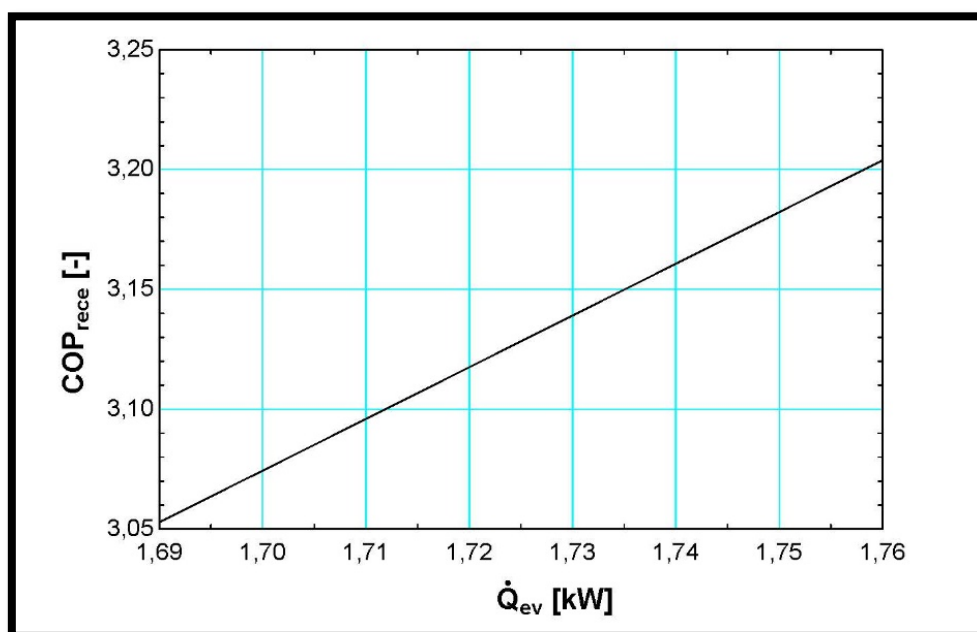


Fig. 4.5 COP variation on the cooling side depending on the cooling capacity

4.4. Validation of experimental data with the mathematical model

4.4.1. Case of refrigerant R134a

The author of the study considered that it is important to consider the cooling load calculated in comparison with the one measured for the R134a refrigerant used in the AIR-WATER HP experimental stand. In Fig.4.6 below is presented for the cooling capacity the proof of validation of the experimental model with the mathematical one, observing a degree of error less than 3%, that falls within the acceptable technical error range. In Fig.4.7 below is presented the COP on the cooling side calculated in comparison with the one measured for the R134a refrigerant used in the AIR-WATER HP experimental stand.

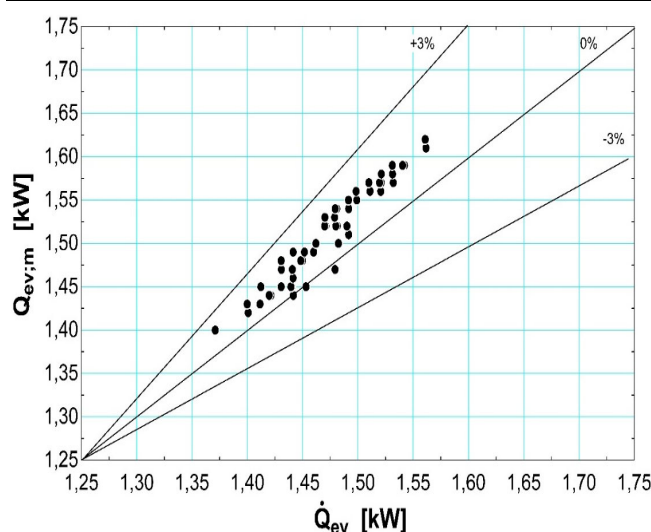


Fig.4.6 The calculated vs. measured cooling capacity of the R134a refrigerant used in the experimental stand of AIR-WATER HP

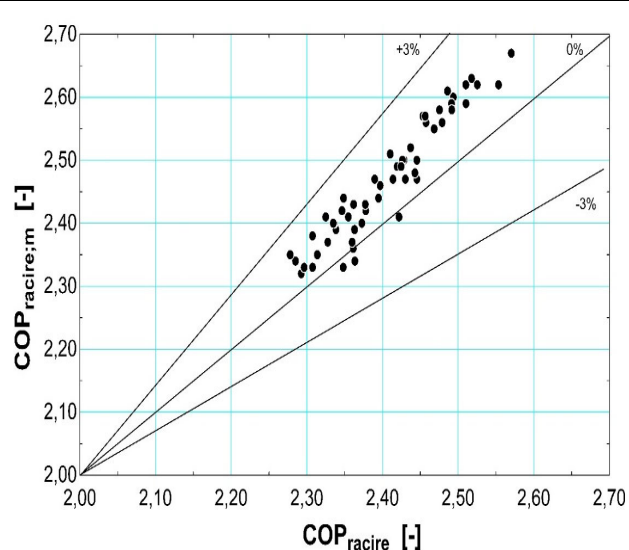


Fig.4.7 The calculated vs. measured cooling COP of the R134a refrigerant used in the experimental stand of AIR-WATER HP

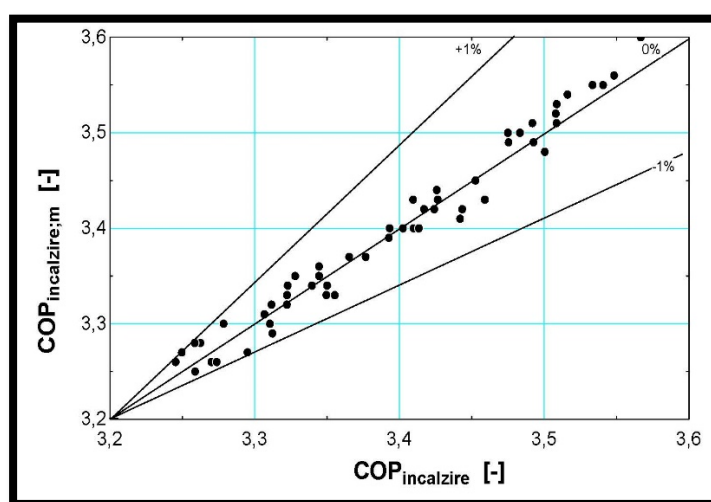


Fig.4.8 COP on the calculated vs. measured heating side of the R134a refrigerant used in the experimental stand of AIR-WATER HP

4.4.2 Case of refrigerant MV3T

In Fig.4.9 is presented, for the cooling capacity, the proof of validation of the experimental model with the mathematical one [61], observing a degree of error less than 4% that falls within under the acceptable technical error range.

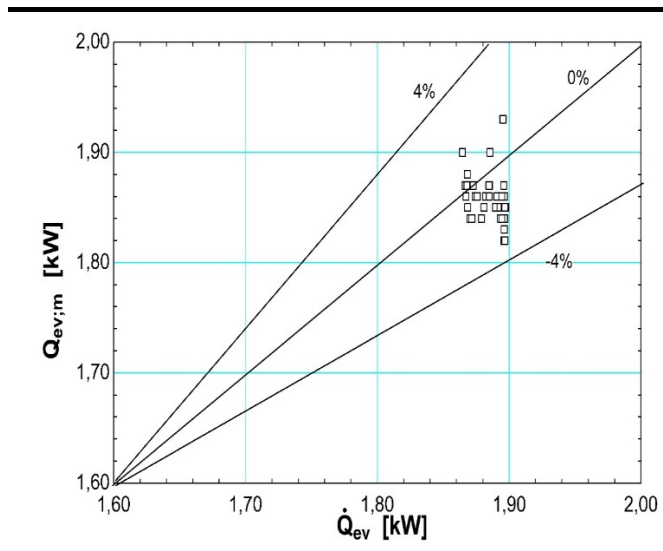


Fig.4.9 Calculated vs. measured cooling capacity of the MV3T refrigerant used in the experimental stand AIR-WATER HP

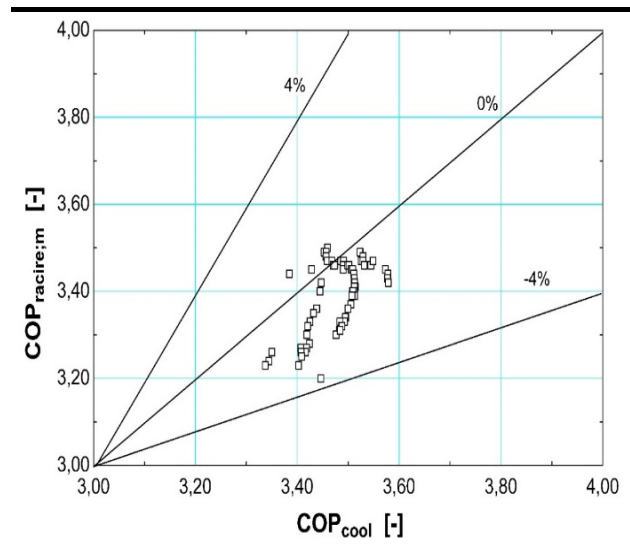


Fig.4.10 Calculated vs. measured cooling COP of the MV3T refrigerant used in the experimental stand AIR-WATER HP

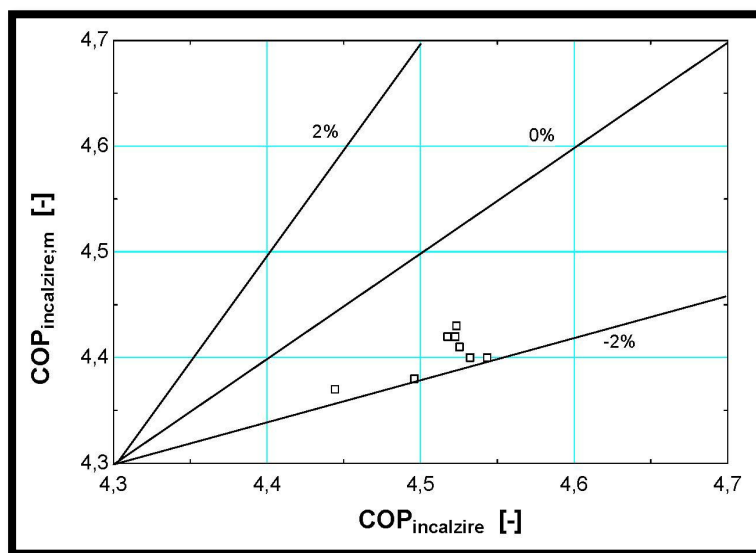


Fig.4.11 COP on the calculated vs. measured heating side of the MV3T refrigerant used in the experimental stand AIR-WATER HP

Also, the degree of error of less than 4% is found, which falls within the acceptable technical error range.

4.4.3 Case of refrigerant MV3TN

Fig.4.12 below shows for the cooling capacity the proof of validation of the experimental model with the mathematical one, observing a degree of error less than 4% which falls within the acceptable technical error range.

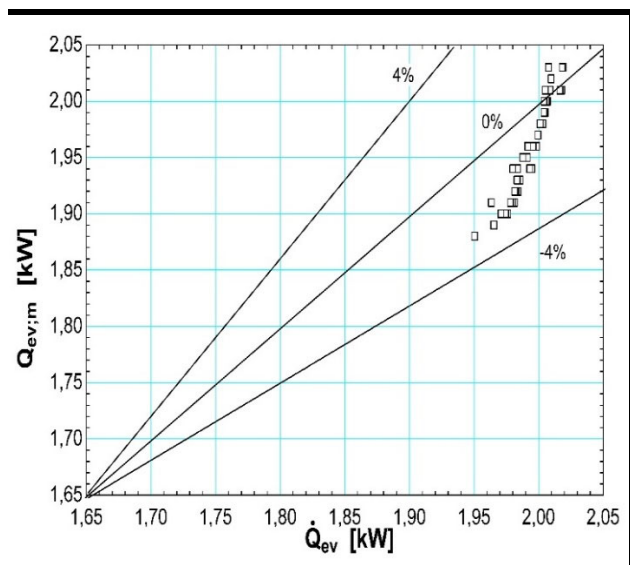


Fig.4.12 Calculated vs. measured cooling capacity of the MV3TN refrigerant used in the experimental stand AIR-WATER HP

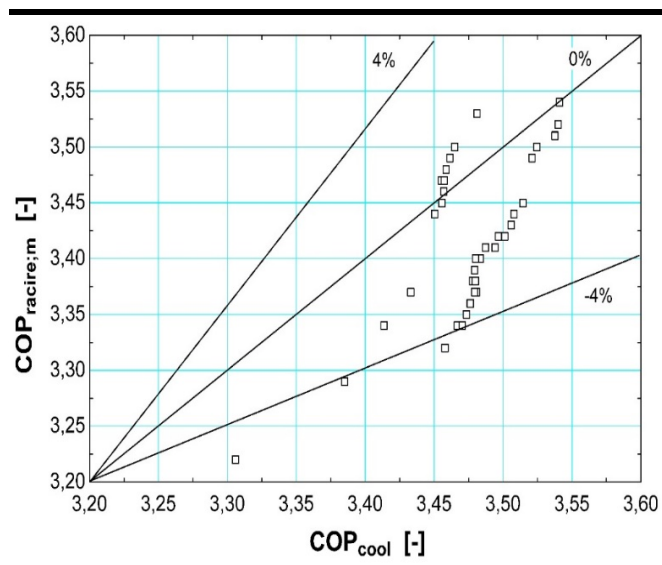


Fig.4.13 The calculated vs. measured cooling COP of the MV3T refrigerant used in the experimental stand AIR-WATER HP

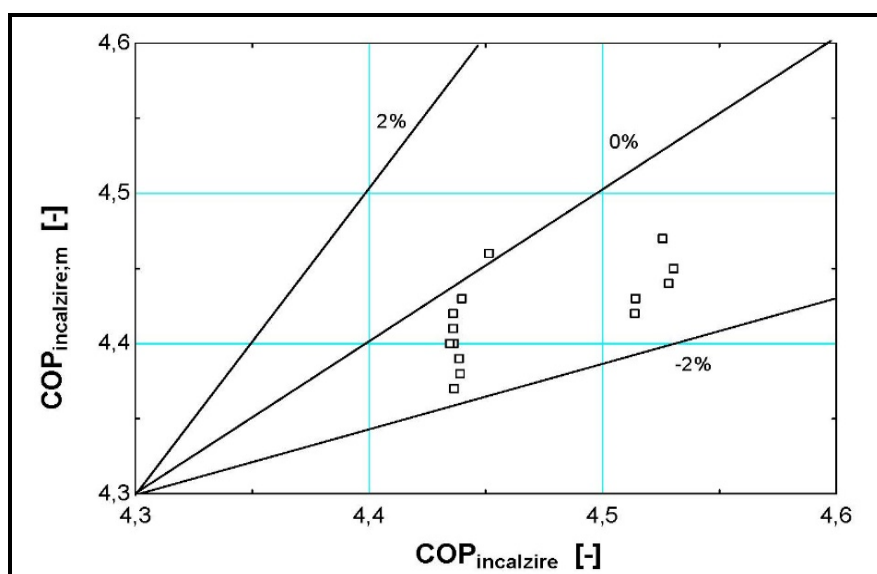


Fig. 4.14 COP on the calculated vs. measured heating side of the MV3TN refrigerant used in the experimental stand AIR-WATER HP

CHAPTER 5. GENERAL CONCLUSIONS AND PERSONAL CONTRIBUTIONS

5.1. General conclusions

The research program proposed in the doctoral thesis "**Research on the contribution of refrigeration systems, air conditioning and heat pumps to global warming**" has accomplished the **principal objective** of the work for studying refrigeration systems both from the point of view of ecological and energy efficiency, with emphasis on the contribution of refrigerants, by greenhouse effect, to global warming.

Also, the **general objective** of the thesis, of carrying out scientific research in order to reduce the emissions of greenhouse gases, with particular reference to the refrigerants that contribute to global warming and climate change, in order to comply with the international legislation in the domain, has been achieved.

In the doctoral thesis entitled: "**Research on the contribution of refrigeration, air conditioning and heat pump systems to global heating**", one objective was the realization of an experimental stand air-water heat pump, designed to determine the performance of the refrigeration system operating with the refrigerant R134a and to find new ecological refrigerants of mixture type MV3T, MV3TN.

This thesis brings together the synthesis of a topical bibliographic material with the results of own theoretical and experimental studies carried out within a complex research program.

Internationally and **nationally**, the issue of refrigerants which contributes to global warming is not yet resolved, this being a topical issue. At **national** level there are very few researches, given the lack of specialists in the area of chemical thermodynamics and of the dedicated equipment (gas chromatograph, spectrophotometer, analyzer) which can experimentally determine the thermophysical and chemical characteristics of some mixtures of refrigerants with various concentrations.

In the thesis are theoretically analyzed both the simple substances and the mixtures proposed on the basis of several programs specific to refrigerants, including the REFPROP software and an EES (Engineering Equation Solver) calculation software with which the COP of the installation and the TEWI factor for each proposed refrigerant were simulated. The thesis presents the current investigation in the domain and a bibliographic material regarding the research of mixtures of refrigerants by the big producers at international level. During the doctoral thesis elaboration, the theoretical partial results were published and communicated in journals and scientific national and international events.

5.2. Personal contributions

In the doctoral thesis, the following personal original contributions were made, accomplishing the several objectives of the doctoral thesis:

- Analysis of the current state of research on the domain of ecological refrigerants that can be used in refrigeration systems (**Chapter 2**);
- Creation of diagrams and tables with thermodynamic properties of the mixtures of refrigerants proposed MV3T, MV3TN, as well as MVIZ1, MVIZ2, MVIZ3 (ANNEX 2);
- Determination of the equations of state of mixtures (**Chapter 3**);
- Development of a new domain of research inside of Faculty of Building Services Engineering (of the UTCB), namely of the refrigerants field;
- Analyzing the different variants of refrigeration systems with various refrigerant fluids and proposing optimal solutions from an energy and ecological point of view (**Chapter 3**);

- The use of high-performance simulation programs for ecological analysis and energy efficiency for various applications in the domain of cold and air conditioning (EES, REFPROP, CLIMACHECK) (**Chapter 3**);
- Realization of an experimental stand - heat pump designed to determine the performance of the refrigeration system that can operate with R134a, MV3T, MV3TN in the Laboratory of atmosphere protection, Colentina Laboratories Complex inside of the Technical University of Civil Engineering Bucharest (UTCB) (**Chapter 4**).

Other personal contributions:

- Making a technical documentary regarding the research in the domain of refrigerants at international level in the last 10 years (**Chapter 1**);
- The use of various simulation programs existing at international level, for ecological analysis and energy efficiency for applications in the domain of refrigeration and air conditioning (**Chapter 3-below chapter 3.1**);
- Making a technical documentation regarding the contribution of refrigeration systems, air conditioning and heat pumps to global warming evidenced by the presented bibliography;
- Proposal of new ecological refrigerants of mixture types for which the mass participations have been established following a thermodynamic analysis (**Chapter 3**) for an experimental stand compressor group – digital condenser with scroll compressor modulation [9];
- Making diagrams and obtaining thermodynamic properties for the mixtures of refrigerants proposed for the experimental stand compressor group – digital condenser with modulation of the scroll compressor [29];
- Elaboration of a calculation algorithm, a mathematical model and a personalized simulation program for the **air-to-water heat pump system operating** with the refrigerant R134a, MV3T, MV3TN;
- Obtaining some mixtures of refrigerants, namely MV3T, MV3TN with GWP less than 750 [according to Regulation (EU) 517/2014] [16], in order to align with the European legislation;
- The processing of experimental data led to results comparable to those from the use of the mathematical model (**Chapter 4**), at the validation of the experimental model with the mathematical one, observing a degree of error less than 3% (0.75-2.9) that falls in the acceptable technical error range.

In accordance with the subject of the doctoral thesis, a number of over 50 scientific articles have been elaborated as follows:

- - 13- articles can be found on the site IIFIIR
- - 25 – Google Academic (from 2014- present)
- - 8 - articles on the site <https://orcid.org/0000-0003-0079-1562> (Scopus - Elsevier)
- - 14 <https://publons.com/researcher/3110311/vinceriuc-mioara/publications/>
- Web of Science Researcher ID Y-1626-2019
- - 1- <http://www.riss.kr/search>

Between the above mentioned papers, 5 (five) are published as first author at national and international scientific events such as SGEM 2018, CLIMA 2019, BELGRAD 2019, TIMISOARA 2019, DSC 2020.

5.3. Issues of perspective

The doctoral thesis can be considered a continuation of the accomplished researches in the domain of refrigerants at national level.

Future research directions may involve:

- Finding ecological alternatives with low or zero GWP in order to align with EU legislation;
- The use of an existing refrigeration system (designed in optimal conditions) that is subjected to different functional regimes from the nominal one with the mixtures MVIZ1, MVIZ2, MVIZ3 and others for the experimental stand of the compressor group – digital condenser with modulation of the scroll compressor;
- Discovery of new green (ecological) refrigerants that do not directly contribute to global warming ($GWP=0$, $ODP=0$);
- Development of the experimental stand of the compressor - digital condenser group with modulation of the scroll compressor and its use for the validation of the theoretical results obtained from the research directions mentioned above;
- Analysis of thermodynamic and ecological performances of refrigerants for automotive climate systems with the realization of mathematical simulations followed by experimental validations;
- Applying on the results of the research in the area of refrigerants for various domain.

The analyses made in the thesis with the title: „**Research on the contribution of refrigeration, air conditioning and heat pump systems to global warming**” can be a basis for future studies in the domain of refrigeration systems that use renewable energies (eg. solar energy) in order to implement in systems with air-water heat pumps with solar panels.

In the thesis, the bibliography chapter includes 131 references of which the most important ones were presented and which are found in the summary of the thesis.

Selective bibliography:

- [1]. A. Leca, I. Prisecaru, Thermophysical and thermodynamic properties of solids, liquids and gases, Technical Publishing House, Bucharest, 1994.
- [2]. A. A. Akopian, „ *Chemical thermodynamics*”, translation from Russian, Didactic and Pedagogical Publishing House, Bucharest, 1968.
- [3]. I. Antohi, Thermodynamic Technique, Didactic and Pedagogical Publishing House, Bucharest, 1971
- [4]. F. Chiriac, F. Băltărețu, C. Mihăilă, **Chemical thermodynamics**, Agir Publishing House, Bucharest, 2006
- [5]. Țârlea G, *Ecological refrigeration installations*, ECOLEX, Bucharest, 2002.
- [6] Code of Good Practice – *The domain of cold and air conditioning*, AGIR Publishing House, Bucharest, 2008-2009
- [7]. The National Institute of Standards and Technology (NIST) - *Refprop version 8.0*, USA, 2007
- [8]. Bitzer - *Refrigerent Report 2008, 2012, 2018*
- [9]. Ion Zabet - *PhD thesis - Contributions to the study of eco-efficiency of refrigeration systems*, 2012
- [10]. *Standard European EN 378-1:2008*, 2017
- [11]. SR EN378- *Refrigerating systems and heat pumps - safety and environmental requirements*’, 2005, European standard, CEN.
- [12]. SOLKANE versiunea 6.0
- [13] KANS, *KansRef*, Datasysteem voor natuurlijke koudemiddelen en koudedragers, versie 1.4
- [14]. DuPont *Refrigerant Expert*TM
- [15]. *ClimaCheck Performance Analyser 8:7* (2008 - Ver 2.2X.Y)
- [16]. *Regulation (EU) no 517/2014* of the European Parliament and of the council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006, <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32014R0517>
- [17]. *The Montreal Protocol on Substances that Deplete the Ozone Layer* (2000), Secretariat for the Vienna Convention for the Protection of the Ozone Layer & the Montreal Protocol on Substances that Deplete the Ozone Layer.
- [18]. *Kyoto Protocol to The United Nations Framework Convention on Climate Change* , United Nations Framework Convention on Climate Change, 1997
- [19-40]. **Eng. Mioara Vinceriuc**, Prof.univ.dr.ing.Gratiela Maria Tarlea, et all. - articles published in journals and in volumes of international conferences during 2009-2018;
- [41]. Directive 2006/40/EC of the European Parliament and of the Council of 17 May 2006 on emissions from air-conditioning systems in motor vehicles and amending Council Directive 70/156/EEC
- [42]. Commission Implementing Regulation (EU) 2015/2067 of 17 November 2015
- [43]. EES Software (*Engineering Equation Solver*)
- [44]. *Amendment to the Montreal Protocol on Substances that Deplete the Ozone Layer Kigali*, 15 October 2016
- [45]. EN 14511-3:2007 - *Air conditioners, liquid chilling packages and heat pumps with electrically driven compressors for space heating and cooling - Part 3: Test methods*- English Version
- [46]. Kamel Sgar Hmooda*, Horatiu Popb, Valentin Apostol, Ahmed Qasim Ahmedd - *Refrigerants Retrofit as Alternative for R12 and R134a in Household Refrigerators*, American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS) ISSN (Print) 2313-4410, ISSN (Online) 2313-4402

- [47]. Gaurav and Raj Kumar- *Thermo economic analysis of environmental friendly refrigerant mixtures for replacement of R134a*, Vol. 13, No. 4, 2018
- [48]. https://ec.europa.eu/clima/news/eu-ratifies-kigali-amendment-montreal-protocol_en
- [49]. Standard AHRI 700 - *Specifications for Refrigerants*, 2017
- [50]. Standard for *Performance Rating of Unitary Air-conditioning & Air-source Heat Pump Equipment*, 2017
- [51] Vinceriuc M., Țârlea G , Tarlea A.- Air-Water-Heat Pump with low GWP refrigerant - CLIMA 2019
- [52] Lemmon, E.W., M.L. Huber, and M.O. McLinden, *NIST standard reference database 23, NIST reference fluid thermodynamic and transport properties—REFPROP*, v. 9.2. Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, MD, 2016
- [53] ASHRAE - *Designation and safety classification of refrigerants*. ANSI/ ASHRAE Standard 34-2016
- [54] Calm, J. C., G. C. Hourahan, A. Vonsild, D. Clodic, and D. Colbourne - *2014 Report of the refrigeration, air conditioning, and heat pumps technical options committee, Ch. 2: Refrigerants*. United Nations Environment Programme (UNEP) Ozone Secretariat, Nairobi, ozone.unep.org/en/assessment-panels/technology-and-economic-assessment-panel, 2015
- [55] M. Vinceriuc, G. Tarlea - Retrofit with mixtures of refrigerants with reduced GWP, Conference: Installations for Construction Energy, Efficiency, Comfort, 2019, ISSN 2559-6985
- [56] M. Vinceriuc – *Low GWP alternative for R404A refrigerant* published in the volume of the conference with international participation, Installations for constructions and environmental comfort, Edition 28, April 12 Timisoara 2019, page 79 -84, Ed.Politehnica ISSN 1842-9491
- [57] Mioara Vinceriuc, Gratiela TARLEA- *Mathematical And Experimental Mv3tn Heat Pump Validation*, 2nd Conference of the UTCB Doctoral School, 25th of October 2019, Hydrotechnics Faculty
- [58]. Mioara Vinceriuc, Gratiela Tarlea - *Comparative refrigerants study of R134a, R1234YF, MV3T and MV3TN* , 50-International Hvac&R Congress And Exhibition (KGH), 299-301 pp, 2019, Belgrad,
- [59]. Gratiela Tarlea, Mioara Vinceriuc, Ion Zabet- *Air-Water Heat Pump Modelling*, 50-International Hvac&R Congress And Exhibition (KGH), 2019, Belgrad
- https://kgh-kongres.rs/images/2019/prezentacije/66_Gratiela_Tarlea.pdf
- [60] Vinceriuc Mioara and Tarlea Gratiela - *TEWI Calculation for AC Technological Application*, 3rd Conference of the UTCB Doctoral School, 27th of November 2020, Bucharest, TUCB; <https://sd.utcb.ro/dsc-2020/programme-2020/>
- [61] Mioara Vinceriuc and Gratiela TARLEA- *Numerical and Experimental Analysis of the MV3T Refrigerant*, Building Services and Energy Efficiency, Modernizing and increasing performance of Building Services, July 2nd, 2020 - July 3rd, 2020, Iași; DOI: [10.2478/9788395720413-004](https://doi.org/10.2478/9788395720413-004), <https://sciendo.com/de/chapter/9788395720413/10.2478%2F9788395720413-toc>
- [62] Gratiela Tarlea, Mioara Vinceriuc, Ana Tarlea -*A Natural Refrigerant DME and HC Eco- Efficient Mixture Alternative*, PAPER ID: 1181, 14th Gustav Lorentzen Conference, Kyoto, Japan, 6th- 9th December, 2020, ISSN: 0151-1637, ISBN: 978-2-36215-040-1, Publication: IIF-IIR - Paris – France, IIR Conference; DOI: <http://dx.doi.org/10.18462/iir.gl.2020.1181>, <https://biz.knt.co.jp/tour/2020/12/gl2020/pdf/program.pdf>
- [63]. Prof. Gratiela Maria Tarlea PhD, Drd.Ing. Mioara Vinceriuc, *Air Conditioning Total Equivalent Warming Impact Comparison*, Presentation at 51. MEĐUNARODNI KONGRES I IZLOŽBA O KGH, 2-4 December 2020; <https://kgh-kongres.rs/index.php/sr/program>
- [64] M Vinceriuc¹ and G M Tarlea¹ - *Total equivalent warming impact calculation for air conditioning technological application*, Published under licence by IOP Publishing Ltd, IOP Conference Series: Earth and Environmental Science, Volume 664, The 7th Conference of the Sustainable Solutions for Energy and Environment 21-24 October 2020, Bucharest, Romania, Online ISSN: 1755-1315, Print ISSN: 1755-1307; DOI:10.1088/1755-1315/664/1/012078