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Thermodynamics, Heat engines, Thermal and Refrigerating Equipment

PH.D. THESIS

CONTRIBUTIONS TO THE OPTIMIZATION OF HEAT PUMP SYSTEMS

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Content

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CHAPTER 1. LIMITING CO_2 EMISSIONS BY REPLACING CLASSIC GAS HEATING EQUIPMENT WITH HEAT PUMP EQUIPMENT

Scientific development offers many solutions for ensuring thermal comfort in residential, commercial and industrial spaces. The most common equipment to satisfy this need is equipment based on the combustion of methane gas. The rational use of resources has a beneficial effect on the economy, environmental protection and sustainable development.

According to data provided by Eurostat regarding energy consumption in 2020, buildings, along with transport, represent the largest energy consumers of the total consumed.

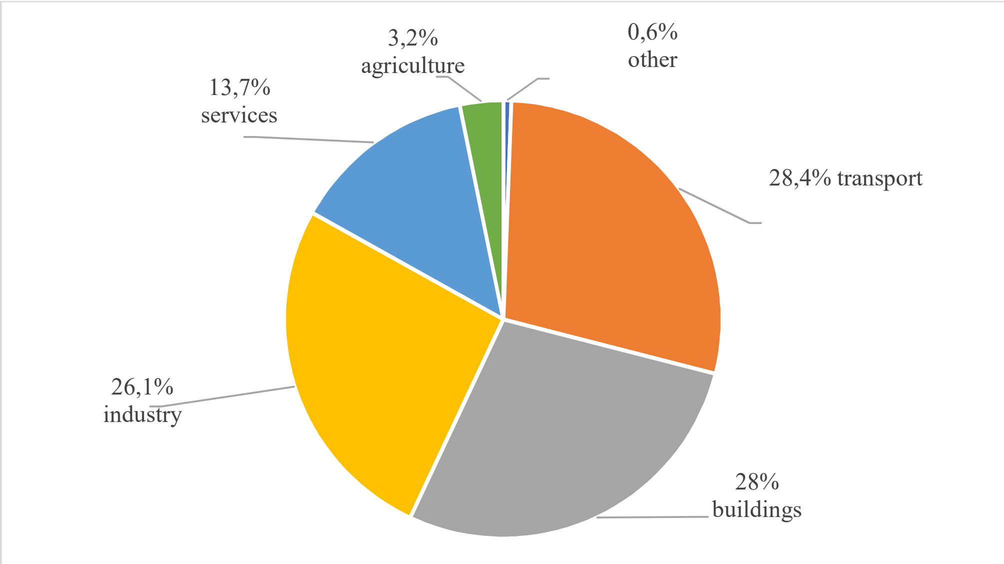

Figure 1.1. The share of total energy consumption at the level of the European Union in 2022

Reducing energy consumption in buildings can be considered an important energy resource, thus making equipment more efficient, but also replacing greenhouse gas generating systems that ensure the thermal comfort of buildings is a priority.

In order to reach this target, an analysis is supposed to be carried out that is able to draw guidelines regarding the efficiency and implementation of new systems that ensure thermal comfort using renewable and recoverable energies.

At the level of the European Union, energy and environmental protection policies are oriented towards sustainable development, energy security and energy efficiency. Thus, the European Union adopted a series of objectives and regulations aimed at reducing primary energy consumption and implicitly reducing greenhouse gas emissions.

On 14 April 2014, the European Parliament adopts regulation 517/2014 on the use of greenhouse gases, which requires that greenhouse gas emissions be reduced by 80 to 95% by 2050 compared to the level of the 1990s.

On 28 November 2018, the European Commission in terms of sustainable development presented its long-term strategic vision for a prosperous, modern, competitive and climate-neutral economy. This is based on a new energy policy framework established within the "Clean Energy for All for Europeans" package which aims to limit the increase in global temperature below 2 [^{0}C] possibly 1.5 [^{0}C] by the year 2050.

In December 2019, the European Commission launched the European Green Park project, which sets out measures that will transform Europe into the first climate-neutral continent by 2050.

The Glasgow conference in October-November 2021, decided to cut emissions to limit global warming by phasing out coal-fired power, halting deforestation, accelerating the switch to electric vehicles and reducing methane emissions. The COP26 climate change decisions will also be successful if heating and cooling based on heat pump solutions are included.

As the cost of energy continues to rise, reducing energy consumption and improving energy performance becomes a necessity. Thus, for the efficiency and reduction of energy consumption consumed by buildings, heat pumps represent an alternative for heating, preparation of domestic hot water and cooling of buildings, because these equipments are efficient from an energy point of view and do not have a destructive effect on the environment.

Improving heat pump performance, reliability and environmental impact has been a continuous concern over the last decade. Achievements and progress in order to improve the performance of heat pumps have focused on the modeling of advanced cycles but also the improvement of the devices that make up the system.

The evolution of new hybrid systems has enabled the efficient operation of heat pumps with the diversification of fields of use.

CHAPTER 2. CURRENT STATE OF RESEARCH IN THE FIELD OF FUNCTIONAL ANALYSIS AND OPTIMIZATION AND CONSTRUCTION OF MECHANICAL VAPOR COMPRESSION HEAT PUMPS

Heat pumps are energy systems that can be used to heat or cool spaces depending on the season. They work after a refrigeration cycle being powered by electricity. Although it is very popular to use fossil fuels or electricity directly in space or water heating applications, it is inefficient compared to using the heat pump. Unlike electric radiators used for heating in the cold season, which have a performance coefficient equal to unity, that is, they provide an amount of heat equal to the electrical energy consumed, or a classic heating system by burning a fuel that has a sub-unit energy efficiency , the heat pump has a super unit efficiency (over 2.5), returning in the heating mode both the consumed electrical energy and the thermal energy taken from a cold source which can be a waste heat or heat taken from the ambient environment. The cold source feature of the heat pump cycle is that it is free.

2.1. BIBLIOGRAPHICAL TRENDS AND RESEARCH

For a qualitative assessment of the evolution of the analyzed subject, the ScienceDirect and Scopus databases were consulted.

In 2019 P. Byrne et al.[1] carry out a theoretical and experimental investigation of a heat pump cycle in a compression stage, evaluating the performance of the working agents R407C and R290 (propane). The energy analysis puts the working agent R407C in a superior position compared to the working agent R290. The exergy analysis indicates the highest exergy destruction at the level of the compressor, and the lowest exergy destruction being recorded at the level of the heat exchangers. The study concludes that exergy analysis is interesting when applied to heat pumps, as it allows for both quantitative and qualitative assessment of energy conversion processes.

Sho F et al. [2] perform a theoretical analysis on low global warming potential agents R1234ze(E) and R1234ze(Z). The purpose of the research is to investigate the performance of working agents at condensing temperatures above 75 [^{0}C]. The comparative analysis proves that the working agents R1234ze(E) and R1234ze(Z) can successfully replace the freon R134a. Evaluations have shown that the working agent R1234ze(Z) is more suitable for applications where the condensing temperature exceeds 100 [^{0}C].

Alptung Y et al. [3] performs a theoretical analysis focused on the replacement of R134a freon in the existing systems of heat pumps and refrigeration installations with mechanical vapor compression, with the ecological freons R1234yf and R1234ze. The exergy analysis indicates that R1234ze performs similarly to R134a.

Bin H et al [4] perform the exergy analysis of heat pump cycles in one compression stage, two compression stages and three compression stages, using R1234ze(Z) freon as the working agent. The study seeks the optimal configuration of a heat pump equipment that is capable of delivering hot water at a temperature of 120 [^{0}C], using as a heat source water from industrial processes at temperatures above 50 [^{0}C]. The results indicate a decrease in exergy losses in the lamination process in the case of multi-stage compression compared to the single-stage compression system. The exergy analysis indicates the highest efficiency in the case of the three-stage compression cycle.

T. Bai et al. [5] carry out a thorough analysis of an ejector heat pump system in which the working agent CO_2 evolves in the transcritical domain. The system performance is investigated based on exergy analysis. The study is focused on identifying the components with the greatest exergy destruction. The results indicate that the highest exergy destruction is registered at the level of the compressor, followed by the exergy destruction in the ejector, but with very close values. The analysis carried out on the ejector indicates a real potential for improvement of the equipment compared to the classic throttling valve equipment.

In 2019 S. Taslimi Taleghani et al. [6] carry out a comparative analysis between the CO_2 heat pump in a compression stage, conventional (with throttling valve) and CO_2 heat pump with ejector. The results indicate that the ejector heat pump installation has a better coefficient of performance than the conventional throttling valve installation, with the coefficient of performance being up to 12% higher for the ejector installation under the same operating conditions.

In 2019 F.Cao et al [7] present the theoretical and experimental analysis of a CO_2 heat pump system intended for heating residential spaces .The equipment includes a main system and a secondary system. Both the main cycle and the secondary cycle use carbon dioxide as a working agent. To maximize the coefficient of performance by reducing exergy destruction at the level of the throttling process, the auxiliary equipment subcools the carbon dioxide at the level of the main cycle. Experimental analysis shows that this equipment can be successfully implemented.

D.Yang et al [8] perform a theoretical and experimental analysis of a combined R134a and CO_2 heat pump for heating residential spaces. The equipment consists of two heat pumping installations, put in contact with the supply water. The experimental results showed that the ambient temperature has the greatest influence on the performance coefficient. The comparative analysis between this equipment and heat pump equipment in one compression stage or two compression stages shows that the combined system offers a higher coefficient of performance, under the same operating conditions.

CHAPTER 3. THERMODYNAMIC ANALYSIS METHODS. ENERGY ANALYSIS. EXERGETIC ANALYSIS

Classical thermodynamics analyzes from a phenomenological point of view the conversion of energy from one to another. In this type of thermodynamic analysis, the microstructure of bodies and their individual behavior is ignored, accounting only for energy and substance exchanges between the body and the environment.

3.1. THE CONCEPT OF EXERGY

The increased interest in identifying the maximum fraction of mechanical work that can be obtained from a disordered form of energy led to the need to introduce the term exergy.

According to A. Dobrovicescu [9] exergy can be defined in two ways:

Definition 1: *Exergy represents the amount of ordered energy that can be obtained from a disordered energy.*

Definition 2: *Exergy represents the maximum amount of mechanical work that a system can release under the specified conditions of the intensive parameters of its ambient environment.*

The importance of applying the exergy method in investigating the performance of heat pumping systems is that it becomes possible to express quantitatively the losses caused by the internal and external irreversibilities caused by the processes carried out during the thermodynamic cycle.

3.1.1. Exergy of a control mass (closed system)

In thermodynamics, the control mass represents a system that does not exchange matter with its surrounding environment, that is, it is a closed system [10,11].

The maximum mechanical work that can be released by a closed system, under given conditions, is called the exergy of the system (Ex), and can be expressed mathematically according to equation (3.1).

$$\mathrm{Ex} = \mathrm{L_{Cmax}} = \mathrm{E} - \mathrm{U_0} + \mathrm{p_0}(\mathrm{V} - \mathrm{V_0}) - \mathrm{T_0}(\mathrm{S} - \mathrm{S_0}) \quad (3.1)$$

3.1.2. Exergy destruction

It is admitted that any process that takes place under finite conditions is accompanied by exergy destruction due to irreversibility. For this reason, the mechanical work released is:

$$\mathrm{L_c} = \mathrm{L_{c_{max}}} - \mathrm{T_0} \cdot \mathrm{S_{gen}} = \mathrm{Ex} - \mathrm{I} \quad (3.2)$$

$\mathrm{I} = \mathrm{T_0} \cdot \mathrm{S_{gen}}$, is called exergy destruction or irreversibility, is known in the literature as the Gouy-Stodola theorem [12].

3.1.3. Exergy of heat

It is considered an elementary amount of heat δQ, located at a temperature T. To evaluate the maximum amount of mechanical work that can be obtained from the specified amount of heat, which is at that temperature, the Carnot engine cycle is used, characterized by the most high yield, respectively the greatest amount of mechanical work that can be obtained [50,51,54].

The heat exergy can be calculated with the relation:

$$\mathrm{Ex_Q} = \int \left(1 - \frac{\mathrm{T_0}}{\mathrm{T}}\right) \delta\mathrm{Q} = \left(1 - \frac{\mathrm{T_0}}{\mathrm{T}}\right) \mathrm{Q} = \mathrm{Q} - \mathrm{T_0} \cdot \Delta \mathrm{S_Q} \quad (3.3)$$

3.1.4. Exergy balance equation for a control mass (closed system)

The exergy balance equation for a control mass is written as follows [13] :

$$\sum \mathrm{Ex_Q} = \Delta \mathrm{Ex} + \left(\sum \mathrm{L} - \mathrm{p_0} \cdot \Delta \mathrm{V}\right) + \sum \mathrm{I} \quad (3.4)$$

3.1.5. Exergy balance equation for a control volume (open system)

An open system is a system that exchanges heat, mechanical work and substance with its surrounding environment [11].

The exergy balance equation for an open system (control volume) is written as follows [55].

$$\frac{\mathrm{dEx_{vc}}}{\mathrm{d\tau}} = \sum \dot{\mathrm{Ex}}_\mathrm{Q} - \left(\sum \dot{\mathrm{L}} - \mathrm{p_0} \cdot \frac{\mathrm{dV}}{\mathrm{d\tau}}\right) + \sum \mathrm{ex_i^f} \cdot \dot{\mathrm{m}}_\mathrm{i} - \sum \mathrm{ex_e^f} \cdot \mathrm{m_e} - \sum \dot{\mathrm{I}} \quad (3.5)$$

Exergy analysis based on both the first and second principles of thermodynamics makes it possible to actually measure the usable energy of each stream of energy or mass that penetrates the boundaries of a system and highlights its inefficient areas.

Exergy analysis has the ability to provide solutions to improve the overall performance of the system, by identifying the irreversibilities in the components that make up the equipment. This type of analysis enters the system boundaries and has the ability to highlight and locate any failure associated with each device and process. The results of the exergy analysis provide solutions for the structural and functional improvement of each system.

CHAPTER 4. MATHEMATICAL MODELING OF REAL GAS BEHAVIOR. THERMAL EQUATIONS OF STATE. RELATIONS FOR THE CALCULATION OF STATE QUANTITIES

In specialized literature, numerous thermal equations of state can be identified, they have the role of specifying the behavior of pure substances in p, V, T space.

In general, most equations of state restrict their scope to the gas or liquid region, but there are also forms of equations of state with applicability in both the gas and liquid phases. The complexity of these forms of state equations depends on the size of the imposed domain and the required rigor.

4.1. THERMAL EQUATIONS OF STATE

The best-known equations of state have been established in practice by their ability to mathematically reproduce the results obtained in the laboratory.

Under these conditions, the best-known thermal equations of state can be listed. In general, these equations of state explain the pressure in the specified state [14-16].

4.1.1. Van der Waals equation

$$p = \frac{R \cdot T}{v - b} - \frac{a}{v^2 + u \cdot b \cdot v + w \cdot b^2} \tag{4.1}$$

4.1.2. Beattie-Bridgeman equation

$$p = \frac{R \cdot T}{v^2}\left[v + B_0\left(1 - \frac{b}{v}\right)\right]\left(1 - \frac{c}{v \cdot T^3}\right) - A_0\left(1 - \frac{a}{v}\right) \tag{4.2}$$

4.1.3. The Martin-Hou equation

$$p = \frac{R \cdot T}{v - b} + \sum_{i=2}^{5} \frac{A_i + B_i \cdot T + C_i \cdot e^{-kT/T_c}}{(v - b)^i} + \frac{A_6 + B_6 \cdot T + C_6 \cdot e^{-kT/T_c}}{e^{\alpha v}(1 + cE^{\alpha v})} \tag{4.3}$$

4.2. WORKING AGENTS IN REFRIGERATION INSTALLATIONS AND HEAT PUMPS

The lack of future use of HFCs in refrigeration and air-conditioning installations has focused the interest of engineers and researchers on natural refrigerants whose category includes water, air, hydrocarbons, ammonia and carbon dioxide [17-18].

The use of these natural working agents is limited by their characteristic disadvantages.

Air can be used in the Bryton cycle as a working agent in refrigeration and heat pump installations but has low efficiency due to the large temperature difference between the hot source and the cold source.

Water is a good working agent, having great availability, but the existence of the triple point at a temperature of 0 [^{0}C] at a pressure of 1 bar makes water to be used as a working agent only in the positive Celsius range.

Hydrocarbons are excellent working agents with acceptable working pressures and favorable thermodynamic properties. But the well-known flammability means that these substances are successfully used only in household refrigerators. These include propane, butane and their mixtures.

Ammonia is in many countries the most used working agent in medium and large equipment. It is completely harmless to the environment, but on the other hand, ammonia is toxic and flammable.

If the working agents listed above such as ammonia and hydrocarbons have good working properties but do not fully satisfy the safety conditions due to toxicity and flammability, carbon dioxide is an excellent solution from the point of view of safety. Carbon dioxide is successfully used in refrigeration equipment.

Refrigerant blends attempt to satisfy a wide range of requirements and characteristic properties. Choosing any working agent is choosing a compromise.

In table 4.1. the thermodynamic properties of some working agents of interest are presented.

Table 4.1. Thermodynamic properties of working agents

Work agent	Normal boiling point [^{o}C]	Critical point	ODP	GWP
R-279	-	-221.0	0	0
R-718	100.0	375.0	0	0
R-744	-55.6	31.0	0	1
R-717	-33.3	135.0	0	0
R-600	-0.8	152	0	4
R-600a	-12	134.7	0	3
R-290	-42.11	96.7	0	3
R-170	-88.58	32.17	0	6
R-601	36.1	196.6	0	20
R-1234yf	-29.48	94.7	0	1
R-1234ze(E)	-18.96	109.37	0	6
R-1234ze(Z)	9.76	153.7	0	10
R-1233zd(E)	18.26	166.4	0	6
R-1336mzz(Z)	33.45	171	0	9

4.3. CALCULATION OF STATE THERMAL AND CALORIC PROPERTIES OF CO_2

In this sub-chapter we try to determine the state properties both on the basis of the analytical model and with the help of the Engineering Equation Solver work program for CO_2.

4.3.1. Enthalpy of CO_2 in gaseous state

The mathematical relation (4.4) represents the caloric equation of state of enthalpy for carbon dioxide in the gaseous state and on the upper limit curve of the saturated gas. With the help of this mathematical expression, the enthalpy values can be calculated with a very good approximation.

$$\mathrm{H}(\mathrm{P},\mathrm{T}) = \left(\mathrm{A} + \frac{\mathrm{B}}{2}\mathrm{T}\right)\mathrm{T} + \frac{(\mathrm{N}+1)}{10^3}\left[\frac{\left(\mathrm{C}_1 + \frac{\mathrm{C}_2}{2}\cdot \mathrm{P_S}(\mathrm{T}=0^0\mathrm{C})\right)\mathrm{P_S}(\mathrm{T}=0^0\mathrm{C})}{2{,}7315^{\mathrm{N}}} - \frac{\left(\mathrm{C}_1 + \frac{\mathrm{C}_2}{2}\mathrm{P}\right)\mathrm{P}}{\left(\frac{\mathrm{T}}{100}\right)^{\mathrm{N}}}\right]$$

$$+ \mathrm{H}''(\mathrm{T}=0^0\mathrm{C}) - 273{,}15\ \left(\mathrm{A} + 273{,}15\frac{\mathrm{B}}{2}\right)\ \left[\frac{\mathrm{KJ}}{\mathrm{KG}}\right] \tag{4.4}$$

In table 4.2. the enthalpy values calculated with equation (4.4) but also with the help of the EES program are presented comparatively.

Table 4.2. Enthalpy of CO_2 in the gas phase. Comparison between the values calculated with equation (4.4) and the EES program

t [ºC]	h (Eq. (4.4)) [kJ/kg]	*Δ*h = h - hg	h_EES [kJ/kg]	Δh_EES = =h_EES – hg_EES	ε [%]
1	2	3	4	5	6
25	-34.2800	40.35	-32.3700	40.79	1.1050
30	-28.1800	46.45	-26.5800	46.59	0.3050
35	-22.1800	52.44	-20.9000	52.26	0.3370
40	-16.2800	58.34	-15.3200	57.84	0.8551
45	-10.4600	64.16	-9.8240	63.34	1.2750
50	-4.7220	69.90	-4.3930	68.77	1.6150
55	0.9531	75.58	0.9826	74.15	1.8910
60	6.5680	81.19	6.3110	79.48	2.1140

4.3.2. Entropy of CO_2 in the gaseous phase

To validate the mathematical model developed for entropy calculation, a comparative study of the results obtained using equation (4.5) determined based on the model developed in the thesis and the EES program was carried out, it is presented in table 4.3.

$$(\mathrm{P},\mathrm{T}) = \mathrm{A}\cdot \mathrm{LN}\,\mathrm{T} + \mathrm{B}\cdot\mathrm{T} - \left[\mathrm{R}_{\mathrm{CO_2}}\cdot \mathrm{LN}\,\mathrm{P} + \frac{\mathrm{N}\cdot\mathrm{P}\left(\mathrm{C}_1 + \frac{\mathrm{C}_2}{2}\mathrm{P}\right)}{\mathrm{T}\left(\frac{\mathrm{T}}{100}\right)^{\mathrm{N}}}\right]10^{-3} +$$

$$+\left\{\mathrm{R}\cdot \mathrm{LN}\,\mathrm{P_S}\,(\mathrm{T}=0^0\mathrm{C}) + \frac{\mathrm{N}\cdot \mathrm{P_S}(\mathrm{T}=0^0\mathrm{C})}{100\cdot(2.7315)^{\mathrm{N}+1}}\left[\mathrm{C}_1 + \frac{\mathrm{C}_2}{2}\mathrm{P_S}(\mathrm{T}=0^0\mathrm{C})\right]\right\}10^{-3} +$$

$$+s''(T = 0^0C) - (A \cdot \ln 273.15 + B \cdot 273.15) \left[\frac{kJ}{kg \cdot K}\right] \quad (4.5)$$

Table 4.3. Entropy of CO_2 in the gas phase. Comparison between the values calculated with equation (4.5) and the EES program

t [ºC]	s (Eq.4.5) [kJ/(kg K)]	Δs = s -sg	s_EES [kJ/(kg K)]	Δs_EES = =s_EES sg_EES	ε [%]
1	2	3	4	5	6
25	-0.7258	0.143	-0.7188	0.1448	1.2630
30	-0.7055	0.1633	-0.6995	0.1640	0.4861
35	-0.6859	0.1829	-0.6810	0.1826	0.1356
40	-0.6669	0.2019	-0.6630	0.2006	0.6367
45	-0.6484	0.2203	-0.6456	0.2180	1.0420
50	-0.6305	0.2382	-0.6286	0.2349	1.3710
55	-0.6131	0.2556	-0.6121	0.2514	1.6380
60	-0.5961	0.2726	-0.5960	0.2676	1.8550

4.4. COMPARATIVE ANALYSIS OF THE CHARACTERISTIC PROPERTIES OF THE WORKING AGENTS CO_2, R404A AND NH_3

For the comparative study of the properties of CO_2, R404A and NH_3, the cycle of a refrigerating plant in a stage with mechanical vapor compression characterized by the condensing temperature and a subcooling $\Delta t_{sr} = 5$ [K] was considered $t_c = 25$ [^{0}C]. The evaluation of the characteristic properties of the mentioned working agents was done for different vaporization temperatures. In order to evaluate the characteristic properties of the investigated working agents, exergy analysis is used, which manages to penetrate into the intimacy of the functional processes specifying the place and magnitude of malfunctions in the system.

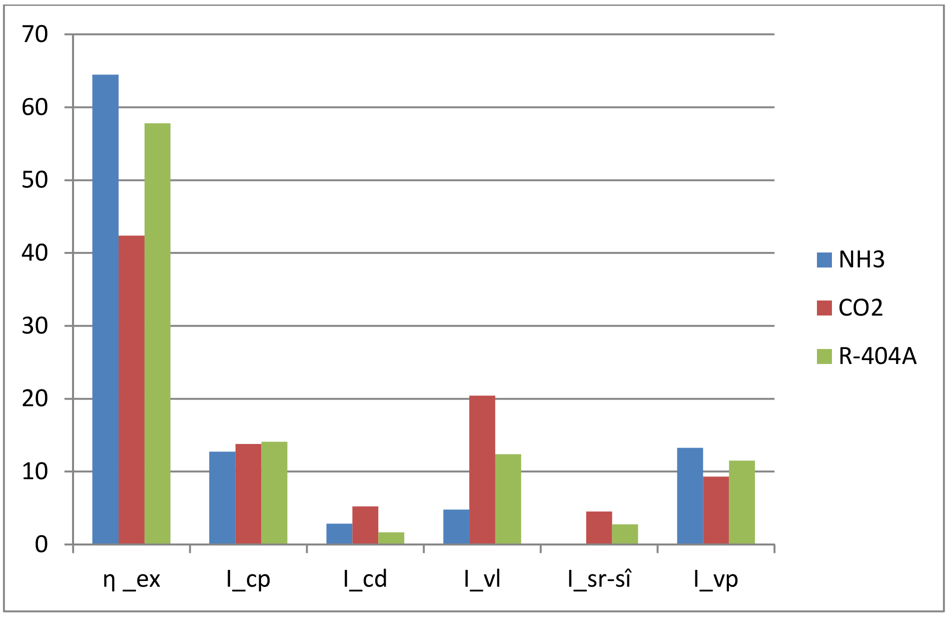

Figure 4.1. Comparative exergy analysis of the single-stage cycle when operating with NH_3, CO_2 and R-404A

In order to highlight the particular aspects of the behavior of refrigeration installations operating with different refrigerants, a comparative analysis was carried out considering ammonia, the best agent for industrial refrigeration, R404 A – a mixture of Hydro-Fluro-Carbons, frequently found in installations from the field of commercial refrigeration and in large capacity air conditioning systems and the carbon dioxide that is imposed by its safety in operation.

A comparative energy and exergy study of the cycle operation with CO_2, NH_3 and R404A was carried out.

A characteristic of the CO_2 refrigeration plant is the compressors' displacement, which is very small compared to the case of using NH_3 or R-404A.

Due to the high working pressure at which CO_2 operates, the compressors and piping corresponding to this refrigerant are small in size.

Ammonia is characterized by the best thermodynamic properties, while CO_2 is the safest refrigerant, a characteristic that represents a strong argument in favor of its use in commercial refrigeration applications, in the food industry or in transport.

The refrigeration efficiency of the cycle operating with R-404A is between the coefficients of performance of the cycles with NH_3 or CO_2. This nearly azeotropic mixture with very little temperature slip in the phase change process is a very good refrigerant but its high GWP limits its future.

The low exergy destruction in the evaporator recommends CO_2 as a good refrigerant in the low pressure stage of a cascade installation or as a volatile cold carrier, while the high exergy destruction in the condenser recommends it for use in heat pumps for heating and preparation of domestic hot water.

CHAPTER 5. SIMULATION OF THE OPERATION AND STRUCTURAL OPTIMIZATION OF A REFRIGERATION-HEAT PUMP COUPLED EQUIPMENT

This study seeks the optimal configuration of equipment capable of generating heat and cold for the industrial sector. The heated water is characterized by an inlet temperature of 20 [^{0}C] and an outlet temperature of 100 [^{0} C]. The chilled water is characterized by an inlet temperature of 12 [^{0}C] and an outlet temperature of 7 [^{0}C]. The heat pump uses a waste water source from an industrial process characterized by an inlet temperature of 50 [^{0}C] as a heat source at the evaporator level .

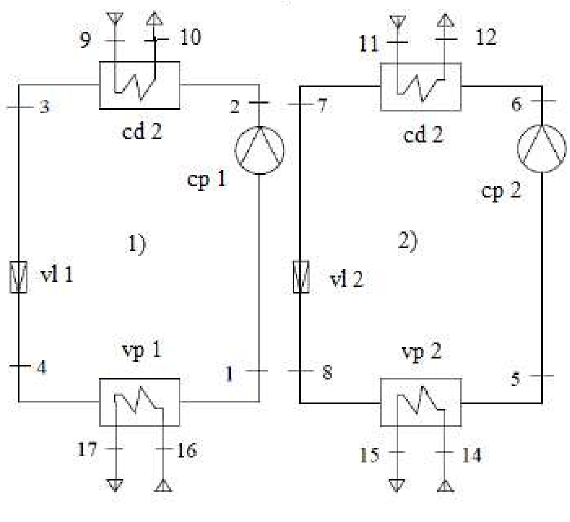

Figure 5.1. Separate cycles : 1) refrigeration cycle; 2) the heat pump cycle

For the first time, an equipment composed of two separate cycles is proposed for the generation of the two products (heat and cold).

The modeling starts from the exergy balance equation for a closed system

$$\sum \dot{Ex}_Q = \sum \dot{L} + \sum \dot{I} \tag{5.1}$$

$$|\dot{L}_{cp1}| + |\dot{L}_{cp2}| + |\dot{Ex}_Q^{Tsc}| = |\dot{Ex}_Q^{Tar}| + |\dot{Ex}_Q^{Taî}| + \sum \dot{I}_1 + \sum \dot{I}_2 + \dot{L}_{cd1} \tag{5.2}$$

The global fuel for the global system:

$$CB_{SG} = |\dot{L}_{cp1}| + |\dot{L}_{cp2}| \tag{5.3}$$

The energy product of the global system:

$$P_{SG}^{en} = |\dot{Q}_{vp1}| + |\dot{Q}_{cd2}| \tag{5.4}$$

The exergy product of the global system:

$$P_{SG}^{ex} = |\dot{Ex}_Q^{Tar}| + |\dot{Ex}_Q^{Taî}| \tag{5.5}$$

According to relations (5.3), (5.4) and (5.5) the energy performance coefficient and the exergy efficiency of the global system become:

$$COP_{SG}^{en} = \frac{P_{SG}^{en}}{CB_{SG}} \tag{5.6}$$

and

$$\eta_{SG}^{ex} = \frac{P_{SG}^{ex}}{CB_{SG}} \tag{5.7}$$

5.1. RESULTS AND DISCUSSION

The calculation program was made based on the thermodynamic model described, the thermodynamic properties of the working fluids were determined using the EES work program.

Since the products $|\dot{Ex}_Q^{Tar}| + |\dot{Ex}_Q^{Taî}|$are fixed, increasing the overall exergy efficiency of the system focuses on decreasing the exergy destruction rates in each apparatus and process.

The optimization procedure will track the devices and processes that consume large amounts of exergy (exergy destructions) and look for a way to reduce them. The decisive parameter is the condensation temperature of the refrigeration cycle.

5.1.1. Separate R717 and R152a systems

The exergy analysis indicates a high loss at the condenser of the refrigeration cycle given by the heat of condensation, which in the first instance is thrown into the environment.

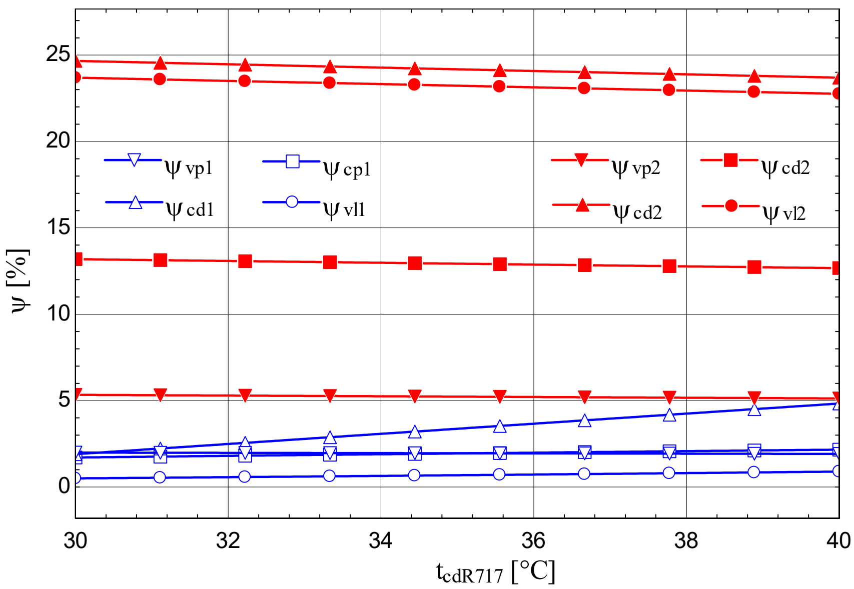

Figure 5.2. The influence of the condensing temperature in the refrigeration system on the exergy losses in each device and process. Separate cycles R717 and R152a

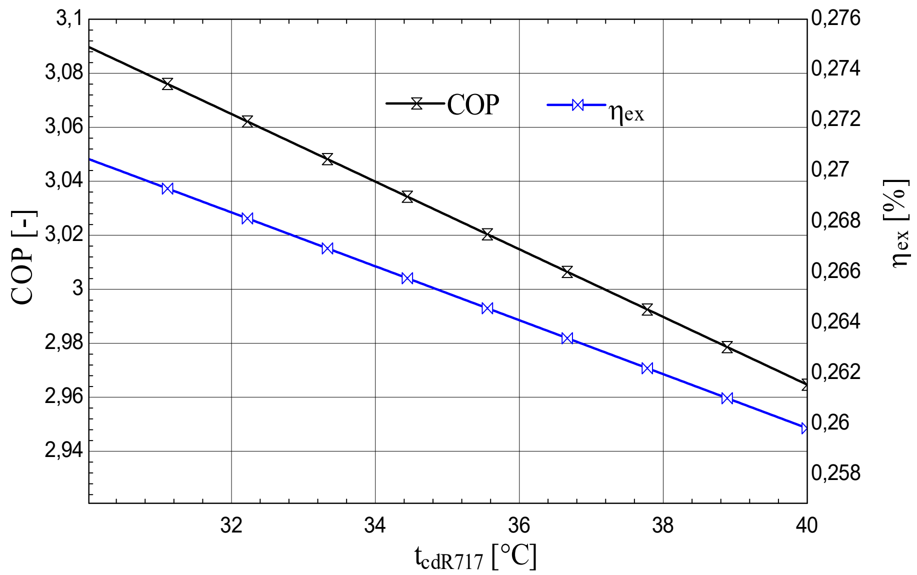

Figure 5.3. Energy performance coefficient and exergy efficiency of the overall system in the case of R717 and R152a separate cycles

5.1.2. Systems coupled by capacitors R717 and R152a

To eliminate the loss of exergy from the condenser of the refrigeration cycle and improve the overall performance of the equipment, the cycles are coupled to the condensers by means of heated water. The heat given off at the refrigeration cycle condenser is used to preheat the water from state 11 to an intermediate state 12. After preheating, the water enters the heat pump condenser where it is heated to the final state 13.

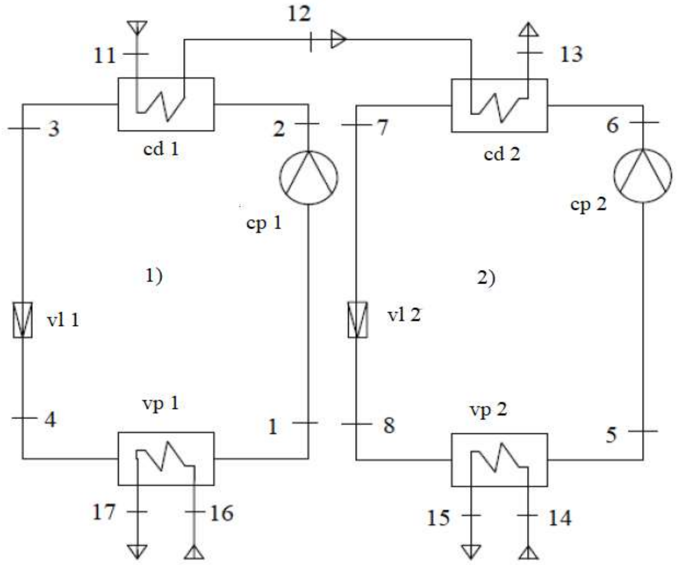

Figure 5.4. Systems coupled by R717 and R152a capacitors: 1) refrigeration cycle; 2) the heat pump cycle

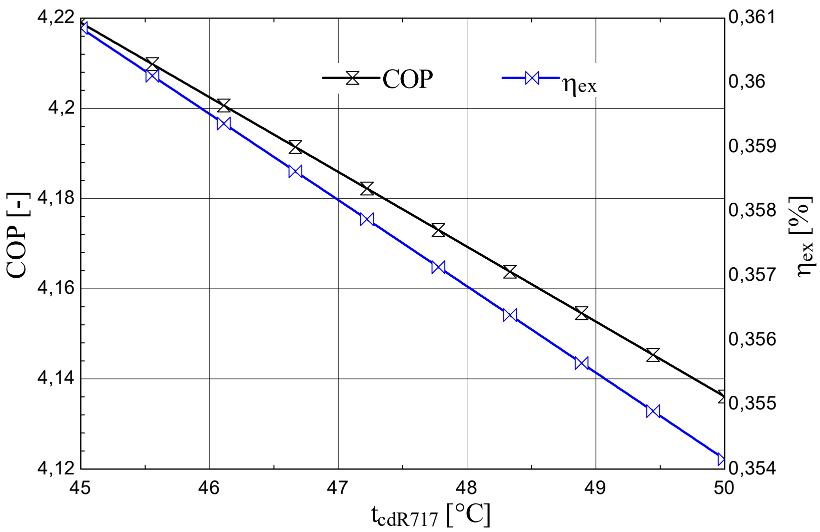

Figure 5.5. Energy performance coefficient and exergy efficiency of the overall system in the case of R717 and R152a capacitor-coupled cycles

5.1.3. R744 and R152a coupled cycles

The results indicate a substantial increase in equipment performance. The simulations carried out showed that to ensure heat transfer in the refrigeration cycle condenser, the condensation temperature must be at least 50 [^{0}C]. Due to the high condensing temperature, the exergy destruction in the refrigeration cycle condenser is the largest destruction in the refrigeration cycle. To reduce it, a functional optimization was carried out by replacing ammonia with carbon dioxide.

For the assessment of exergy destruction at the level of each device and process, but also for the investigation of the performance of the R744 and R152a coupled cycles, the discharge pressure at the level of the refrigeration cycle is chosen as a decision-making parameter.

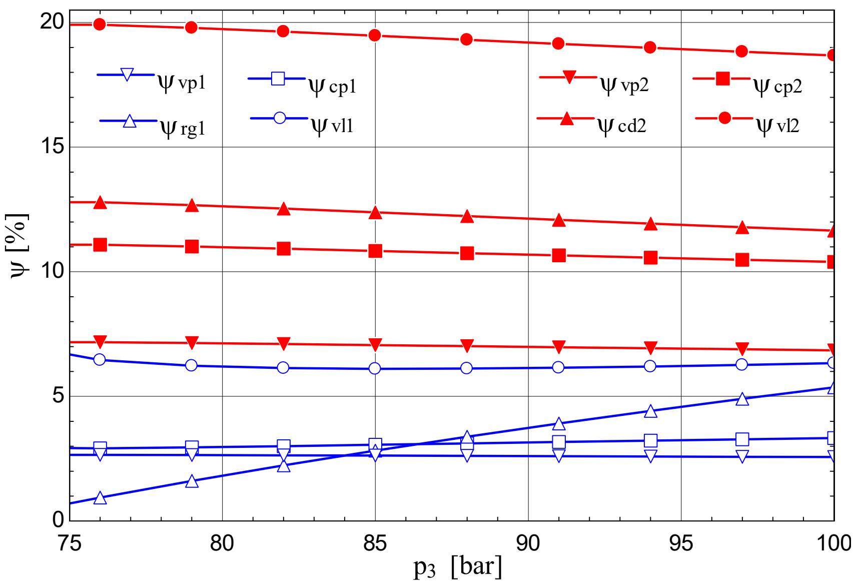

Figure 5.6. Influence of gas cooler discharge pressure on exergy losses in each apparatus and process. R744 and R152a coupled cycles

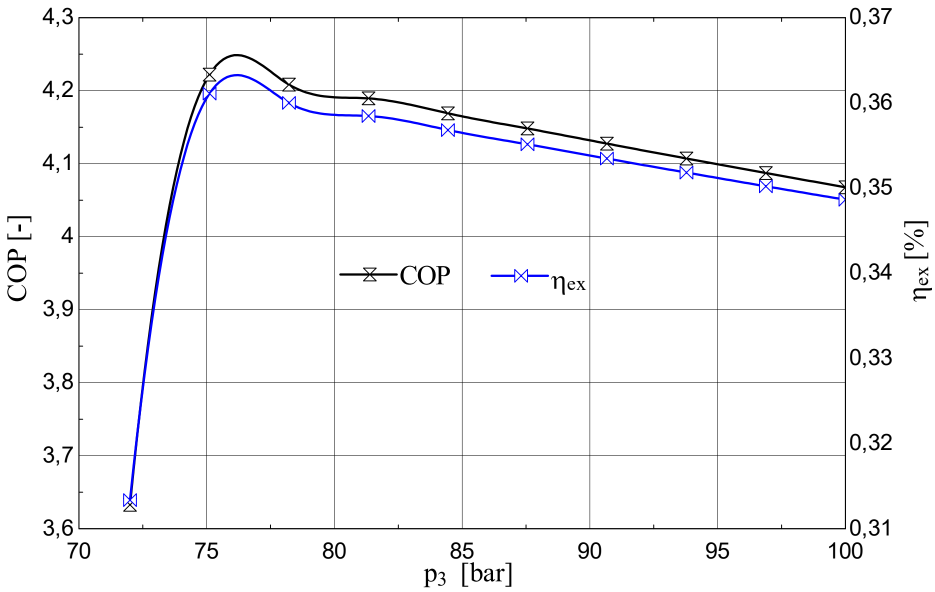

Figure 5.7. Energy performance coefficient and exergy efficiency of the overall system in the case of R744 and R152a coupled cycles

5.1.4. Coupled cycles and regenerative subcooling in the refrigeration cycle using R744 and R152a working agents

The replacement of ammonia with carbon dioxide led to the increase of the overall performance of the equipment by reducing the exergy destruction at the level of the heat exchange process between the heated water and the working agent, but the exergy destruction at the level of the throttling process increases. In order to reduce exergy destruction at the level of the throttling process, an internal regenerative heat exchanger was introduced that ensures subcooling of the carbon dioxide.

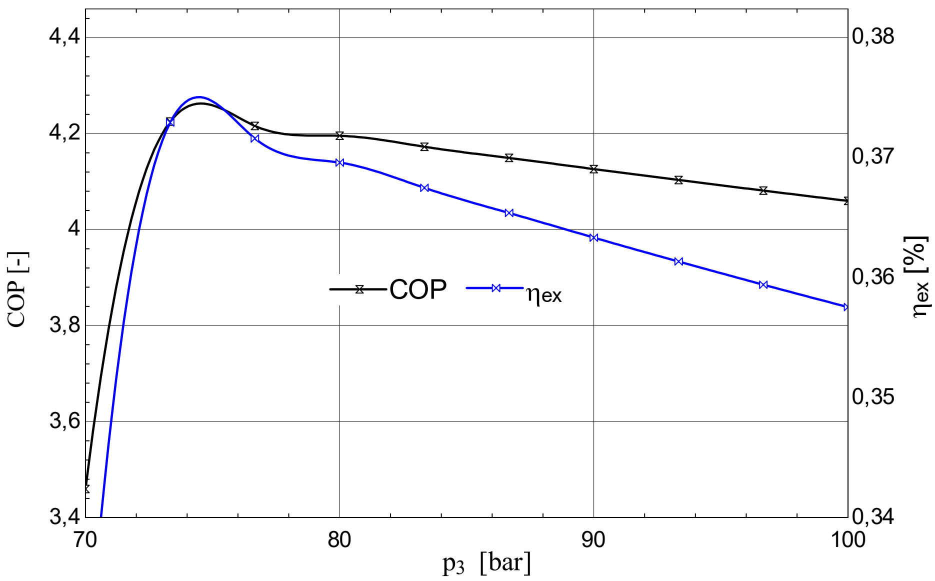

Figure 5.8. Energy performance coefficient and exergy efficiency of the overall system in the case of coupled cycles and regenerative subcooling at the refrigeration cycle level using R744 and R152a working agents

5.1.5. Analysis and behavior of coupled cycles and internal heat exchanger using working agents R744 and R152a

In order to optimize the heat pump cycle, the introduction of a heat exchanger was carried out, which has the role of subcooling the working agent at the level of the heat pump. The heat taken is passed to the refrigerating cycle realizing an overheating of the working agent at the suction in the compressor.

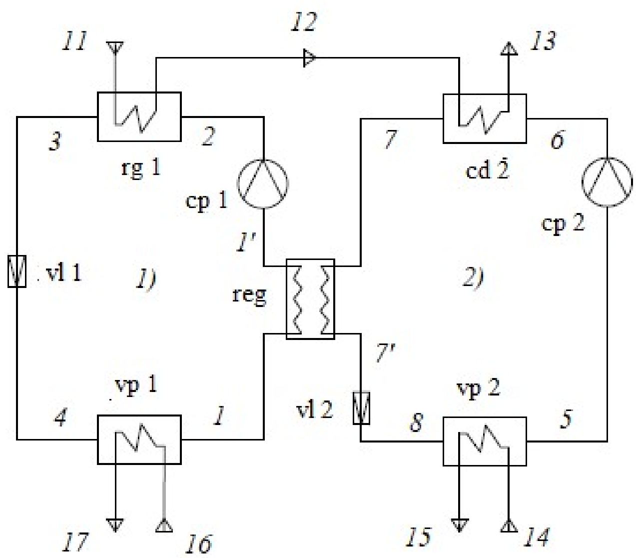

Figure 5.9. Coupled cycles and internal heat exchanger using R744 and R152a working agents: 1) refrigeration cycle; 2) the heat pump cycle

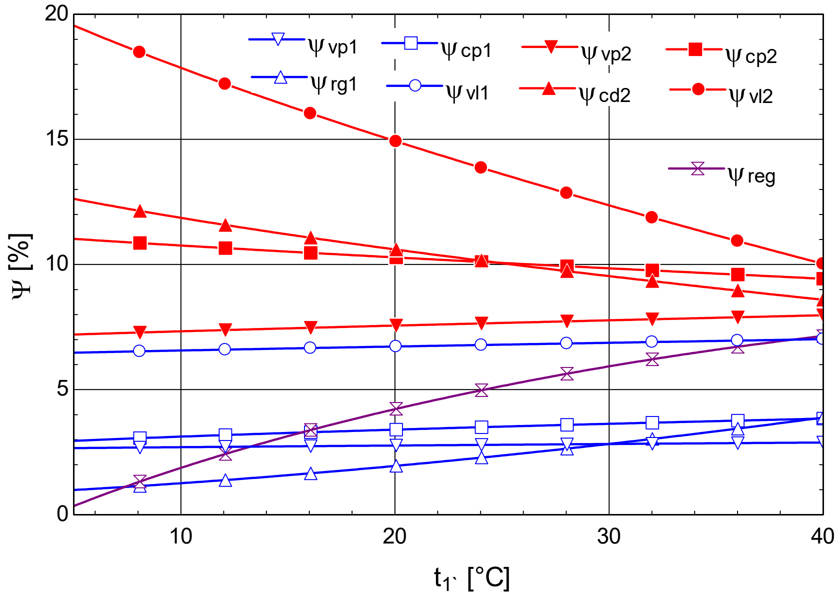

Figure 5.10. Influence of superheat temperature on exergy destructions in each apparatus and process. Coupled cycles and internal heat exchanger using R744 and R152a working agents

By introducing the internal heat exchanger, the exergy losses at the level of the throttling process in the heat pump cycle are significantly reduced.

In this case, the performance coefficient and exergy yield show the highest value among the 5 cases presented.

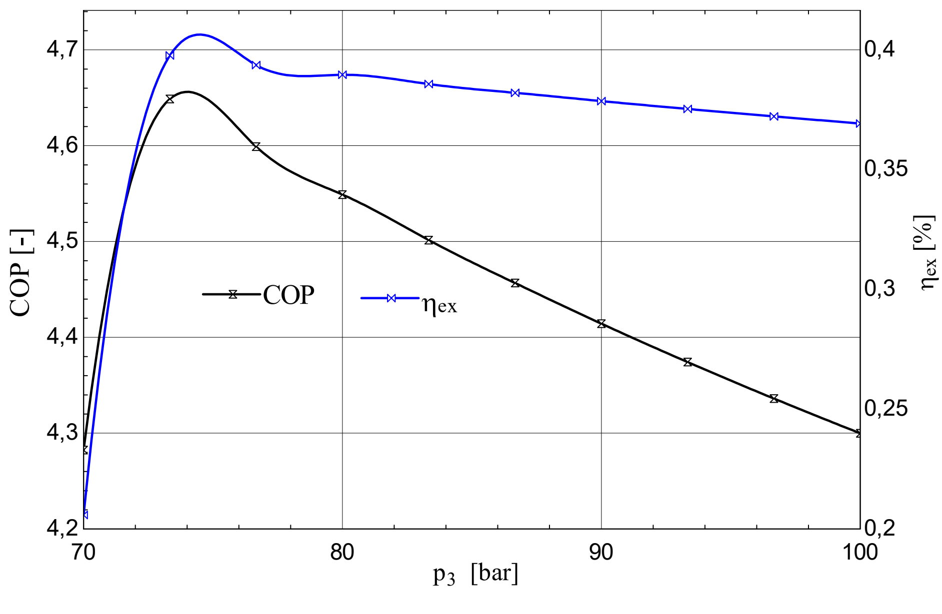

Figure 5.11. Energy performance coefficient and exergy efficiency of the overall system in the case of coupled cycles and internal heat exchanger using working agents R744 and R152a

The continuous increase of the global performance indices is possible by tracking the exergy destruction in each device and process. Based on the exergy analysis, it is possible to identify and locate the malfunctions in the system.

This study proves the importance of using exergy analysis in the optimization of thermal equipment. Evaluation of the exergy destruction rate charts for each piece of equipment indicated priority areas for optimization. The exergy analysis led to an optimal configuration of the equipment and enabled the significant improvement of the overall performance of the equipment.

CHAPTER 6. HEAT EXCHANGE MODELING IN THE GAS COOLER OF A CO_2 HEAT PUMP OPERATING IN THE SUPERCRITICAL DOMAIN

The paper deals with the design and simulation of a gas-water heat exchanger used for heating purposes. The heat exchanger is the gas cooler / water heater of a transcritical CO_2 heat pump. The logarithmic mean temperature difference and the NTU-ε method are compared. The heat transfer surface can be calculated by both methods, but the real strength and what makes the difference when using the NTU-ε method is that it can easily be used to simulate the behavior of an existing heat exchanger.

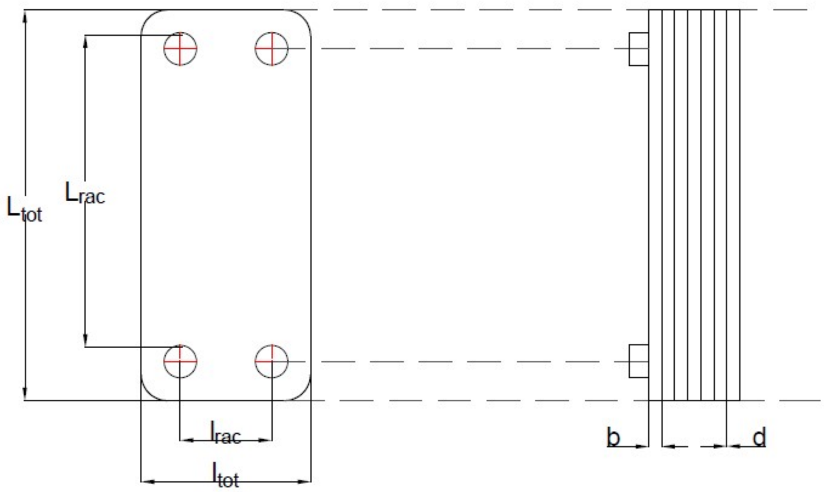

Figure 6.1 . Gas Cooler Configuration

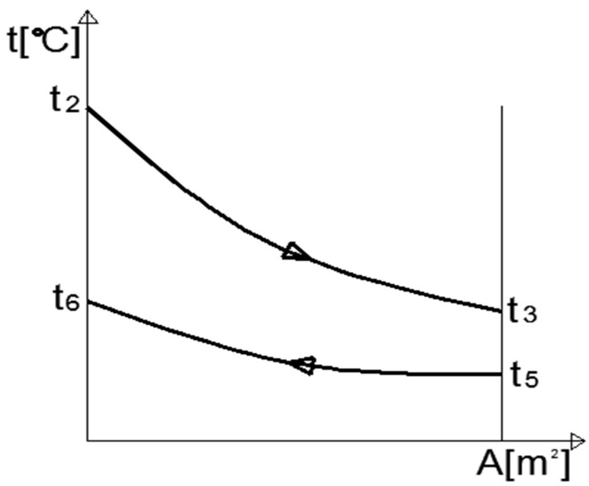

Figure 6.2. Countercurrent gas cooler. Temperature variation in the heat exchanger.

6.1 . RESULTS AND DISCUSSION

6.1.1. Determination of the overall heat exchange coefficient

To determine the global transfer coefficient, the following criterion equation was selected from the specialized literature for carbon dioxide [19].

$$\mathrm{Nu_{CO_2}} = 0.021 \cdot \mathrm{Re_{fCO_2}^{0.8}} \cdot \mathrm{Pr_{fCO_2}^{0.43}} \cdot \left(\frac{\mathrm{Pr_{fCO_2}}}{\mathrm{Pr_p}}\right)^{0.25} \tag{6.1}$$

For water it was selected [20]:

$$\mathrm{Nu_a} = 0.0508 \cdot \mathrm{Re_{fa}^{0.7304}} \cdot \mathrm{Pr_{fa}^{0.33}} \cdot \left(\frac{\mu_{ma}}{\mu_p}\right)^{0.14} \tag{6.2}$$

Table 6.1. Flow and heat transfer characteristics

[um]	Carbon dioxide	The water
t_m [^{o} C]	86.2	57.5
t_p [^{o}C]	71.8	71.8
λ [W/mK]	0.03697	0.6386
μ_f [m ^{2} /s]	8,862 $\cdot 10^{-8}$	4.924 $\cdot 10^{-7}$
μ_p [m ^{2} /s]	7,945 $\cdot 10^{-8}$	4.037 $\cdot 10^{-7}$
a_f [m ^{2} /s]	6.435 $\cdot 10^{-8}$	1,551 $\cdot 10^{-7}$
a_p [m ^{2} /s]	4,419 $\cdot 10^{-8}$	1,591 $\cdot 10^{-7}$
ṁ[kg/s]	0.2064	0.956
Re $_f$	123338	28803
Prof _	1,377	3,175
Fr $_p$	1,798	2,537
Not	261.6	122.3
α [W/m ^{2} K]	742	5881
k [W/m ^{2} K]	655.2	

6.1.2. Method based on logarithmic mean temperature

The logarithmic mean temperature difference method is mainly used for the design or selection of a heat exchanger.

Determination of the heat flux changed by the heat exchanger, the method based on the logarithmic mean temperature difference:

$$\dot{Q} = k \cdot A \cdot \Delta T_{med} = k \cdot A \frac{(t_2 - t_6) - (t_3 - t_5)}{\ln \frac{t_2 - t_6}{t_3 - t_5}} \tag{6.3}$$

6.1.3. The method based on the number of heat transfer units

If C_{CO2}, C_a , k, A (or kA) and the inlet temperatures t_2 and t_5 are known , the three equations contain three variables and the two outlet temperatures t_3 and t_6 .

By eliminating two equations, we are left with two unknowns t_3 and t_6.

$$C_{CO_2}(t_2 - t_3) = C_a(t_6 - t_5) \tag{6.4}$$

$$C_{CO_2}(t_2 - t_3) = k \cdot A \frac{(t_2 - t_6) - (t_3 - t_5)}{\ln \frac{t_2 - t_6}{t_3 - t_5}} \tag{6.5}$$

Defining P as:

$$P = k \cdot A \left(\frac{1}{C_{CO_2}} - \frac{1}{C_a} \right) \tag{6.6}$$

$$\varepsilon = \frac{e^P - 1}{e^P - \frac{C_{CO_2}}{C_a}} \tag{6.7}$$

$$NTU = \frac{k \cdot A}{C_{CO_2}} = \frac{k \cdot A}{C_{min}} \tag{6.8}$$

The heat transfer area can be calculated:

$$A = \frac{NTU \cdot C_{CO_2}}{k} \tag{6.9}$$

For the specific case, the following are given: C_{min} , C_{max} and k and the inlet and outlet temperatures. When it is desired to determine the heat transfer area, the following steps must be taken:

1. Calculate ε (equation 6.7);
2. Determine P (equation 6.6.) and NTU (equation 6.8);
3. Determine the heat transfer area A (equation 6.9).

The heat transfer area was calculated using the two methods presented (the method based on the logarithmic average temperature and the method based on the number of transfer units and the thermal efficiency of the heat exchanger). Table 6.2 shows the results obtained for a heat flow given off by carbon dioxide $\dot{Q}_{Gc}$ = 19.98 [kW]; C_{CO2} =0.4614 [kW/K];

C_a = 3.998 [kW/K]; C_r =0.1154; t_2 =108.3 [^{0}C]; t_3 =65 [^{0}C]; t_5 =55 [^{0}C]; t_6 = 60 [^{0}C].

Table 6.2. The results obtained by the two methods (ΔT_{med}) and NTU- ε

ΔT_{med}[K]	$A_{\Delta T_{med}}$[m ^{2}]	ε [-]	NTU [-]	A_{NTU} [m ^{2}]
24.32	1,254	0.8124	1.78	1,254

The heat transfer area can be calculated with the same accuracy by both methods, but the real strength and what makes the difference when using the NTU- ε method is that based on it the simulation and behavior of an existing heat exchanger can be easily done.

CHAPTER 7. STUDY OF THE INFLUENCE OF CARBON DIOXIDE SUBCOOLING AT THE OUTLET OF THE HEAT PUMP GAS COOLER BY COUPLING TWO HEAT PUMP CYCLES

The present study focuses on identifying the optimal configuration of an air-to-water heat pump that is capable of providing hot water at 70 [^{0}C]. The heat pump shown in figure 7.1. it takes heat with low energy potential from the surrounding environment, and through a process of mechanical compression raises the temperature level of the heat, corresponding to the customer's request. Due to the low critical temperature that characterizes carbon dioxide, the cycle evolves in the transcritical zone. Water is heated in a round-trip system where the inlet and outlet water temperatures are t_{10} = 50 [^{0}C] and t_{11} = 70 [^{0}C].

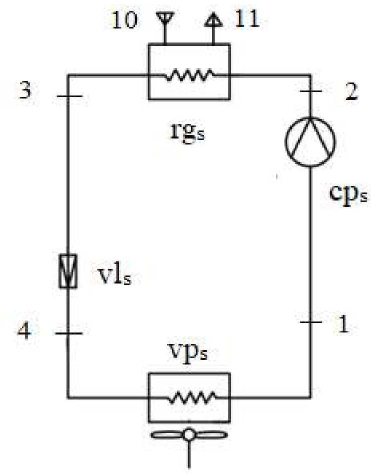

Figure 7.1. CO_2 heat pump in a compression stage. Standard cycle

The exergy balance equation

$$\left|\dot{L}_s\right| = \left|\dot{Ex}_{Q_{rg_s}}^{T_{aî}}\right| + \dot{I}_{vp_s} + \dot{I}_{cp_s} + \dot{I}_{rg_s} + \dot{I}_{vl_s} \tag{7.1}$$

The exergy performance coefficient of the heat pump is:

$$\eta_{ex} = \frac{\dot{Ex}_{Q_{rg_s}}^{T_{aî}}}{\dot{L}_s} \tag{7.2}$$

7.1. RESULTS AND DISCUSSION

7.1.1. Results and discussion. Standard cycle

A parametric analysis of the sensitivity to the variation of the discharge pressure (p2) in the gas cooler is performed.

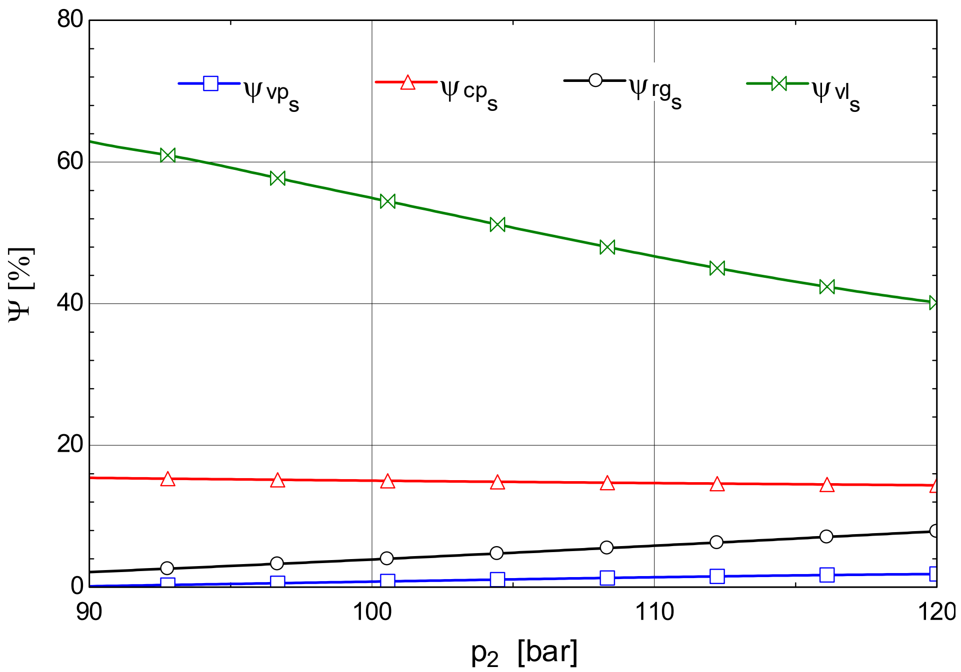

Figure 7.2. Exergy destruction rate versus gas cooler discharge pressure for key system components

Exergy destruction rate in compression mechanical work input and energy and exergy efficiency were calculated.

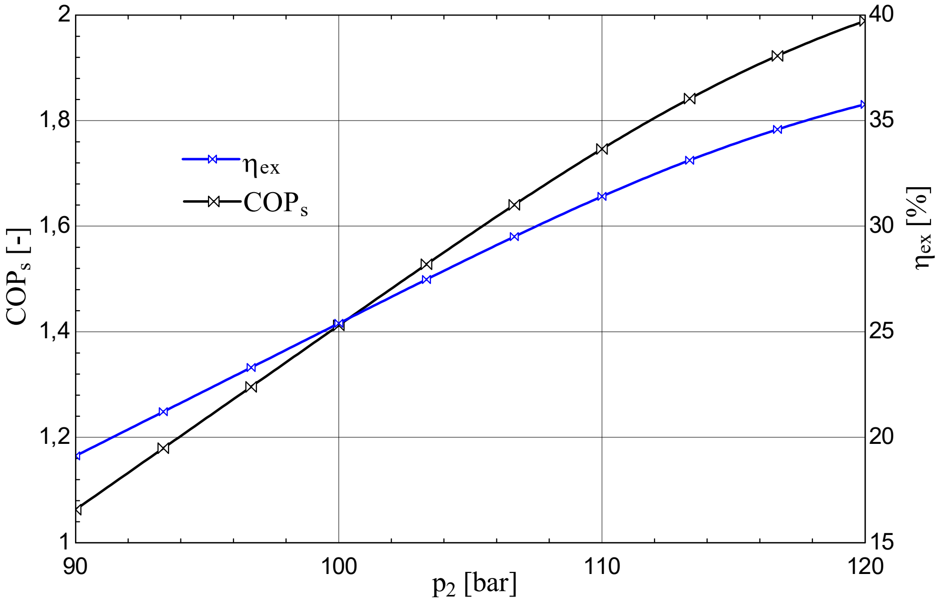

Figure 7.3. Coefficient of energy performance and exergy efficiency of the standard CO_2 heat pump cycle at the variation of the discharge pressure in the gas cooler

7.2. CO_2-CO_2 COUPLED CYCLES

To increase the performance coefficients of the standard heat pump cycle, the optimization strategy must focus on decreasing the exergy destruction associated with the throttling process.

In order to further reduce the exergy destruction in the throttling process in addition to increasing the compression pressure, a change must be made to the input parameters at the level of the throttling valve.

In order to lower the temperature of the CO_2 at the inlet of the lamination valve, a subcooling of the gas after the gas cooler, by means of an external subcooler, can be imagined. This can be done by coupling the standard cycle with an auxiliary one.

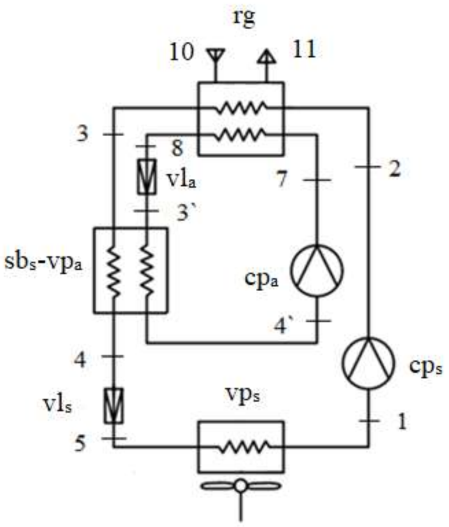

Figure 7.4. Scheme of the coupled cycle of the heat pump

$$\left|\dot{L}_{cp_s}\right| + \left|\dot{L}_{cp_a}\right| = \left|\dot{Ex}_{Q_{rg_s}}^{T_{aî}}\right| + \left|\dot{Ex}_{Q_{rg_a}}^{T_{aî}}\right| + \left|\dot{Ex}_{Q_{vps}}^{T_{vps}}\right| + \dot{I}_{\Delta T_{rg_s}} + \dot{I}_{\Delta T_{rg_a}} + \dot{I}_{cp_s} + \dot{I}_{cp_a} + \dot{I}_{vl_s} + \dot{I}_{vl_a} + \dot{I}_{\Delta T_{sb_s - vp_a}} \quad (7.3)$$

The total fuel for the coupled system is given by the relation:

$$CB_c = \left|\dot{L}_s\right| + \left|\dot{L}_a\right| \quad (7.4)$$

The energy product and the exergy product of the coupled system are:

$$P_c^{en} = \left|\dot{Q}_{rg_s}\right| + \left|\dot{Q}_{rg_a}\right| \quad (7.5)$$

And

$$P_c^{ex} = \left|\dot{Ex}_{Q_{rg_s}}^{T_{aî}}\right| + \left|\dot{Ex}_{Q_{rg_a}}^{T_{aî}}\right| \quad (7.6)$$

According to the mathematical relations (7.4), (7.5) and (7.6) the energy performance coefficient of the coupled cycles COP_c^{en} becomes:

$$COP_c^{en} = \frac{P_c^{en}}{CB_c} \quad (7.7)$$

The exergy efficiency of the coupled cycles can be written:

$$\eta_c^{ex} = \frac{P_c^{ex}}{CB_c} = \frac{\left|\dot{Ex}_{Q_{rg_s}}^{T_{aî}}\right| + \left|\dot{Ex}_{Q_{rg_a}}^{T_{aî}}\right|}{\dot{L}_s + \dot{L}_a} \quad (7.8)$$

7.2.1 . CO_2 -CO_2 coupled cycles results and discussion

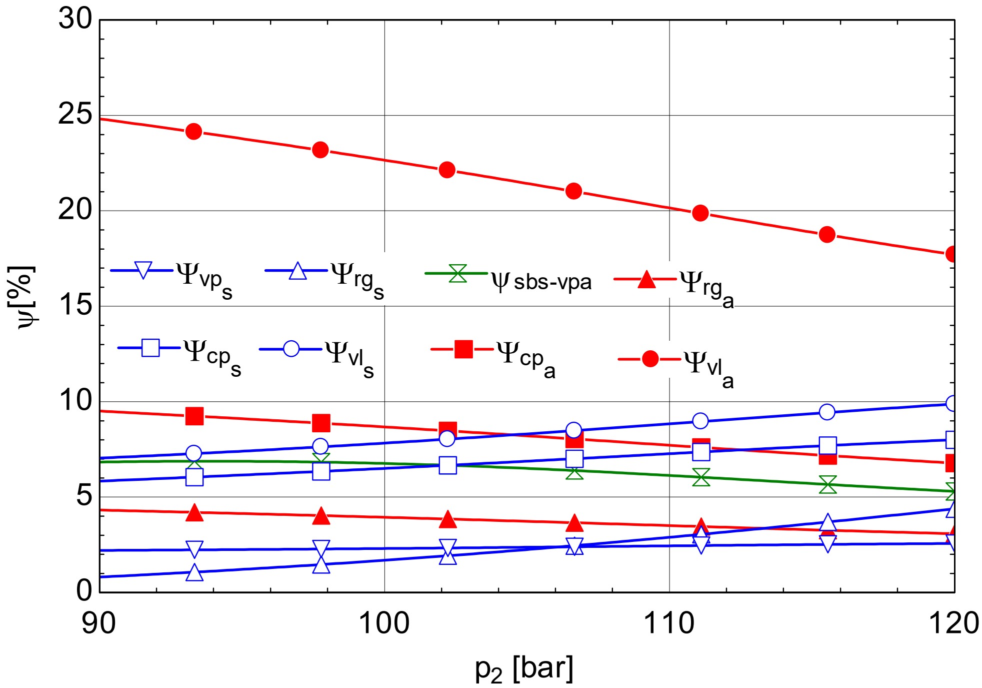

Figure 7.5. The exergy destruction rate of CO_2 -CO_2 coupled cycles at the variation of the discharge pressure of the standard cycle

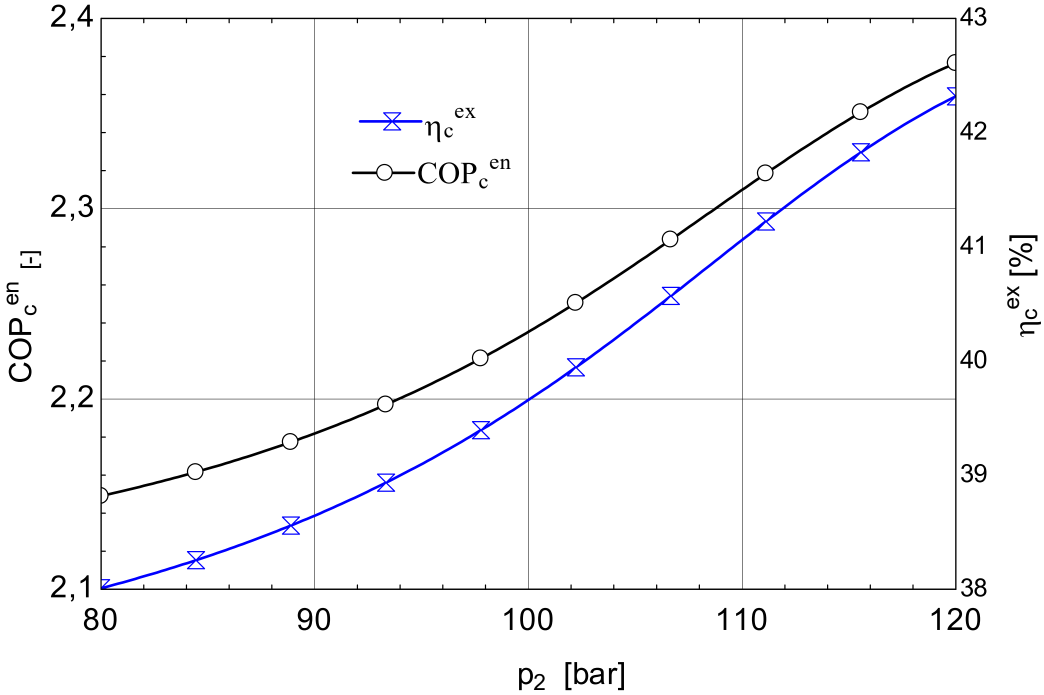

Figure 7.6. CO_2 -CO_2 coupled cycle performance indices

Comparing performance indices ($COP_c^{en}$and η_c^{ex}) in the case of the coupled CO_2 -CO_2 heat pump with the case of the standard heat pump cycle, an improvement in the global energy and exergy coefficients of the coupled CO_2 -CO_2 system is observed . This overall improvement in performance indices comes from the application of subcooling which leads to a substantial decrease in exergy destruction in the standard cycle throttling process.

CHAPTER 8. HEAT PUMPS FOR HIGH TEMPERATURES

The present study focuses on the delivery of hot water at 90 [^{0}C]. The refrigerant is CO_2 whose use in heat pumps is mainly recommended for cold regions of the globe characterized by an average annual temperature that does not exceed t_0=15 [^{0}C]. Such systems are recommended when a waste heat source is available or for cogeneration heat and cold applications [21-24].

Three constructive schemes are considered:

- a transcritical system with a compression step considered as the reference system;
- a two-stage system with cold vapor injection between the two compression stages;
- a two-stage compression cycle with intermediate external cooling by preheating a stream of water.

Carbon dioxide is a natural, non-toxic and non-flammable refrigerant. These qualities recommend it for use in a wide range of activities such as the food industry or industrial processes where water at high temperatures is required.

Due to its low critical temperature, the use of carbon dioxide in heat pumps is particularly recommended in cold climate regions.

Different configurations with one compression stage and two compression stages were modeled and parametrically tested.

Exergy analysis was used in the search for the optimal structure and operating regime.

For the two-stage compression system, the existence of two lamination valves removes the positive effect of decreasing the exergy destruction in the gas cooler.

The two-stage cycle with external intercooling manages to achieve the best efficiency while retaining only one throttling valve.

8.1. RESULTS AND DISCUSSION

8.1.1. Heat pump for high temperatures in a CO_2 compression stage . Transcritical system with one compression stage

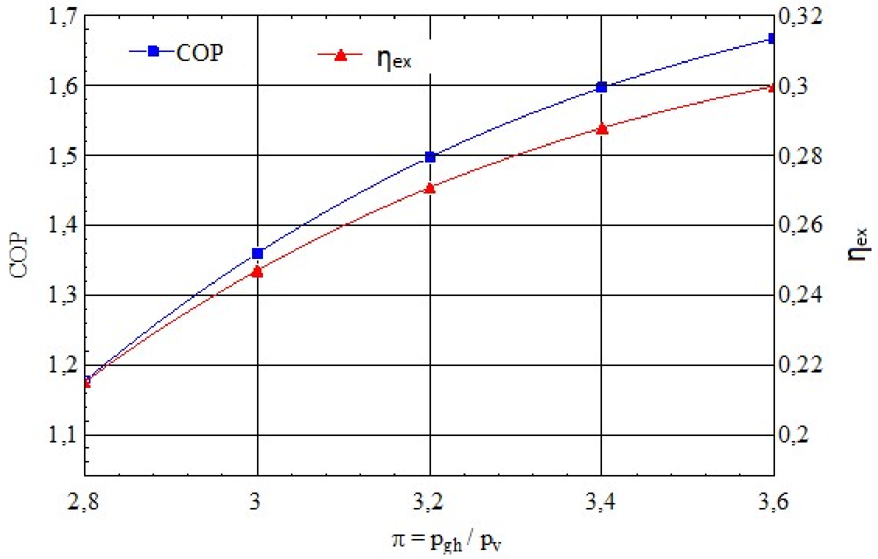

Figure 8.1. Performance indices COP_{en} and η_{ex} at variation of compression ratio. Heat pump for high temperatures in a CO_2 compression stage . Transcritical system with one compression stage

8.1.2 Two-stage compression heat pump with cold vapor injection between the two compression stages

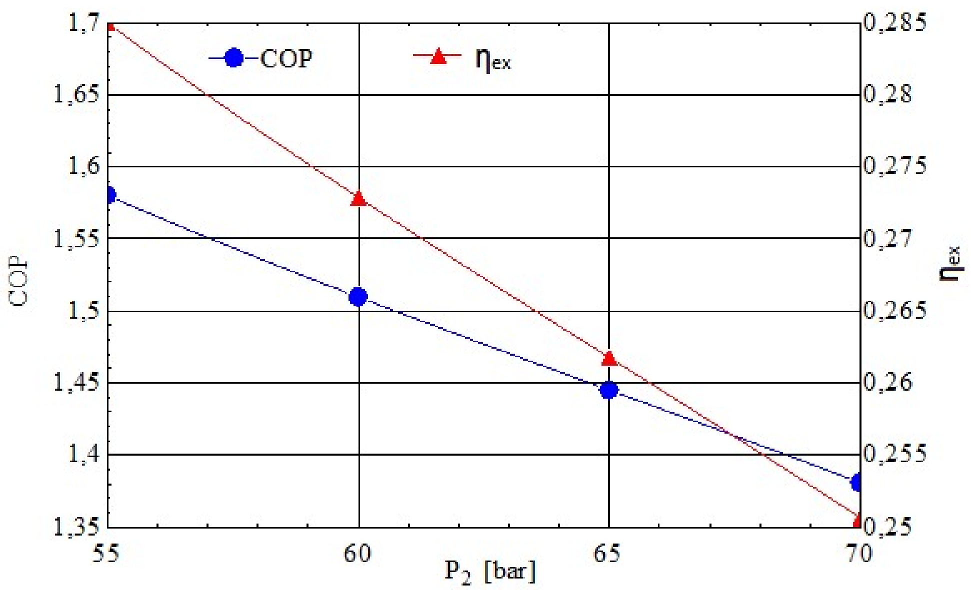

Figure 8.2. Energy and exergy performance indices of the two-stage compression system with injection of cold vapors between the two compression stages, at the variation of the intermediate pressure

8.1.3 . Two-stage compression heat pump with external cooling between the two compression stages

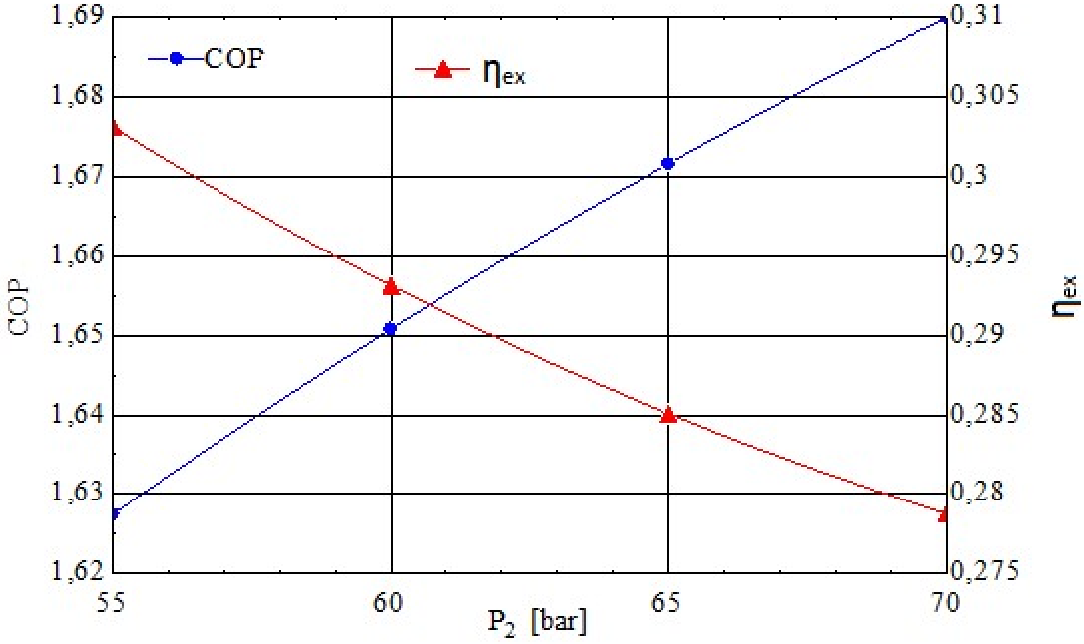

Figure 8.3. Energy and exergy performance indices of the system in two stages of compression with external cooling between the two stages of compression, at the variation of the intermediate pressure

FINAL CONCLUSIONS

Heat pumps represent one of the most practical solutions for reducing greenhouse gas emissions. This process of pumping heat from the environment or as waste from an industrial process, provides energy efficient and environmentally friendly heating and cooling solutions.

The PhD thesis investigates heat pump cycles through the lens of the second law of thermodynamics which is able to provide qualitative information of each form of energy entering or leaving the system.

To identify malfunctions in each device and process, exergy analysis is used, which makes it possible to enter the system boundary and has the ability to identify the extent and location of each failure.

The paper presents the simulation, behavior and energy and exergy performance indices of one-stage compression heat pump cycles and different two-stage compression schemes using environmentally friendly working agents.

Simulations performed on carbon dioxide heat pump cycles show that this working agent can be successfully used in heat pump applications that ensure the thermal comfort of buildings but also for high temperature heat pumps that are able to deliver water at temperatures above 90 [^{0}C].

Although carbon dioxide exhibits high exergy losses in the lamination process based on the exergy analysis, an optimization strategy could be identified that led to a considerable improvement in the overall performance of the equipment.

The optimization study of heat pump cycles as a whole, based on exergy analysis, represents an original contribution of the doctoral thesis.

PUBLISHED ARTICLES

1) **D. Dima** , A. Dobrovicescu*, Exergy analysis, coupled heat pump and refrigeration system using waste heat, The XXIII rd National Conference on Thermodynamics with International Participation, NACOT 11-13 May 2023, Galati, Romania .

2) **D. Dima** , A. Dobrovicescu, C. Dobre*, Energy and exergy analysis of the heat pump cycle using working agents with low environmental impact, The 11 th International Conference of Thermal Equipment, Renewable Energy and Rural Development, TE-RE-RD 8-10 June 2023, Bucharest, Romania.

3) Claudia Ionita*, Alexandru Dobrovicescu, **Daniel Dima** , EXERGETIC ANALYSIS OF A VAPOR INJECTION COMPRESSION HEAT PUMP, XXII th International Multidisciplinary Scientific GeoConference Surveying, Geology and Mining, Ecology and Management – SGEM 2022, Albena, Bulgaria.

4) Claudia Ionita*, Alexandru Dobrovicescu, **Daniel Dima,** SELECTING THE OPTIMAL LIQUEFACTION CYCLE FOR CRYOGENICS ENERGY STORAGE, XXII th International Multidisciplinary Scientific GeoConference Surveying, Geology and Mining, Ecology and Management – SGEM 2022, Albena, Bulgaria.

5) Talaba, **D Dima*** , V Buiuc, C Ionita, MF Stefanescu, A Serban and A Dobrovicescu, CO_2 high temperature heat pump – a promising solution, IOP Conference Series: Materials Science and Engineering , Volume 997 , The 9th International Conference on Advanced Concepts in Mechanical Engineering - ACME 2020 4-5 June 2020, Iasi, Romania .

6) **D Dima** , C Ionita, EE Vasilescu, AT Gheorghian and A Dobrovicescu*, Analysis of a dual-purpose refrigerating and heat pump system, IOP Conference Series: Materials Science and Engineering , Volume 997 , The 9th International Conference on Advanced Concepts in Mechanical Engineering - ACME 2020 4-5 June 2020, Iasi, Romania .

7) S Bucsa, **D Dima** , A Serban, MF Stefanescu, V Popa and A Dobrovicescu*, Heat exchanger design based on minimum entropy generation, IOP Conference Series: Materials Science and Engineering , Volume 595 , The XXIInd National Conference on Thermodynamics with International Participation, NACOT 23–24 May 2019, Galati, Romania .

8) **D Dima** , S Bucsa, C Ionita, EE Vasilescu, A Dobrovicescu* and E Niculae, Heat transfer characteristics of a gas cooler, IOP Conference Series: Materials Science and Engineering , Volume 595 , The XXIInd National Conference on Thermodynamics with International Participation, NACOT 23–24 May 2019, Galati, Romania .

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