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PRELIMINARY ASSESSMENT OF CARNOT BATTERIES AS AN INNOVATIVE ELECTRICAL ENERGY STORAGE

VOLUME 1

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Preliminary assessment of Carnot Batteries as an innovative electrical energy storage

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Avaliação preliminar das Baterias de Carnot como uma forma inovadora de armazenamento de energia elétrica.

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“Combati o bom combate, terminei a corrida, guardei a fé”

2 Timóteo, 4 :7

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Abstract

Increased world-wide demand for energy (especially electricity), rising energy costs, and heightened environmental concerns are factors that continually press for the adoption of technologies to exploit the renewable energy sources (RES). However, due to the ever increasing share of RES in the energy mix, large-scale energy storage systems are considered essential to ensure the security of supply in energy systems.

The purpose of this work arises from the need to find a new form of energy storage technology, which works without any restriction of location, with low-cost materials and a high storage capacity. The technology studied comprehends a combination of a heat pump that transforms electrical energy into thermal energy in the charge phase, that can be stored for several hours to a few days, and an organic Rankine cycle (ORC) that transforms the thermal stored energy in electrical energy again in the discharge situation. This technology is known as Carnot Batteries

Three different configurations of the Carnot Batteries were tested using models created in Matlab programming software. The first model is a simple model in which both the heat pump and the organic Rankine cycle are described in the simplest configuration. The second model adds a new stage in the heat pump and an organic Rankine's cycle regenerator. The third and last model uses an additional heat source (waste heat, geothermal or solar) to the cycle.

Six working fluids were used to run the tests in the three configurations, R1233zd(E), R1234yf, R11, R236ea, R245fa, and iso-pentane. The second configuration makes the system more complex but increases the P2P efficiency relatively to the first one. The third configuration achieves P2P efficiencies higher than 100%, where the resulting electrical energy of the system is bigger than the provided one. The best results were obtained using the third configuration with iso-pentane as the working fluid.

Keywords Energy Storage, Heat Pump, Organic Rankine Cycle, Waste heat, Iso-Pentane.

Resumo

O aumento da demanda mundial por energia (especialmente eletricidade), os custos crescentes da energia e as preocupações ambientais aumentadas são fatores que pressionam continuamente para a adoção de tecnologias para explorar as fontes de energia renováveis (FER). No entanto, devido à participação cada vez maior de FER no cabaz energético, os sistemas de armazenamento de energia em grande escala são considerados essenciais para garantir a segurança do abastecimento dos sistemas energéticos.

O objetivo deste trabalho surge da necessidade de encontrar uma nova forma de tecnologia de armazenamento de energia, que funcione sem qualquer restrição de localização, com materiais de baixo custo e elevada capacidade de armazenamento. A tecnologia estudada compreende a combinação de uma bomba de calor que transforma energia elétrica em energia térmica na fase de carga, que pode ser armazenada por várias horas a alguns dias, e um ciclo Rankine orgânico (ORC) que transforma a energia térmica armazenada em elétrica energia novamente na situação de descarga. Esta tecnologia é conhecida como Baterias Carnot

Três configurações diferentes das baterias Carnot foram testadas usando modelos criados no software de programação Matlab. O primeiro modelo é um modelo simples no qual a bomba de calor e o ciclo Rankine orgânico são descritos na configuração mais simples. O segundo modelo adiciona um novo estágio na bomba de calor e um regenerador de ciclo de Rankine orgânico. O terceiro e último modelo usa uma fonte de calor adicional (calor residual, geotérmico ou solar) para o ciclo.

Seis fluidos de trabalho foram usados para executar os testes nas três configurações, R1233zd (E), R1234yf, R11, R236ea, R245fa e iso-pentano. A segunda configuração torna o sistema mais complexo, mas aumenta a eficiência P2P em relação à primeira. A terceira configuração atinge eficiências P2P superiores a 100%, onde a energia elétrica resultante do sistema é maior que a fornecida. Os melhores resultados foram obtidos usando a terceira configuração com isopentano como fluido de trabalho.

Palavras-chave: Armazenamento de Energia, Bomba de Calor, Ciclo de orgânico de Rankine, Waste heat, Iso-Pentano.

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LIST OF SIMBOLS AND ACRONYMS/ ABBREVIATIONS

List of Symbols

p – Pressure [kPa]

h – Enthalpy [kJ/mol]

s – Entropy [J/K]

T – Temperature [ºC]

$\dot{m}$ – Mass debit [kg/s]

W_{in} – Work input [kW]

W_{out} – Work output [kW]

Acronyms/Abbreviations

P2P – Power to Power

COP – Coefficient of performance

ORC – Organic Rankine Cycle

HP – Heat Pump

PHS – Pumped Hydro Storage

GES – Grid Energy Storage

CAES – Compressed Air Energy Storage

LAES – Liquid Air Energy Storage

Li-Ion B – Lithium Ion Battery

Flow B – Flow Battery

FC – Fuel Cells

PTES – Pumped Thermal Energy Storage

1. FRAMEWORK

The change from fossil fuels to renewable energy sources has been the top priority of our society since global warming became a major problem and climate changes started to affect the way the world works, fossil fuels are considered to be one of the most pollutant sources. To solve the problem of global warming, most countries tried to find an agreement to reduce carbon dioxide emissions and so, since the Paris agreement decarbonization goals have been included on their political agendas. Portugal has presented the "Roteiro para a neutralidade carbónica para 2050" and the "Plano Nacional de Energia e Clima 2030" which define a goal of reducing the emissions of CO_2 by 45% to 55%, an increase of 35% of energy efficiency, an increase of 47% or renewable energy sources, 20% increase on renewable vehicles and a 15 % of electrical interconnections.

As most countries still depend on fossil fuel energy to produce electrical power is important to understand that the biggest difference between renewable energy sources and fossil fuel energy, besides all the pollution inherent to fossil fuels, due to the unpredictability of the first, such as eolic and solar, which suffer significant daily fluctuations, and for that reason require a more agile, flexible, and intelligent grid. This is the main reason why research about ways to store the electric energy produced from renewable sources is of high priority. There is an urgent need to store this energy, so it can be provided in times of need and prevent it from being wasted, ergo, a balance between the demand and supply needs to be matched. In the future, the energy produced from fossil fuels should not be needed as we can control when and how much energy we produce.

Currently, the conventional energy storage systems are several and although they present high qualities, they have a lot of high downsides as well. There are three main types of the energy storage system in use, the first and most common one, representing ninety-six percent of the world storage capacity (Frate et al., 2020), is pumped hydro energy storage systems (PHES), which works by pumping water from a lower to a higher level reservoir. These types of systems run with renewable electric power when the supply exceeds the demand and, during the high peaks of electric consume, the water stored at the high-level reservoir is released through hydro turbines which produce work and therefore electric power (Rehman et al., 2015). This technology is limited mainly due to its geographical specificities.

The second type of energy storage system is the one relying on Lithium-Ion Batteries. This is a technology that uses lithium ions batteries as a key component. During the discharge cycle, the lithium atoms on the anode are ionized and separated from their electrons, after that they move through the electrolyte and reach the cathode where they recombine with their electrons and electrically neutralize. This type of technology is highly efficient, but its life cycle is very short and it is relatively expensive.

The third energy storing technology is based on the compression (and storage) of air. The storage is charged using electrically driven compressors, which convert the excess of electric energy into potential energy of pressurized air. The pressurized air is stored and in the discharge phase, it is released producing energy while expansion within a gas turbine. However, this technology has several reasons for its limited success compared to pumped hydro energy storage, such as the geological restrictions, the lower cycle efficiencies, and the lack of off-the-shelf machinery (Budt et al., 2016).

To resume these types of technology, they present several disadvantages, such as the cost, the limited number of resources (Lithium), the environmental impact, the geological restrictions, and the lack of legislation. Therefore, there is a need to search and invest in alternative ways to store energy.

The thermally integrated thermal electricity storage, which stores electric energy as thermal energy, is a group of energy storage technology often referred to as Carnot Batteries (Frate et al., 2020). In this thesis we will focus on one of many types of Carnot Batteries: the heat pump integrated with an organic Rankine cycle.

The two active devices of this system (the heat pump and the heat engine) work exchanging energy with two thermal energy reservoirs. The heat pump is used, when there is excess of renewable electrical energy, to rise the temperature of one of those thermal reservoirs pumping thermal energy from the other, which temperature decreases. With the thermal energy preserved at a high-temperature the (re)conversion to electrical energy will be done reoccurring to a Organic Rankine based heat engine that absorbs the heat from the high-temperature reservoir and converts the thermal exergy into work with the use of a turbine. The high-temperature fluid cools down during the process and returns to the original state. These reservoirs can store the thermal energy either through sensible heat, or latent heat.

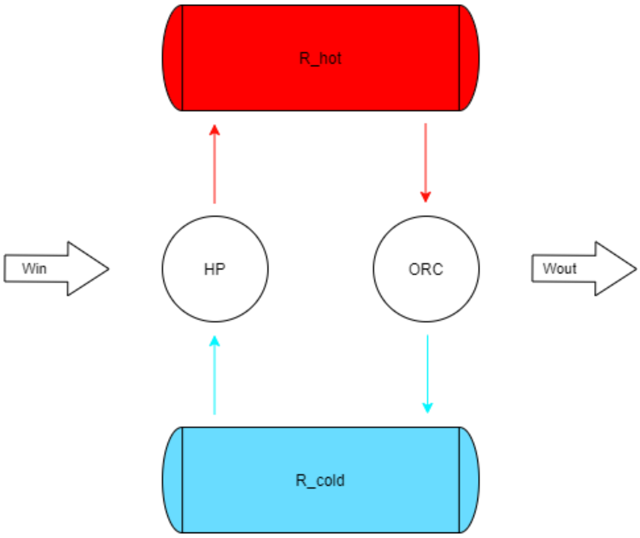


Figure 1 - Carnot Battery configuration

This technology can be seen as a major future alternative to the current energy storage systems, not only due to its low cost but also due to the absence of geographical barriers. Therefore, this thesis focuses on this new technology and i) presents an actualized review of the work done in the area, ii) describe the development of a model of the system encompassing and analysis of a three-model configuration modeled on MATLAB and the comparison and discussion of the results achieved.

1.1. State of the art

A Carnot Battery is an electric energy storage system, where the energy that exceeds from the grid is used as an input, to establish a temperature difference between two reservoirs, one with high temperature and another with low temperature. Consequently, the electric energy is stored as thermal energy. In the discharge phase, which happens when the demand for electric energy overcomes the production, the thermal energy is discharged by taking advantage of the heat flow between the high-temperature reservoir and the low temperature, through an organic Rankine cycle, which allows its turbine to transform part of that heat into electric energy.

Throughout recent years the studies on Carnot Batteries have increased and began to be a priority for academic researchers in the field of the energy storage system, the possibility to create a simple and low-cost energy storage system which primarily seemed to be theoretically impossible, increased the interest of the academic community.

The first step to understand the importance and possible interest in this new technology was to compare it to other existing storage technologies. This allowed the academic community to understand if it was something worth the study and a viable alternative. (O. Dumont & Lemort, 2020) presented in his work a comparison between eight different and well-stablished storage systems presented here in Table 1.

Table 1 – Typical characteristics of the main energy storage technologies: Pumped Hydro-storage (PHS), Gravity Energy Storage (GES), Compressed Air Energy Storage (CAES), Liquid Air Energy Storage (LAES), Lithium Batteries, Flow Batteries, Fuel Cells (FC) and Pumped Thermal Energy Storage systems (PTES) according to (O. Dumont & Lemort, 2020)

Technology	Energy Density [kWh/m^3]	Energy Price [$/kWh]	Installation cost [$/kW]	P2P [%]	Lifetime [years]	Specific geographical conditions required
PHS	0,5-1,5	5-100	300-5200	65-87	30-60	Yes
GES	0,5-1,5	N/A	-	70-86	30-40	Yes
CAES	3-12	2-200	400-2250	40-95	20-60	Yes
LAES	50	260-530	500-3500	40-85	20-40	No
Li-Ion B	300	500-2500	270-1500	85-95	5-15	No
Flow B	16-60	120-1000	175-10000	57-85	5-15	No
FC	500-3000	1-10	3500-10000	20-50	5-30	No
PTES	0,25-6,9	62-107	533-627	70-80	25-30	No

The comparison of the three most common and used technologies referred in Chapter 1 with the Pumped Thermal Energy Storage systems (PTES), on which the Carnot Batteries are included, are favorable to the last. In fact, and despite of the similarity in what refers to the energy price of the pumped thermal and of the pumped hydro energy storage systems, (being the later the most common energy storage systems in use), when comparing the installation costs the differences can be considerable, with the values of the PTES smaller than those of the PHS. This permits to classify the PTES as more economic system than the PHS. When looking at the power to power ratio, which can be seen as a measure of the system efficiency in energy storage, the values presented by the PTES competes with every other technology. The lifetime of 25 to 30 years represents a high upside as well as not having any geographical restriction. To sum up, the PTES technology is a promising technology for energy storage due to all of these characteristics.

After concluding that implementing a PTES as a storage system for renewable energy power plants will enhance the share of these type of energies in the Portuguese electric mix, studies need to be made on what is the best specific solution to be implemented. There are several solutions included in the pumped thermal energy storage family. In (Olivier Dumont et al., 2020) a summary of the different types is made, using different references. The following table compares four of these different configurations:

Table 2 – Characteristics of different PTES configurations according to (Olivier Dumont et al., 2020)

Cycle	Brayton Cycle	Electrical heater and Rankine Cycle	Heat Pump and Rankine cycle	Liquid air
Power [MW]	Up to 100	Up to 100	Up to 10	[10-7800]
Energy [MWh]	Up to 400	Up to 400	Up to 40	[50-650]
Temperature [ºC]	[-70:1000]	Up to 750	Up to 150	-196
Compactness [kW/m^3]	25	~4	[0,05-1,72]	[6-46]
Compactness [kWh/m^3]	200	~36	[0,2-207]	[32-230]
Self-discharge	medium	Very low		
P2P [%]	[60-70]	[12-55]	[30-73]	[12-60]
			[70-150]	
Price [$/kW]	[395-875]	~376	[272-468]	[329-3846]
Price [$/kWh]	[55-198]	~94	[68-117]	[66-666]
Typical fluids	Argon, Air	Water	R1233zd(E), CO2, NH3, water	Air
References	(Ni & Caram, 2015; Smallbone et al., 2017)	(Olivier Dumont et al., 2020)	(O. Dumont & Lemort, 2020)	(Peng et al., 2004)

As we can analyze in the different configurations, the preferential one is using a heat pump and a Rankine cycle, due to its compactness, price and achieves the best overall performance. This configuration has the smaller power and energy which suits them to small and decentralized energy production.

Different authors study distinct models for the application of the Carnot Batteries. For instance (Staub et al., 2018) studied the use of reversible heat pump-Organic Rankine Cycle in PTES. According to the article this heat-pump is dependent on three variables, the first being the chosen working fluid, the second the type of the expander and the third being the way how the system is integrated. The development of this technical concept resulted in a combination of a heat pump with an organic Rankine cycle with a simple hot tank and with the atmosphere as the cold medium.

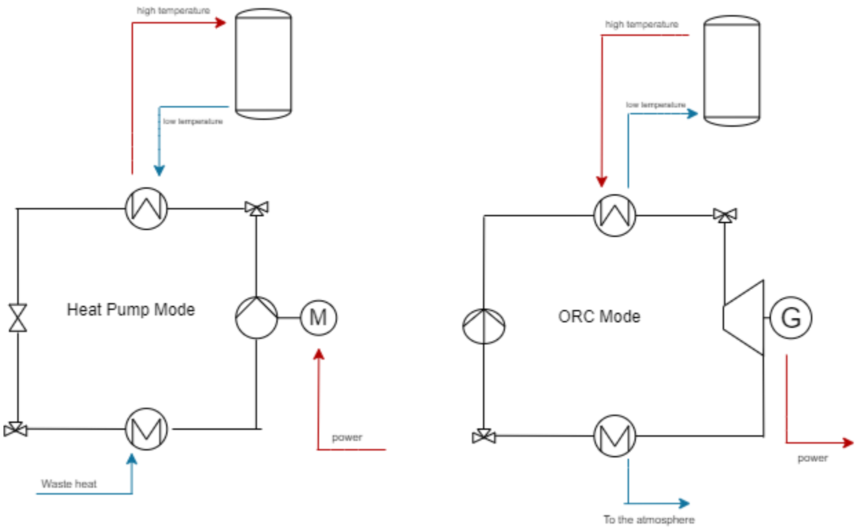


Figure 2 - Reversible Heat Pump–Organic Rankine Cycle system configuration according to Staub et al. (2018)

While the heat pump coefficient of performance requires high temperature for the waste heat and low temperature for the thermal storage to have the best efficiency, the organic Rankine cycle requires the opposite. Just a simple apparatus is needed for this configuration. The heat pump components can be used for the organic Rankine cycle, like the condenser and the evaporator, while the compressor of the heat pump can be used as an expander for the organic Rankine cycle. The efficiency will depend mainly on the isentropic efficiencies of both the compressor and the expander.

Whereas (O. Dumont & Lemort, 2020) performed simulations of PTES based on theoretical approaches. Two configurations were considered: one with hot water storage, and other with cold-water storage. The heat pump and the Rankine cycle use the same working fluid to simplify the analysis and 16 different working fluids pondered. In another paper (Olivier Dumont et al., 2020) are reviewed the different types of technologies and configurations (Brayton Cycle, ORC, thermal integrated Carnot batteries, and Lamm-Honigmann process). The first configuration described is the Brayton Carnot Battery, which is usually comprised of a Brayton heat pump and a Brayton heat engine. Due to its layout, the complete system contains two thermal reservoirs and four main components, two compressors, and two expanders. The functioning principle is that the heat is transferred from the low-temperature reservoir to the high-temperature reservoir through the compression of a gas. During the discharge phase the energy contained in the high-temperature reservoir is used to heat a high-pressure gas before its expansion in a turbine. This system is described as having lower efficiency compared to batteries or PHES, but its high energy density and low estimated capacity prices make this type of technology an interesting option. The second configuration is the one which this thesis is focused on: a heat pump combined with an Organic Rankine cycle. The working principle is the same as in (O. Dumont & Lemort, 2020). The third configuration is a Lamm-Honigmann process which is a thermochemical energy storage process based on the vapour pressure difference between the one of the pure working fluid and the one of a mixture of the working fluid with salts. The fourth, and last, configuration reviewed is the integration of waste heat on the Carnot battery which is also a matter of study in the next chapter.

Other authors like (Steger et al., 2020) purpose the development of a Heat Pump-Organic Rankine cycle pilot plant.

In (Frate et al., 2020) each technology is described and analyzed and then a thermodynamic, technical, and target system size analysis was made. The working fluid that presents the best performance converges towards the same as the other authors, R1233zd(E) is the most successful although it is not the one with the maximum figure is the one that performs better in all the standard ranges of operating conditions. Some other fluids may also be considered, such as R1234ze(Z), R245fa, etc. A conclusion that is possible to design a Carnot Battery with an environmentally friendly, cheap, and possibly nonflammable fluid, without sacrificing its performance, was reached.

Reversible systems are preferential for small-scale models since they present a lower cost. However, the efficiency reached using this reversible system is currently unclear. Large scale systems may in theory use dynamic machines, hence achieving higher rates of performance, but fully reversible systems like the ones used for small-scale machines might not be viable.

An additional paper studied during the preparation of this thesis was (Olivier Dumont & Lemort, 2020) where the authors explain how the first experimental investigation of a Carnot Battery was made. Based on the previous papers written by these authors they were able to implement a live scale Carnot Battery.

The conclusions reached throughout this paper show a roundtrip electrical energy ratio of 75% with the organic Rankine cycle efficiency of 5% and the COP of the HP of 14.4 with a lift of eight Kelvin. These results show a promising future for this technology and also show that it can be easily improved.

With all the articles revised some converging points can be found:

- The use of R1233zd(E) as the working fluid is common to every author, even though it is not the one reaching the highest performance values is the one that presents the best performance on all of the standard tests;
- The use of waste heat as a low-temperature source improves the efficiency of the heat pump by almost 100%;
- Using a heat pump combined with an organic Rankine cycle presents the best performance, although a combination with a Brayton cycle can be a possibility as well;
- The use of a reversible machine on small scales can also improve the efficiency of the batteries but further studies, especially in a real-size model are needed.

1.2. Motivation

Being the Carnot Batteries a recent subject, with a really short bibliography a more profound approach is needed.

The study starts by creating a simple model to validate all the posterior models, this is done by comparing the results with the ones from a reviewed article. The second model created was a combination of a multi-stage heat pump with an organic Rankine cycle with regeneration, it is important to see whether the implementation of a regenerator on the ORC improves the efficiency of the cycle.

The last model is the addition of waste heat as the input for the heat pump. By doing this it is expected that the COP rises because of the smaller differences between the temperatures of the two reservoirs. The use of waste heat from a geothermal energy source, or solar collectors, creates a way to reuse lost energy.

With these three models, it is expected that answers to some research questions are found such as is it possible to increase the efficiency by combining a multi-stage heat pump with an organic Rankine cycle with regeneration? What is the impact of waste heat in the COP of the HP?

1.3. Structure

This thesis is structured in five chapters, being this one the first one, the second one is the methodology in which the three models are explained, and the simple model is validated using the results studied previously by other authors. The third chapter is the discussion of the results gathered through the three models. The last chapter is the conclusion

2. MODEL DEVLOPMENT

2.1. Simple Heat Pump combined with a Simple Organic Rankine Cycle

To begin with, a simple model was used, which combined a simple compressed vapor cycle heat pump with an organic Rankine cycle working between two thermal reservoirs: a cold and a hot one. The isentropic efficiency of the pump, the compressor, and the expander were assumed to be fifty percent, seventy-five percent, and seventy percent, respectively, these values were chosen according to (O. Dumont & Lemort, 2020)

The temperatures of the cold and hot thermal reservoirs were parametrically changed from minus ten degrees to one hundred and twenty degrees Celsius for the hot reservoir, and for the cold, it fluctuates according to:

$$T_{cold,min} = T_{hot,min} - 20\ ºC \ \ and \ \ T_{cold,max} = T_{hot,max} - 20\ ºC \qquad (1)$$

Six working fluids were used throughout the tests, R1233zd(E), R1234yf, R11, R236ea, R245fa, and iso-pentane as they are the five with better results shown in different circumstances and the one that it is currently more used in industry. The fluid used in both the reservoirs is water.

Table 3 - Reference values for the models

Parameter	**Value**
Heat exchangers pinch point	0ºC
Subcooling	0ºC
Superheating	0ºC
Pump isentropic efficiency	50%
Compressor isentropic efficiency	75%
Expander isentropic efficiency	70%

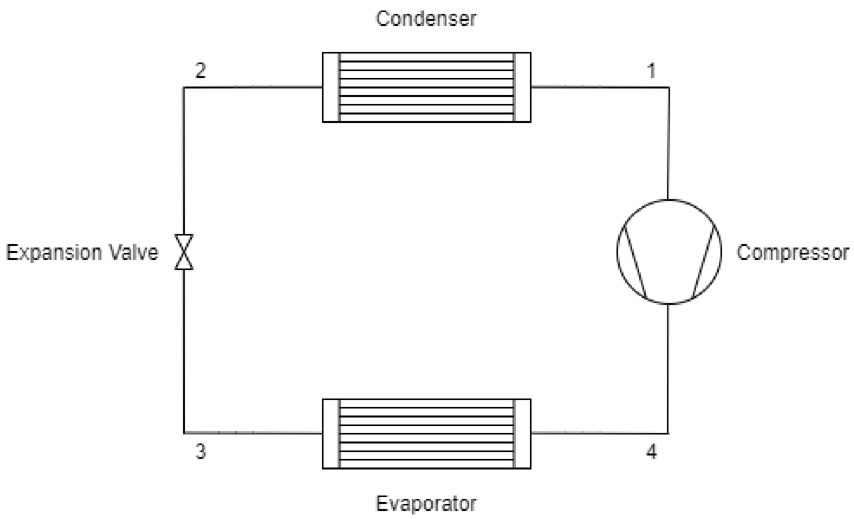
The subcooling degree is the difference between the temperature of saturation with subcooling fluid temperature before it enters the pump. It grants that only liquid enters in the pump and avoids cavitation. The superheating temperature degree is the surplus of temperature above the saturation temperature before it enters in the turbine. It ensures that only vapor fluid enters in the turbine as the liquid can severally damage the component.

Finally, the pinch point in the heat exchangers is the minimum temperature difference that occurs during the condensing and evaporation of the fluid at constant temperature in the condenser and evaporator. In this case study, all of those parameters were considered as 0 in order to perceive the full capacity of the Carnot Batteries despite in the real conditions these assumptions cannot be attained.

2.1.1. Heat Pump

The heat pump design is the simplest possible, a compressor, two heat exchangers, and an expansion valve, as is showed in the next figure:

a)



b)

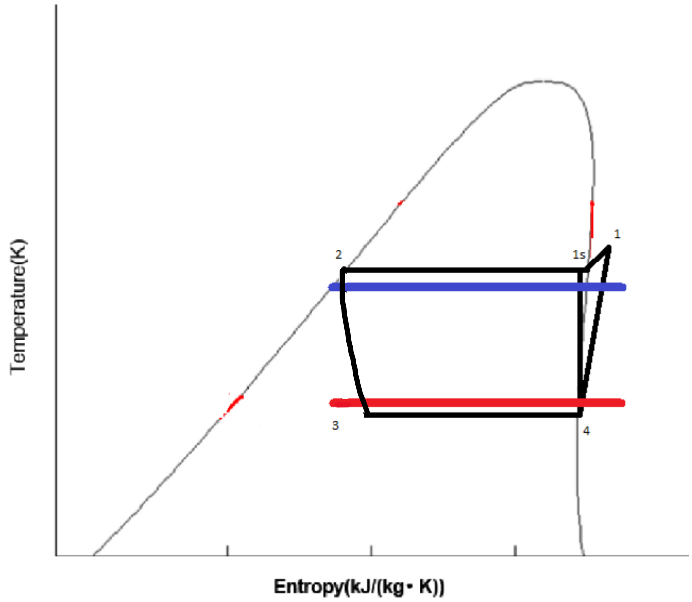


Figure 3 - a) Heat Pump schematic configuration b) T-s diagram of the vapor compression cycle of the heat pump

The thermodynamic cycle shown above involves four processes. Firstly, heat is transferred to the working fluid in the evaporator (state 3 to state 4), where its temperature is lower than the one of the water in the reservoir. At state 4 the working fluid is in a saturated vapor state, this transformation (3 to 4) occurs at a constant pressure which justifies why the pressure in points 3 and 4 are the same in the equations forward. The temperature at the exit of the evaporator can theoretically be considered the same as the temperature of the low temperature reservoir (minus the pinch point temperature difference). To this process follows an adiabatic compression at which the compressor does work, using electricity from the grid, as the low pressure and temperature saturated vapor enter the compressor and is taken from state four to one. The result at the compressor outlet is a compressed working fluid vapor at high pressure and temperature. The third process occurs afterwards when the high pressure and temperature compressed working fluid vapor enters the condenser and releases heat to the high temperature reservoir, because of the higher temperature of the working fluid compared to the water in the thermal sink. At the outlet of the condenser, a saturated liquid appears, which can theoretically be considered to have the same temperature as the high temperature reservoir (plus the pinch point temperature difference). The process between states 1 to 2 can be considered to occur at constant pressure, both these theoretical considerations justify the equations written below. The final process before the working fluid reenters the evaporator and restarting the cycle occurs from state 2 to state 3. During this process the working fluid goes through an expansion valve where an adiabatic pressure drop occurs, resulting in a decrease of temperature and pressure. (Meyer, Josua Petrus, 2011)

To calculate the coefficient of performance for the heat pump, the values for the enthalpy in the points shown on the figure needed to be determinate, with the help of REFPROP, an extension for MATLAB that contains the different thermodynamic properties for several working fluids.

To begin with, the temperature on point two was considered to be the same as the temperature of the hot reservoir and so the pressure and enthalpy were calculated with the use of REFPROP. A similar consideration was used for point number four, the temperature on that point is assumed to be the same as the cold reservoir, and so the pressure, enthalpy, and entropy were found throughout REFPROP. It was assumed that the designed heat exchangers are big enough to the temperatures of the fluid in the evaporator and condenser outlets are close to the temperatures of the cold and heat source.

The following expressions appeared:

$$T_2 = T_{hot} \tag{2}$$

$$p_2 = p_{l,sat}(T_2) \tag{3}$$

$$h_2 = h_{l,sat}(T_2) \tag{4}$$

$$T_4 = T_{cold} \tag{5}$$

$$p_4 = p_{v,sat}(T_4) \tag{6}$$

$$h_4 = h_{v,sat}(T_4) \tag{7}$$

$$s_4 = s_{v,sat}(T_4) \tag{8}$$

Having the fourth and second points all figured out, we still need to calculate the first and third point enthalpy. Considering that the pressure on the first point remains the same throughout the heat exchanger:

$$p_1 = p_2 \tag{9}$$

$$h_{1s} = h(p_1, s_4) \tag{10}$$

Therefore, we can get the value of h_{1s} which is the enthalpy considering an isentropic compression. Considering the isentropic efficiency of the compressor stated before and having the pressure and the specific enthalpy we can calculate the real enthalpy on the first point using the next equation:

$$h_1 = \frac{h_{1s} - h_4}{\eta_{i_{compressor}}} + h_4 \tag{11}$$

The only point missing now is the point three having the following considerations we can discover the temperature on this point using REFPROP:

$$h_3 = h_2 \tag{12}$$

$$p_3 = p_4 \tag{13}$$

$$T_3 = T(p_3, h_3) \tag{14}$$

From this point forward, the coefficient of performance is easily calculated using the following expression:

$$COP_{HP} = \frac{Q_{out}}{W_{in}} = \frac{h_1 - h_2}{h_1 - h_4} \tag{15}$$

2.1.2. Organic Rankine Cycle

An organic Rankine cycle is a characteristic operating cycle of power production technical solution that generates electrical energy through thermal energy, that means, of a heat-engine. The basic cycle works with a working fluid being pumped to a boiler, where it evaporates, and continues to an expansion device, in this case, a turbine, which produces the mechanical work afterwards transformed in electrical energy, then it flows to a condenser heat exchanger where its condensed, and brought to the initial state, creating a closed cycle. The following picture represents schematically, and in the T-s property space, the components and the process, of this cycle.

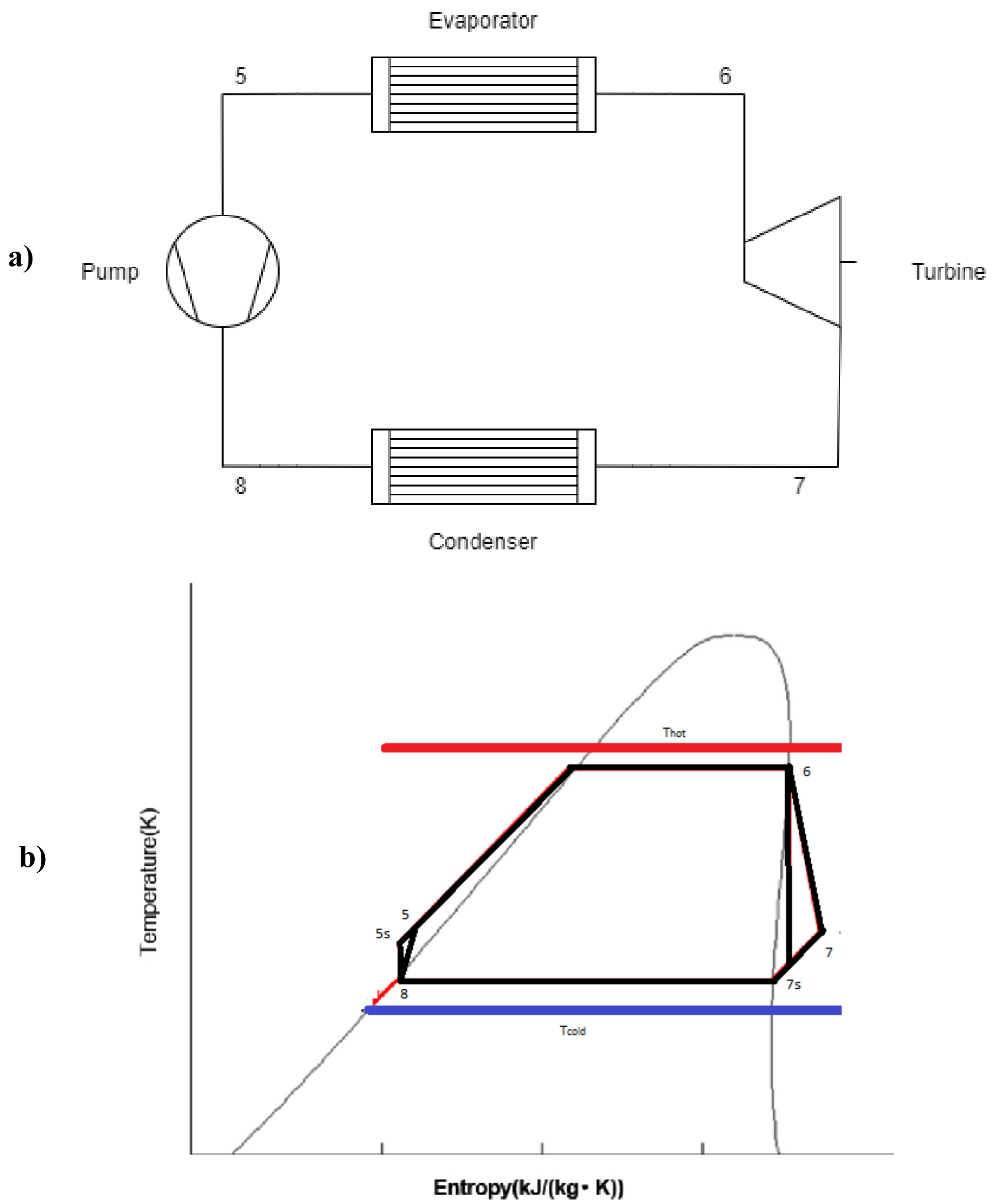


Figure 4 - a) ORC schematic configuration b) T-s diagram of the organic Rankine cycle

At state eight the working fluid enters the pump, as saturated liquid, and suffers an isentropic compression, this increases its temperature due to a slight increase in the enthalpy of the working fluid. At state 5, the working fluid enters the evaporator as a compressed liquid and leaves as saturated vapor at state 6. This vapor enters the turbine where it expands and produces work by rotating a shaft connected to an electric generator. During the process on the turbine, the pressure and temperature of the vapor drops reaching state 7 where the steam enters the condenser. At this state, the vapor has a higher superheating degree due to the non-isentropic expansion in the turbine. After the condenser, the mixture exits as saturated liquid going back to state 8 and closing the cycle. (Toffolo et al., 2014)

This system was combined with the heat pump to generate electricity, therefore the same considerations mentioned above were made. The cycle was then programmed in MATLAB, using the following equations, and using REFPROP to get the thermodynamical properties of the working fluids.

$$T_8 = T_{cold} \tag{16}$$

$$p_8 = p_{l,sat}(T_8) \tag{17}$$

$$h_8 = h_{l,sat}(T_8) \tag{18}$$

$$s_8 = s_{l,sat}(T_8) \tag{19}$$

$$T_6 = T_{hot} \tag{20}$$

$$p_6 = P_{v,sat}(T_6) \tag{21}$$

$$h_6 = h_{v,sat}(T_6) \tag{22}$$

$$s_6 = s_{v,sat}(T_6) \tag{23}$$

The other thermodynamic properties, such as enthalpy and entropy of points eight and six were calculated using the program mentioned earlier for the liquid and vapor saturation points.

The remaining points were then calculated using both REFPROP and thermodynamic assumptions. The following equations show how the calculations were made:

$$p_7 = p_8 \tag{24}$$

$$h_{7s} = h(p_7, s_6) \tag{25}$$

$$h_7 = h_6 - \eta_{i_{exp}} * (h_6 - h_{7s}) \tag{26}$$

$$T_7 = T(p_7, h_7) \tag{27}$$

$$p_5 = p_6 \tag{28}$$

$$h_{5s} = h(p_5, S_8) \tag{29}$$

$$h_5 = \frac{(h_{5s} - h_8)}{\eta_{i_{pump}}} + h_8 \tag{30}$$

$$T_5 = \ T(p_5, h_5) \tag{31}$$

With all the proprieties discovered it is now easy to calculate the efficiency of the organic Rankine cycle:

$$\eta_{ORC} = \frac{Wout - W_{in}}{Qin} = \frac{(h_6 - h_7) - (h_5 - h_8)}{h_6 - h_5} \tag{32}$$

2.1.3. Power to Power Ratio

The P2P efficiency is defined as the ratio between the amount of electric energy that is discharged and the amount of electric energy that the cycle needs to charge. In the case studied this power to power can be written by the product between the COP of the HP and the efficiency of the ORC.

$$P2P = \frac{W_{out}^{ORC}}{W_{in}^{HP}} = \frac{\eta_{ORC} \times Q_{in}}{\frac{Q_{in}}{COP^{HP}}} = COP_{HP} \cdot \eta_{ORC} \tag{33}$$

2.1.4. Validation of the model

A validation of this model is needed. The control results and the variables reproduced could not match the ones produced in any of the papers due to the lack of information however, the results are similar to the ones found in (Hassan et al., 2020).

For the simple model which is the base model for this study the values for the power to power ratio values vary from 25-49% as it will be exposed later on. According to the work of (Hassan et al., 2020), a basic Carnot Battery (simple heat pump and simple organic Rankine cycle) should have a power to power ratio (P2P) of 30-55%.

Another way to validate this model was to try to approach the results of a specific case study in another article, (Trebilcock et al., 2020). Using the first model, with the high temperature reservoir working temperatures between 75 to 78 degrees Celsius and the cold temperature reservoir working temperature running between 40 to 45 degrees Celsius, using R1233zd as the working fluid, the results of the power to power ratio (P2P) vary from 41 to 43 percent which is concordant with what the article refers. The following table present some of the results achieved:

Table 4 - Results from the validation model according to (Trebilcock et al,2020)

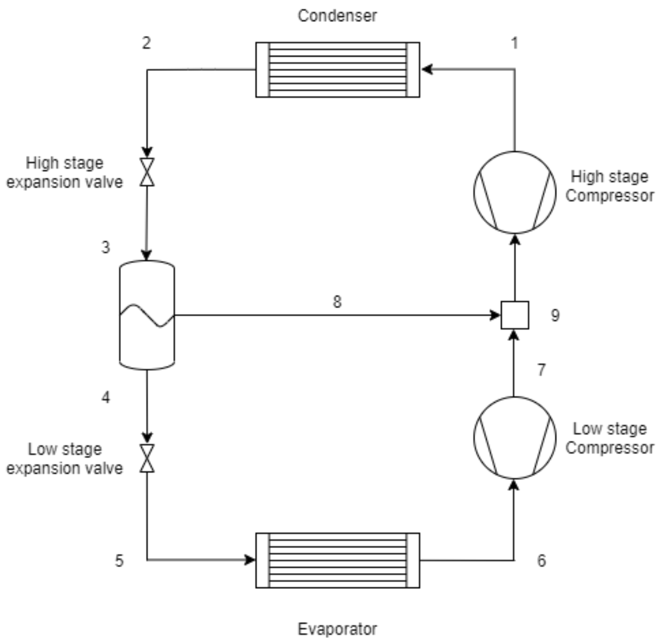
Fluids	T_{hot} [ºC]	T_{cold} [ºC]	COP [-]	η [%]	P2P [%]	P2P [%] according to (Trebilcock et al,2020)
R1233zd	75	40	6,63	6,41	42,50	~45%
R1234yf	76	42	6,85	6,22	42,66	~45%
R11	77	42	6,65	6,37	42,38	~45%
R236ea	78	42	6,46	6,52	42,10	~45%

2.2. Two-Stage Heat Pump combined with an Organic Rankine Cycle with regeneration

After designing the basic model, alterations were made to increase the power to power ratio that will be shown later. The assumptions shown in the table 3 were preserved from the basic model to this new one.

2.2.1. Multi-stage Heat Pump

On the first model, a simple stage HP was used to pump the heat from the low to the high temperature reservoir however studies have shown that a multi-stage heat pump presents a reduced work consumption rather than the simple stage heat pump used on the previous model. The cycle works by using the evaporator for the heat source, such as the previous one, a condenser as a heat sink, and a separator vessel between the two stages. The upgrade made for the multi-stage heat pump configuration and its T-s diagram is shown in the following figures:



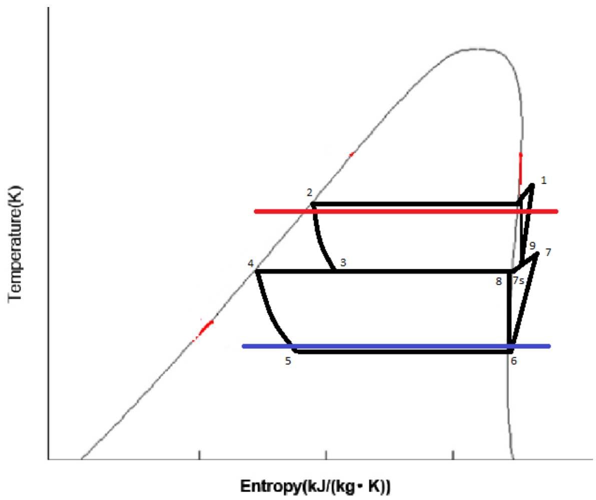


Figure 5 - a) Multi-stage heat pump schematic configuration b) T-s diagram of the vapor compression cycle of the multi-stage heat pump

Consequently, an update on some equations was made to include the new stage of the heat pump. Points two, five, and six kept the equations of points one, two, three, and four, written above, respectively.

For point number three the enthalpy is the same as point number two and the pressure was, as usual for these systems calculated with the equation (35). Once calculated the pressure the temperature could easily be determined using the REFPROP and the equation 36.

$$h_3 = h_2 \tag{34}$$

$$p_3 = \sqrt{p_1 * p_6} \tag{35}$$

$$T_3 = T_{sat}(p_3) \tag{36}$$

On point number four, the pressure is the same as in point number three, so:

$$p_4 = p_3 \tag{37}$$

$$T_4 = T_{l,sat}(p_4) \tag{38}$$

$$h_4 = h_{l,sat}(p_4) \tag{39}$$

After the expansion valve (point 5), the pressure and enthalpy are equal to point 6 defined à priori.

$$p_5 = p_6 \tag{40}$$

$$h_5 = h_6 \tag{41}$$

$$T_5 = T(p_5, h_5) \tag{42}$$

Point seven has the same pressure as point three and therefore:

$$p_7 = p_3 \tag{43}$$

$$h_{7s} = h(p_7, s_6) \tag{44}$$

$$h_7 = \frac{(h_{7s} - h_6)}{\eta_{i_{comp}}} + h_6 \tag{45}$$

$$T_7 = T(p_7, h_7) \tag{46}$$

With only points one, eight, and nine missings, we needed to calculate the variables on point eight to be able to find out the mass flow rate, and then calculate the variables on point nine, and then we can calculate point one.

$$p_8 = p_3 \tag{47}$$

$$T_8 = T_3 \tag{48}$$

$$h_8 = h_{v,sat}(T_8) \tag{49}$$

$$\dot{m}_8(h_3 - h_8) = \dot{m}_4(h_4 - h_3) \tag{50}$$

$$\dot{m}_4 = \dot{m}_3 - \dot{m}_8 \tag{51}$$

$$\dot{m}_7 = \dot{m}_4 \tag{52}$$

$$\dot{m}_9 * h_9 = \dot{m}_8 * h_8 + \dot{m}_7 * h_7 \tag{53}$$

$$p_9 = p_7 \tag{54}$$

$$T_9 = T(p_9, h_9) \tag{55}$$

$$s_9 = s(p_9, h_9) \tag{56}$$

$$h_{1s} = h(p_1, s_9) \tag{57}$$

$$h_1 = \left(\frac{h_{1s} - h_9}{\eta_{i_{comp}}}\right) + h_9 \tag{58}$$

$$T_1 = T(p_1, h_1) \tag{59}$$

With all the points discovered we can recalculate the COP of the HP through the following expression:

$$COP_{HP} = \frac{h_1 - h_2}{(h_1 - h_9) + (\dot{m}_4/\dot{m}_3) * (h_7 - h_6)} \tag{60}$$

2.2.2. Organic Rankine Cycle with regeneration

Similar to what was done for the HP there was a need to upgrade the ORC so it would get the best performance possible. The inclusion of a regenerator means that the heat of the superheated vapor at the expander outlet is used to preheat the working fluid before it enters the evaporator, consequently, a higher η is achieved as less heat input is required for the same work produced. The following figure shows the configuration of the regenerative organic Rankine cycle and its T-s diagram.

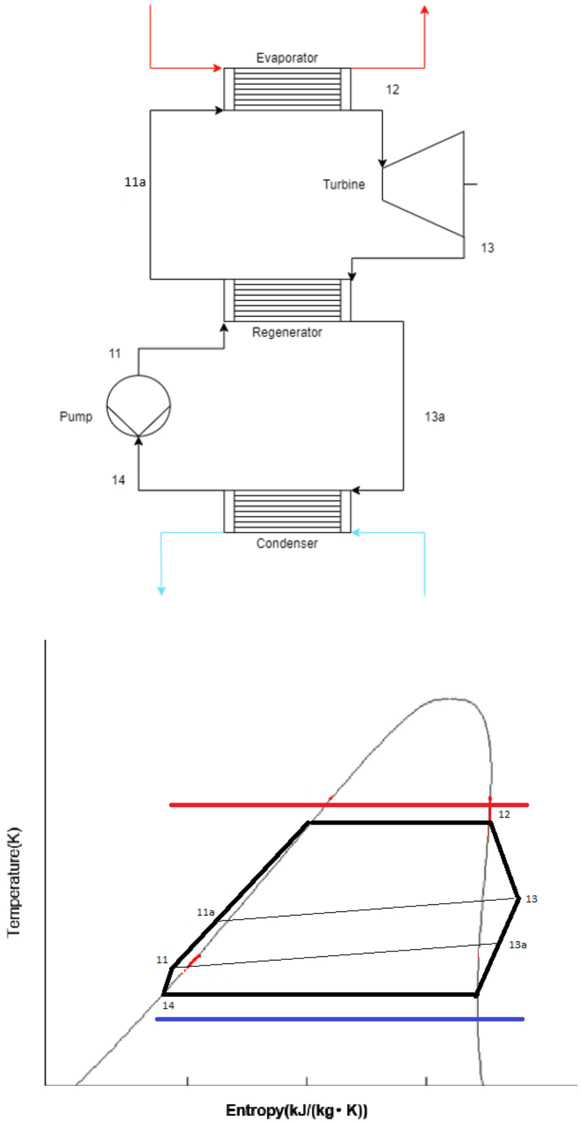


Figure 6 - a) Regenerative ORC schematic configuration b) T-s diagram of the regenerative organic Rankine cycle

The inclusion of points eleven a and thirteen a was made by adding the following equations to MATLAB.

$$T_{13a} = T_{11} + 5 \tag{61}$$

$$p_{13a} = p_{13} \tag{62}$$

$$h_{13a} = h(T_{13a}, p_{13a}) \tag{63}$$

$$p_{11} = p_{11a} \tag{64}$$

$$h_{11a} = h_{13} - h_{13a} + h_{11} \tag{65}$$

$$T_{11a} = T(p_{11a}, h_{11a}) \tag{66}$$

With all of the cycle equations, we can now calculate its efficiency.

$$\eta_{ORC} = \frac{(h_{12} - h_{13}) - (h_{11} - h_{14})}{h_{12} - h_{11a}} \tag{67}$$

2.2.3. Power to Power Ratio

The power to power ratio of the Carnot battery on this new configuration is calculated using equation (33).

2.3. Two-Stage Heat Pump combined with an Organic Rankine Cycle with regeneration using waste heat recovery

As mentioned earlier, using waste heat as a cold source for the heat pump is reported to decrease the power consumption in the heat pump for the same electrical power from the ORC cycle, therefore it is expected that the power to power ratio of the cycle modeled in chapter 2.2. increases to a value higher than 100%. The addition of waste heat to the model only changed the temperature of the cold reservoir for the heat pump, therefore no alterations were made to the equations written above.

The temperature of the waste heat was considered to be 30 degrees Celsius below the temperature of the hot source. The waste heat consider can be from several different sources, the main two considered that may need a deeper study are waste heat from geothermal energy, and waste heat from solar collectors.

For domestic use, it is interesting to see how the waste heat that results from solar collectors can be used to diminish the gap from the cold to the hot reservoir, and therefore increase the coefficient of performance of the heat pump. This solution on a small scale model used only for domestic purposes can decrease the amount of wasted water, but also be an interesting solution in terms of economic savings.

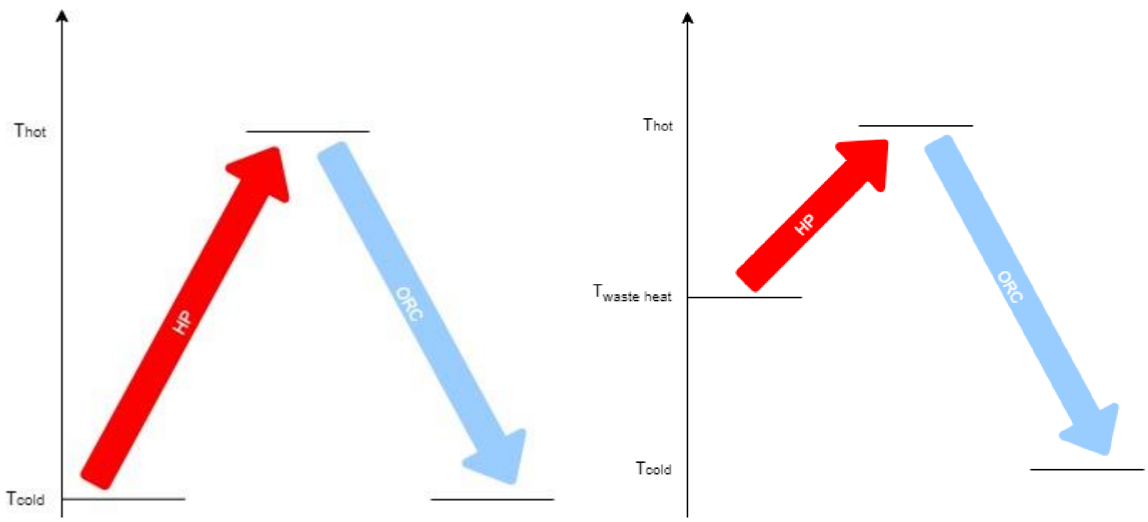


Figure 7 – Schematic of the temperature differences between the use or not of waste heat

3. RESULTS AND DISCUSSION

The following chapter presents the results and a profound discussion of the models described above.

The working temperatures of the reservoirs depend on the model and the working fluid since some can only work until 100 degrees Celsius due to the critical temperature limitation. The graphical comparison will be done for only the best two working fluids, being the rest of the results in the annex.

3.1. Simple Heat Pump combined with a Simple Organic Rankine Cycle

This simple model was validated above comparing the results to two in the bibliography, the best results for each fluid are shown in Table 5:

Table 5 - Results for the simple model

Fluids	T_{hot} [ºC]	T_{cold} [ºC]	COP [-]	η [%]	P2P [%]
R1233zd	40	20	11,15	4,15	46,35
R1234yf	40	20	10,39	3,80	39,43
R11	40	20	11,36	4,23	48,09
R236ea	40	20	10,89	4,06	44,18
R245fa	40	20	11,07	4,13	45,77
Isopentane	40	20	11,14	4,16	46,30

The best result is for R11 which present a power to power ratio of 48 % with the hot reservoir at a temperature of 0 and cold reservoir temperature of -20 degrees. Despite of this result, this kind of working fluid has been banned from use and has been tested only for research purposes therefore the best result is using Iso Pentane or the R1233zd, the biggest difference is that the first one is inflammable but that does not \represent a problem in this particular case.

The following graphics present the results for Isopentane, for the COP of the heat pump, the η of the organic Rankine cycle and the last for the power to power ratio.

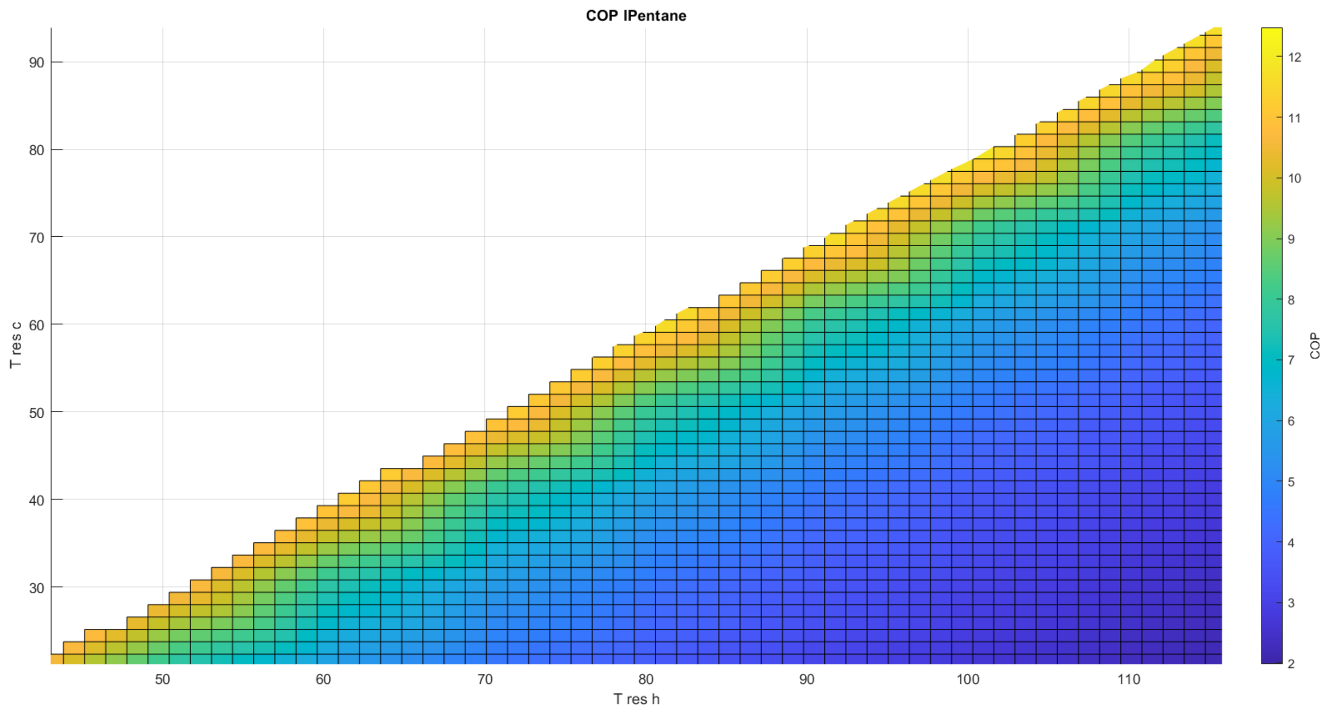


Figure 8 - Isopentane COP as a function of the hot and cold reservoirs temperatures

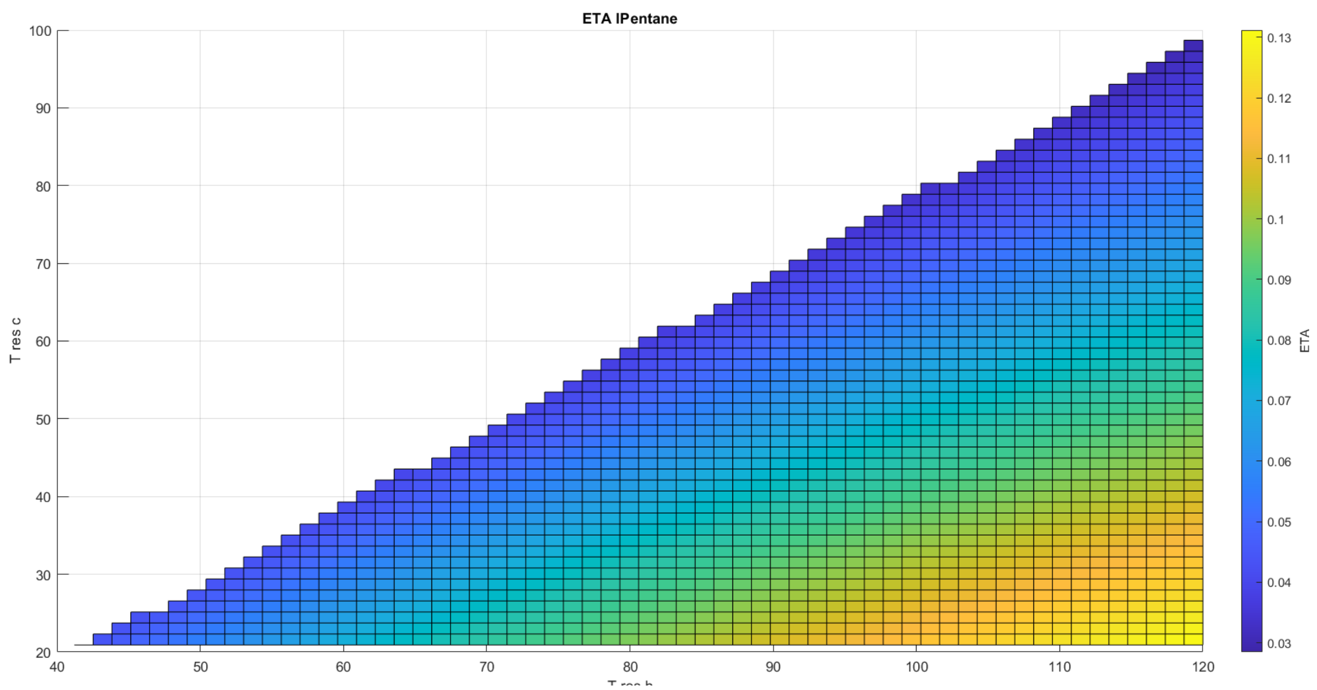


Figure 9 - Isopentane efficiency as a function of the hot and cold reservoirs temperatures

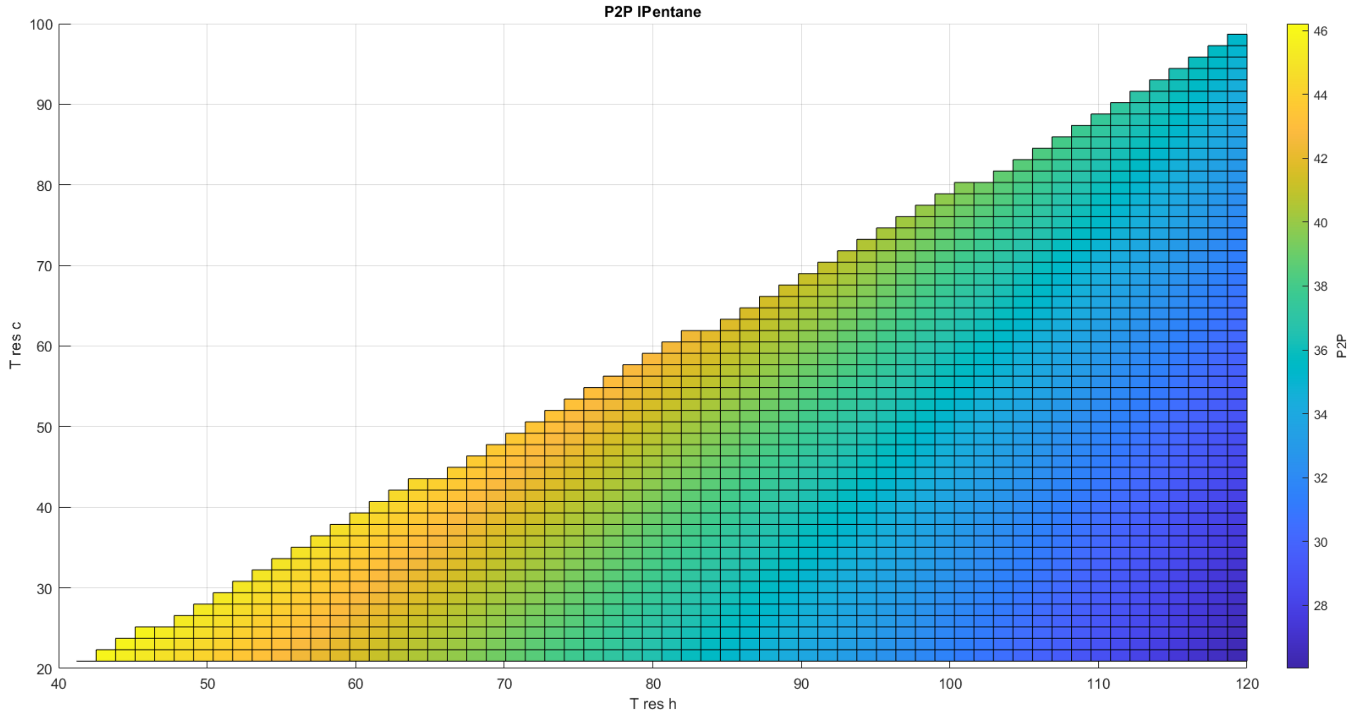


Figure 10 - Isopentane P2P as a function of the hot and cold reservoirs temperatures

As we can see from Figure 8, the COP of the heat pump increases when the difference of temperature between the two reservoirs is smaller, for instance when we have 120 degrees Celsius as the hot reservoir temperature and a temperature of 100 degrees Celsius for the cold reservoir, we get the higher COP for the heat pump. The opposite occurs for the efficiency of the Organic Rankine cycle which is higher for a larger gap between the temperature of the cold and hot reservoir.

The maximum P2P occurs for lower temperatures and for a small gap between the temperatures due to the balance between the heat pump COP and the organic Rankine cycle efficiency. This is related with the values of specific enthalpies variation with the temperature which affects the expansion and compression of the cycles.

With the basic Carnot Battery model, the results of P2P are lower than 50%, leading to a need of an improvement to try to achieve higher results.

3.2. Two-Stage Heat Pump combined with an Organic Rankine Cycle with regeneration

As stated earlier, the values of the basic configuration have relatively low efficiencies but is expected that the next configurations achieve higher values od efficiencies. The following table, shows the best results for the six fluids:

Table 6 - Results for the two-stage HP with a regenerative ORC

Fluids	T_{hot} [ºC]	T_{cold} [ºC]	COP [-]	η [%]	P2P [%]
R1233zd	40	20	14,87	4,17	62,14
R1234yf	40	20	14,03	3,76	52,86
R11	40	20	15,05	4,20	63,35
R236ea	40	20	14,64	4,11	60,32
R245fa	40	20	14,80	4,15	61,50
Iso pentane	40	20	14,90	4,22	62,92

The results show that R11 is the best fluid out of the six, the following graphics represent the 2D evolution of the fluid, with the difference of temperatures.

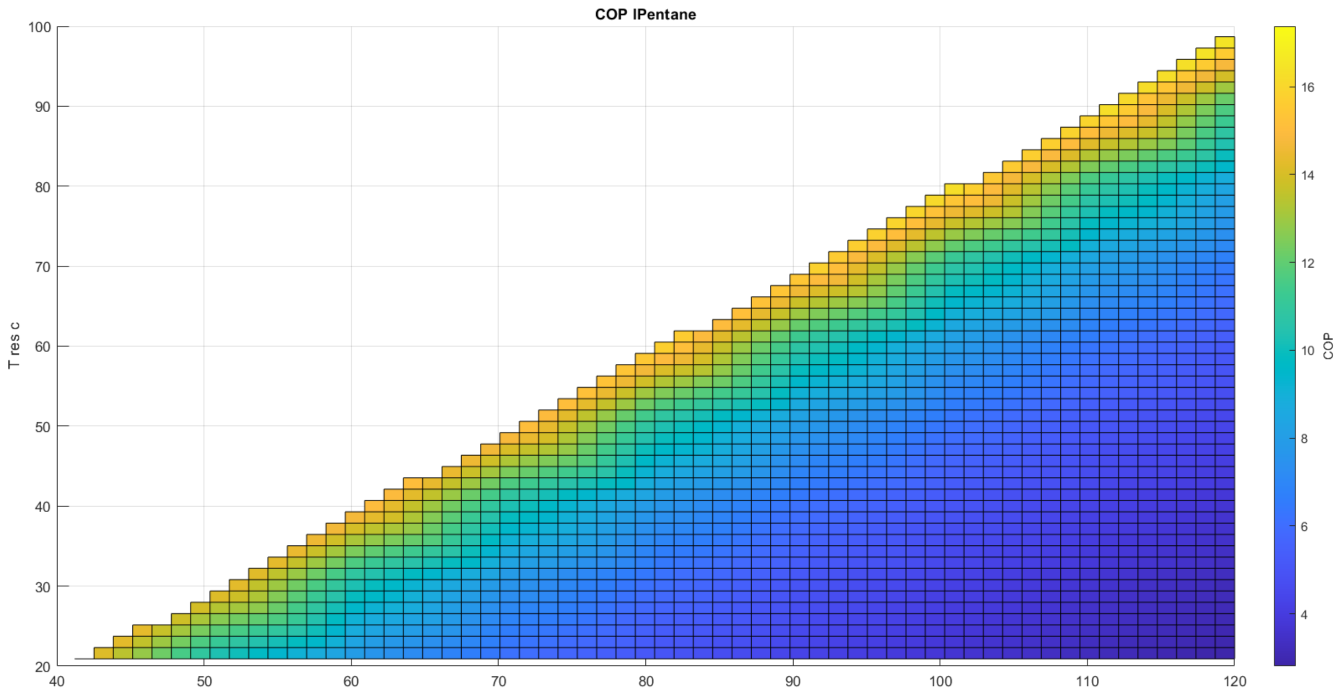


Figure 11 – Isopentane HP COP as a function of the hot and cold reservoirs temperatures

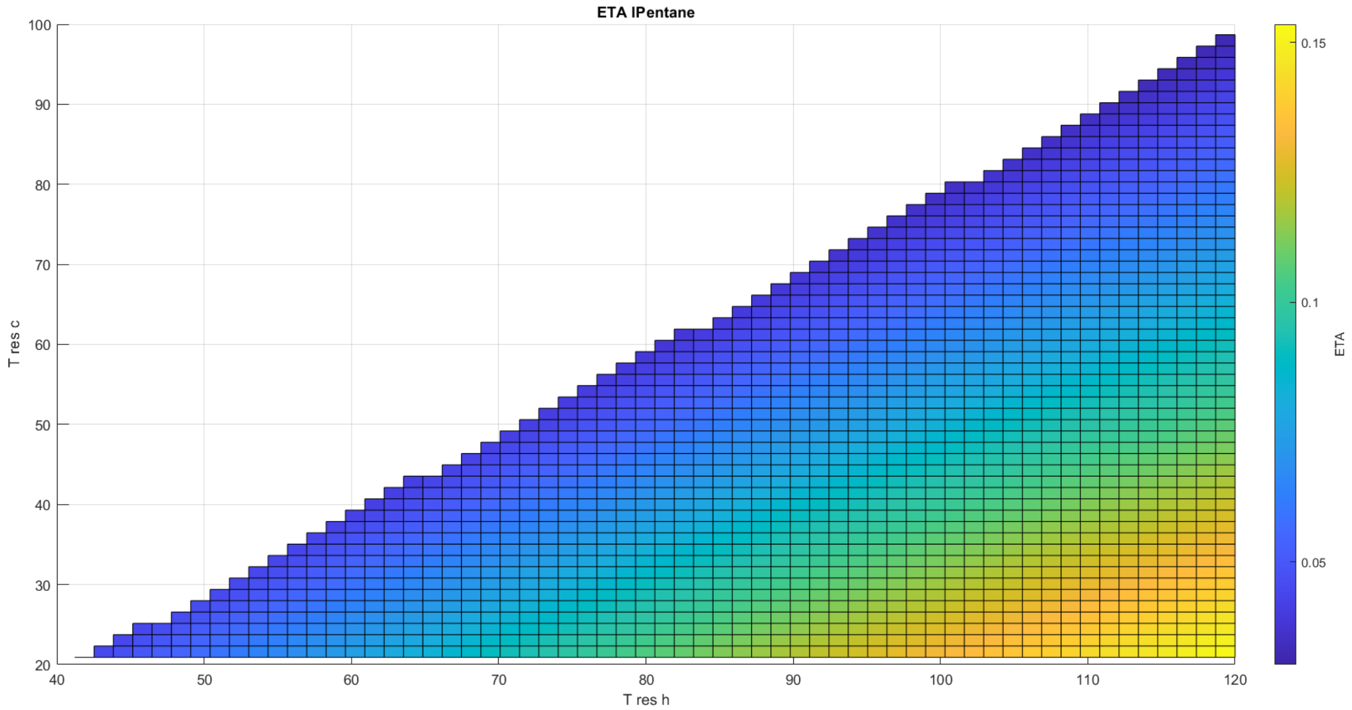


Figure 12 – Isopentane ORC efficiency as a function of the hot and cold reservoirs temperatures

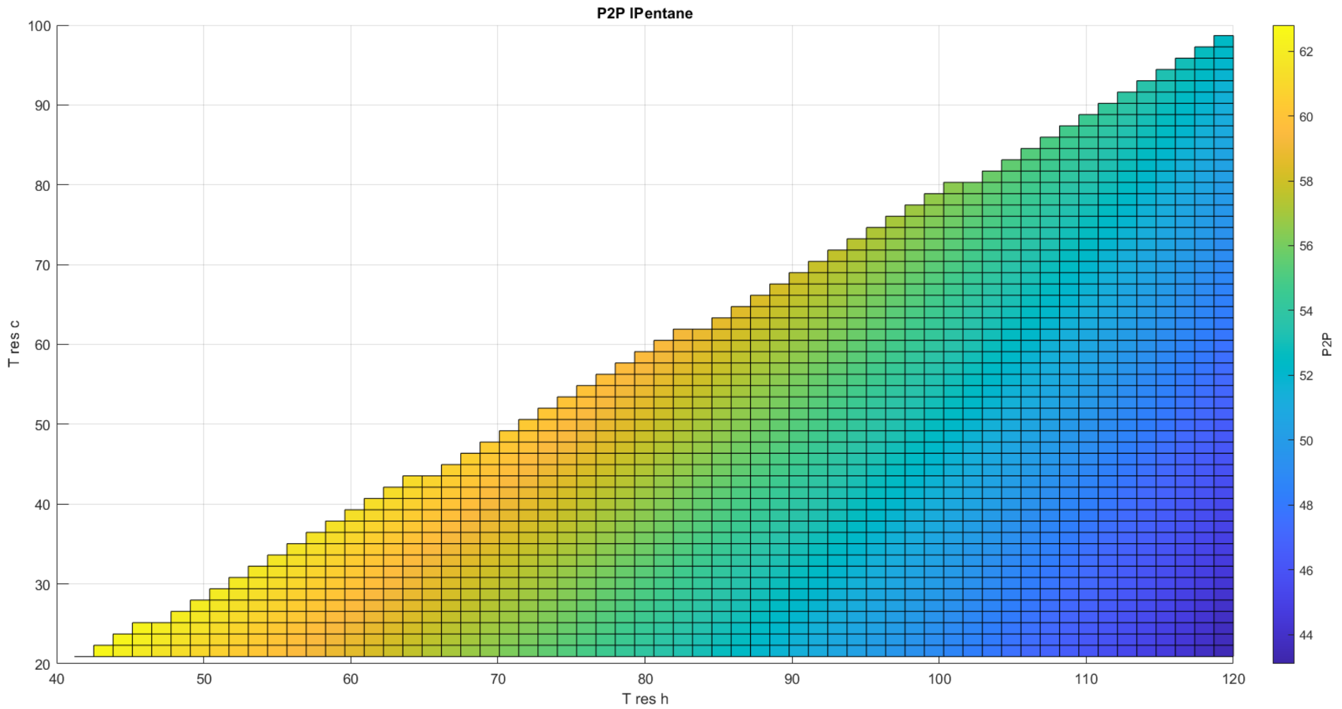


Figure 13 – Isopentane P2P as a function of the hot and cold reservoirs temperatures

The improvement between the previous simple model and the new model, is notorious, the COP rises from values of 13 to values around 17 which indicates that the multi-stage heat pump can be an addition for this system.

The addition of a regenerator in the organic Rankine cycle it is proved to be an improvement to the cycle efficiency, increasing the eta from 0,13 to 0,15.

The biggest improvement is on the power to power ratio where the increment is of 15%.

These results are very promising and show that a real life scale model of a two-Stage Heat Pump combined with an Organic Rankine Cycle with regeneration can increase the efficiency of the cycle.

3.3. Two-Stage Heat Pump combined with an Organic Rankine Cycle with regeneration using waste heat recovery

The use of waste heat was included to improve the efficiency of the heat pump, and therefore increase the power to power ratio of the Carnot battery. The following table includes the results for the improved model.

Table 7 - Results with the addition of waste heat recovery

Fluids	T_{hot} [ºC]	$T_{waste\ heat}$ [ºC]	T_{cold} [ºC]	COP [-]	η [%]	P2P [%]
R1233zd	120	90	20	11,04	14,40	159,16
R1234yf	80	50	20	8,52	7,84	66,84
R11	120	90	20	11,75	14,79	173,83
R236ea	120	70	20	9,69	13,61	132,01
R245fa	120	90	20	10,57	14,10	149,15
Iso pentane	120	90	20	11,26	15,5	174,67

Like the other models, the iso pentane had the best results for the waste heat addition, the following graphics show the different results for different temperature.

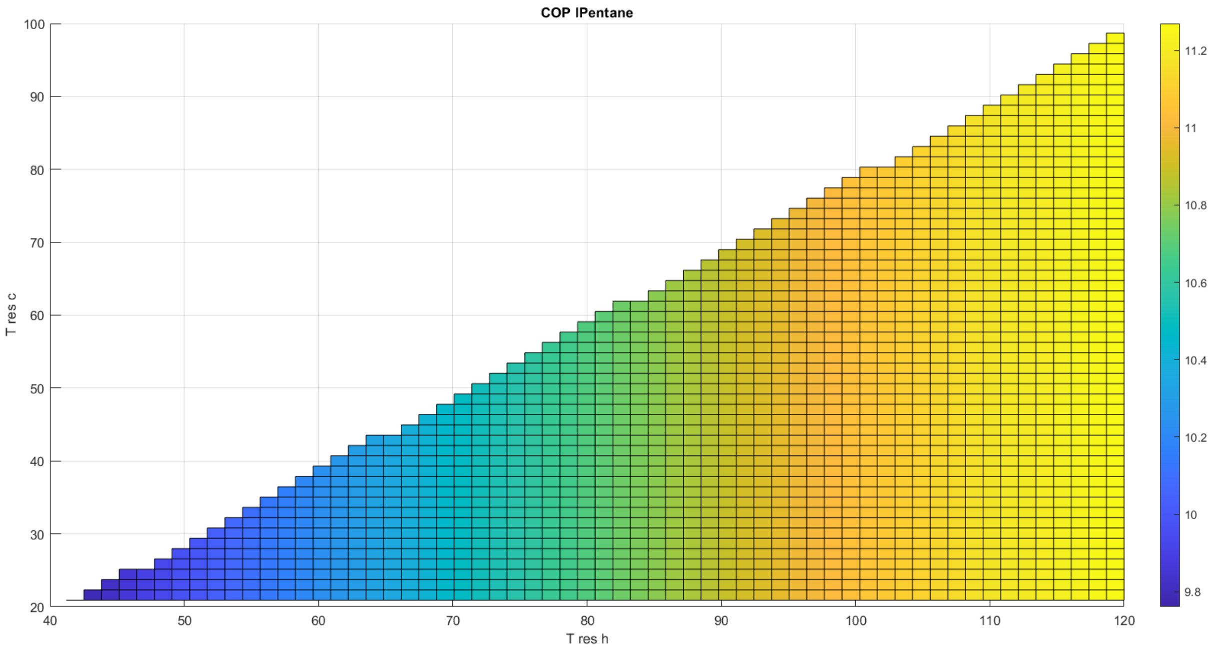


Figure 15 - Isopentane COP as a function of the hot and cold reservoirs temperatures

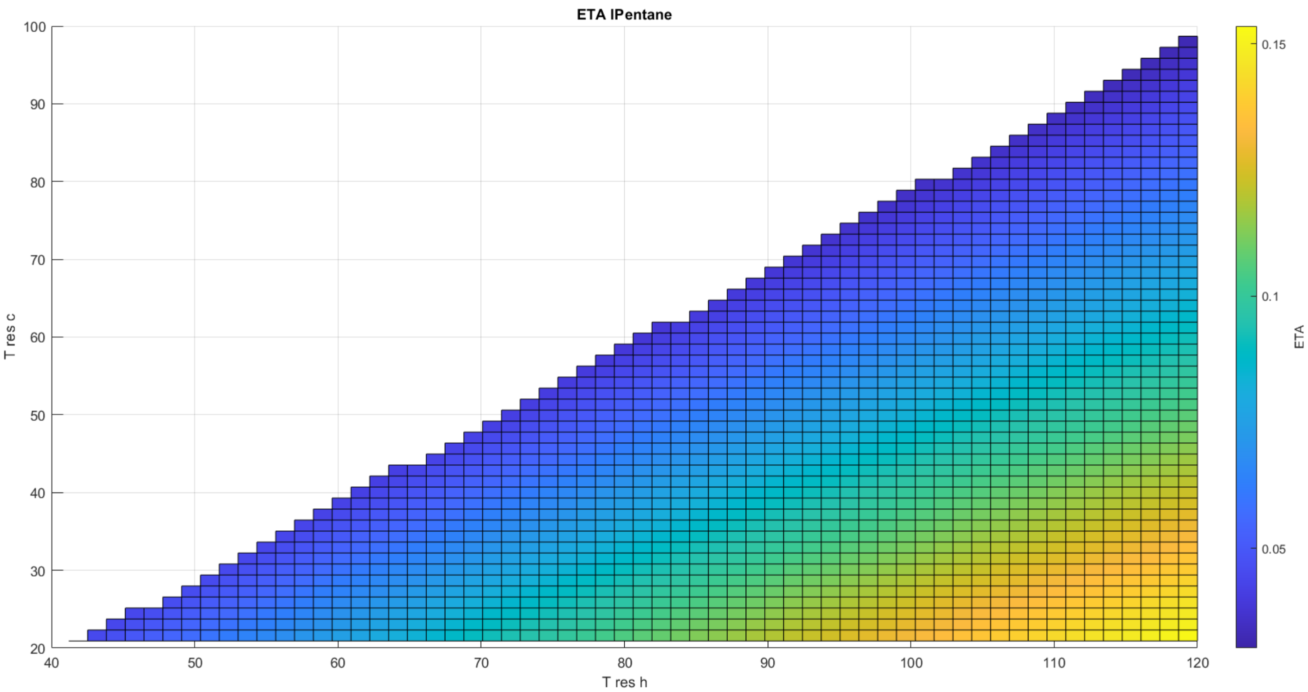


Figure 14 -Isopentane ORC efficiency as a function of the hot and cold reservoirs temperatures

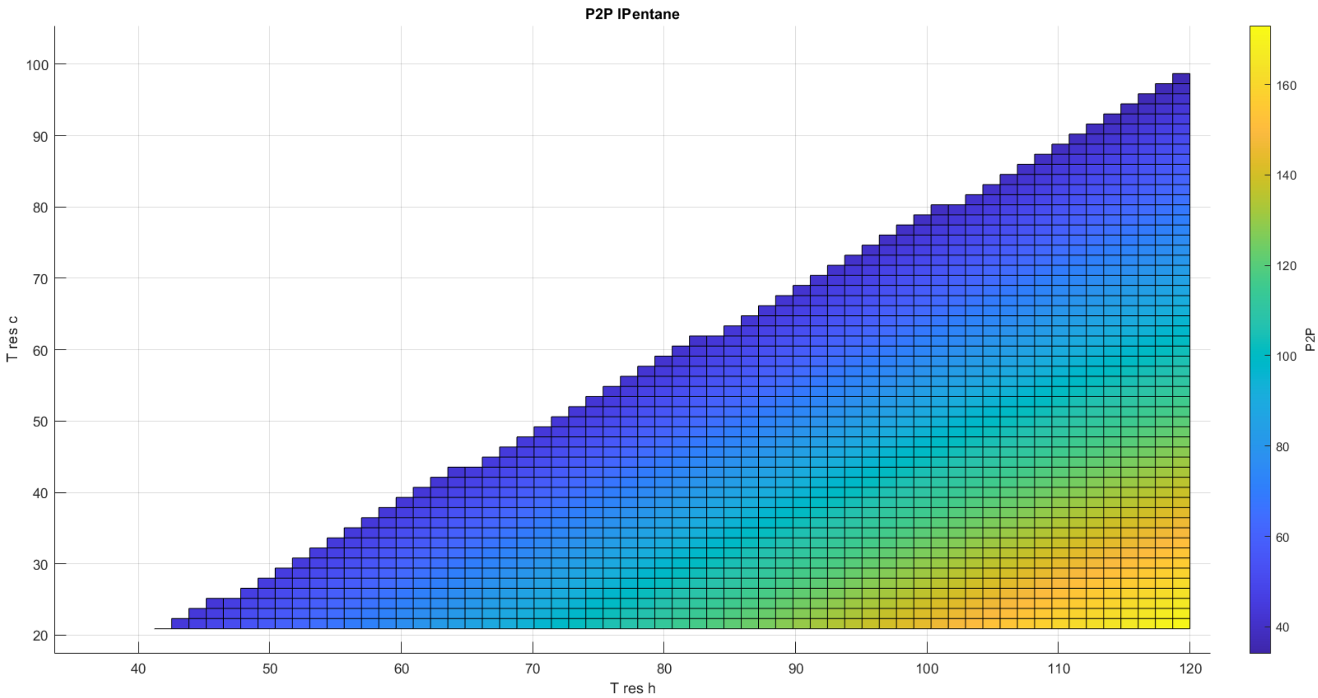


Figure 16 - Isopentane P2P as a function of the hot and cold reservoirs temperatures

As predicted the addition of a waste heat source increased the P2P ratio, the values above are higher than 100% due to the fact that the waste heat is recovered from another source therefore the thermodynamic considerations for this waste heat are not applied since it is energy that is already wasted.

Although the eta and the COP values are lower than what we achieve from the previous model, the working temperatures have a larger difference since the input liquid temperature for the hot reservoir is not the same as the temperature of the low reservoir. Therefore, the heat pump works with temperatures closer to each other and the organic Rankine Cycle works with temperatures apart from each other, gaining a higher power to power efficiency.

4. CONCLUSIONS

Throughout this work different approaches were made to find a solution for energy storage systems. Having revised all papers on the subject of pumped thermal energy storage, the path chosen was a heat pump combined with an organic Rankine cycle.

To begin with a model was made for a simple cycle, with a simple stage heat pump and a basic organic Rankine cycle.

The results for this model show that the iso pentane is the best working fluid of those who are still in the market, and that there is a need for improvement on this model.

Therefore, the solution created was to add a new stage to the heat pump improving its COP and a regenerator to the ORC which means as said earlier that the heat of the superheated vapor at the expander outlet is used to preheat the working fluid before it enters the evaporator, consequently, a higher η is achieved. These predictions were confirmed by the results achieved which maintaining iso pentane as the best working fluid got an improvement on the P2P of fifteen percent.

Lastly, the inclusion of waste heat was a complete success due to having a wasted source of energy included which improved the systems P2P to values where the energy output is bigger than the energy input. This only occurs because the work done to create the waste heat is not included on the calculations.

In this study, a preliminary assessment of a Carnot batteries as an innovative electrical energy storage system was made. The study converged in several points with the bibliography already made and presented an interesting new perspective for future studies.

The main conclusions reached in this assessment were:

- The best working fluid is the isopentane which has not been tested yet;
- The addiction of a new stage to the heat pump increased the coefficient of performance by 5 percent;
- The organic Rankine cycle efficiency remained the same with the addiction of the regenerator although this happened in the second model, the real impact of this addiction was noted in the third model with the addiction of the waste heat;

- The addiction of waste heat increased the power to power of the cycle, which shows that the complex model with this addiction of waste heat as a hot source is the model that should be used for a real life model.
- New studies should be made to the inclusion of phase change materials instead of water.

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ANNEX A

```
clc
clear all


% Variavéis de projeto

working_fluid='IPentane';
reservoir_fluid='water';


% Inputs
Eff_i_pump=0.5;
Eff_i_comp=0.75;
Eff_i_exp=0.7;
dT_sup=0;
dT_sub=0;
dT_pp=2;

i=1
```

```
i = 1
```

1. PROGRAM

```
for T_res_h = [0:10:100]
    for T_res_c = [ -30:10:T_res_h-20]


% bomba de calor

T2=T_res_h;
p2 = refpropm('P','T',T2+273.15,'Q',0,working_fluid);
h2 = refpropm('H','T',T2+273.15,'Q',0,working_fluid);

T6 = T_res_h-30;
p6 = refpropm('P','T',T6+273.15,'Q',1,working_fluid);
h6 = refpropm('H','T',T6+273.15,'Q',1,working_fluid);
```

```
s6 = refpropm('S','T',T6+273.15,'Q',1,working_fluid);

h3=h2;
p1=p2;

p3= sqrt(p1*p6);
T3 = refpropm('T','P',p3,'H',h3,working_fluid)-273.15;

p4=p3;
T4 = refpropm('T','P',p4,'Q',0,working_fluid)-273.15;
h4 = refpropm('H','P',p4,'Q',0,working_fluid);

p5=p6
h5=h6
T5 = refpropm('T','P',p5,'H',h5,working_fluid)-273.15;

p7 = p3;
h7s = refpropm('H','P',p7,'S',s6,working_fluid);
h7 = ((h7s-h6)/Eff_i_comp) + h6;
T7 = refpropm('T','P',p7,'H',h7,working_fluid)-273.15;

p8=p3
T8=T3
h8= refpropm('H','T', T8+273.15,'Q',1, working_fluid)

p9=p7
m8=(h4-h8)/(h3+h4-2*h8);
m4=1-m8;
m7=m4;
h9=m8*h8+m7*h7;
T9=refpropm('T','P',p9,'H',h9,working_fluid)-273.15;
s9 = refpropm('S','P',p9,'H',h9,working_fluid);


h1s = refpropm('H','P',p1,'S',s9,working_fluid);
h1 = ((h1s-h9)/Eff_i_comp) + h9;
T1 = refpropm('T','P',p1,'H',h1,working_fluid)-273.15;

COP = (h1-h2)/((h1-h9)+m4*(h7-h6));

%Rankine
T12 = T_res_h;
p12=refpropm('P','T',T12+273.17,'Q',1,working_fluid);
h12=refpropm('H','T',T12+273.17,'Q',1,working_fluid);
s12=refpropm('S','T',T12+273.17,'Q',1,working_fluid);

T14=T_res_c;
```

```
p14=refpropm('P','T',T14+273.17,'Q',0,working_fluid);
h14=refpropm('H','T',T14+273.17,'Q',0,working_fluid);
s14=refpropm('S','T',T14+273.17,'Q',0,working_fluid);

p13=p14;
h13i=refpropm('H','P',p13,'S',s12,working_fluid);
h13=h12-Eff_i_exp*(h12-h13i);
T13=refpropm('T','P',p13,'H',h13,working_fluid)-273.15;

p11=p12;
h11i=refpropm('H','P',p11,'S',s14,working_fluid);
h11=(h11i-h14)/Eff_i_pump+h14;
T11=refpropm('T','P',p11,'H',h11,working_fluid)-273.15;

T13a=T11+5;
p13a=p13;
h13a=refpropm('H','T',T13a+273.17,'p',p13a,working_fluid);

p11a=p11;
h11a=h13-h13a+h11;
T11a=refpropm('T','P',p11a,'H',h11a,working_fluid)-273.15;

eta=(h12-h13)/(h12-h11a)



P2P = eta*COP*100;

Output1(:,i) =  [T_res_h T_res_c COP eta P2P T2 T6];
 i=i+1
 Output = transpose(Output1)
    end


end
```