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Analysis of Thermodynamic Cycles of Heat Pumps and Magnetic Refrigerators Using Mathematical Models

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Abstract: This paper proposes a critical review of the different aspects concerning magnetic refrigeration systems, and performs a detailed analysis of thermodynamic cycles, using mathematical models found in the literature. Langevin’s statistical mechanical theory faithfully describes the physical operation of a refrigeration machine working according to a magnetic Ericsson cycle. Results of mathematical and real experimental models are compared to deduce which best describes the Ericsson cycle. The theoretical data are not perfectly consistent with the experimental data; there is a maximum deviation of about 30%. Numerical and experimental data confirm that very high Coefficient of Performance (COP) values of more than 20 can be achieved. The analysis of the Brayton cycle consisted of finding the mathematical model that considers the irreversibility of these machines. Starting from the thermodynamic properties of magnetocaloric materials based on statistical mechanics, the efficiency of an irreversible Brayton regenerative magnetic refrigeration cycle is studied. Considering the irreversibility in adiabatic transformations, the lower limit of the optimal ratio of two magnetic fields is determined, obtaining a valid optimization criterion for these machines operating according to a Brayton cycle. The results show that the Ericsson cycle achieves a higher Coefficient of Performance than the Brayton cycle, which has a higher cooling capacity as it operates with a larger temperature difference between the magnetocaloric material and source.

Keywords: heat pump; magnetocaloric technology; thermodynamic cycles

1. Introduction

The disproportionate use of fossil fuels has prompted the formulation of policies to reduce primary energy demand and carbon emissions globally [1]. The maximum exploitation of renewable resources as an alternative to fossil energy sources is still crucial to ensure a high level of energy and environmental sustainability [2,3]. This framework has led to the progressive development of the heat pump.

Refrigeration and heating are based on the mechanical compression of vapor. A viable alternative to vapor compression is magnetic refrigeration, based on the magnetocaloric effect and the use of a solid as a refrigerant. The magnetocaloric effect is the ability of a solid substance to heat up when magnetized and to cool down by eliminating the external magnetic field. This effect consists of an adiabatic change in temperature due to the magnetization/demagnetization of the material. A substantial difference between the classical and the magnetic system is the refrigerant, respectively, fluid and solid, characterized by a constant pressure throughout the cycle. Magnetic refrigeration is not noisy, is a technology with low environmental impact, has zero Ozone Destruction Potential (ODP) and has no direct impact on global warming. A strong disadvantage is related to the achievable temperature difference. To overcome the limits of the inverse magnetic cycle, it is possible to implement the principle of regeneration, thus obtaining the so-called Active Magnetic Regenerator (AMR) cycle, in which the magnetic substance acts not only as a refrigerant, providing a temperature change against a magnetization or demagnetization,
but also as a regenerator of a fluid capable of transferring thermal energy. The AMR cycle consists of the same transformations as the non-regenerative cycle, but the refrigerant can be traversed by the regenerating fluid, which associates it with the hot and cold source heat exchangers. The regenerator, therefore, is immersed in the flow of the regenerating fluid which, through pistons or pumps, can move through it. The significant advantage of this solution is the achievement of a higher $\Delta T$ than that imposed by the magnetocaloric material ($\Delta T_{ad}$) and, therefore, the possibility to transfer more energy between the two sources.

Magnetic refrigeration is much more efficient than traditional refrigeration without the use of harmful substances, it can potentially reach 60% of the cycle Carnot efficiency against about 40% of gas compression cycles [4]. This paper proposes a review of the different aspects concerning this technology, and performs a detailed analysis of thermodynamic cycles, using mathematical models found in the literature. The purpose is to evaluate the functionality, validity, and weaknesses of each model. Results of the hypothetical mathematical models and those derived from a real experiment were compared to deduce which mathematical model best describes the Ericsson cycle. Regarding the Brayton cycle, the analysis consists of finding the mathematical model that considers the irreversibility of these machines. This has resulted in an assessment of how critical issues in this cycle affect its performance, allowing the identification of strategies to minimize them and increase the performance of the entire machine.

1.1. Heat Pumps

The first classification of heat pumps can be made according to the type of energy required for operation distinguishing mechanical vapor compression heat pumps and thermal energy absorption heat pumps.

The main components of mechanical vapor compression heat pumps are a compressor, an expansion valve, and two heat exchangers (evaporator and condenser), connected by a closed circuit in which there is volatile liquid flow. In the evaporator, the temperature of the working fluid is kept below that of the heat source; this temperature difference creates heat transfer allowing the refrigerant to evaporate and thus absorb heat energy. Inside a compressor, the fluid, in the form of steam, is drawn in and compressed to a higher level of pressure and temperature. The fluid passes into the condenser where it is cooled, transfers useful heat to the user fluid, and then condenses. Finally, the refrigerant exiting the condenser is expanded by a lamination valve that lowers its pressure, thus ending the cycle. The compressor is usually driven by an electric motor or an internal combustion engine. The electric motor allows the compressor to operate with minimal transformation losses, leading to a conversion efficiency of more than 90% of electrical energy to mechanical energy.

Absorption heat pumps exploit the ability of liquids and salts to absorb the vapor from the working fluid operating between the high- and low-pressure zones. The most used substances are water (operating fluid) and lithium bromide (absorbent), or ammonia (operating fluid) and water (absorbent).

Adsorption heat pumps and refrigeration systems can directly use primary thermal energy sources (such as solar and geothermal) and waste heat generated in various industrial processes; they also use refrigerants with zero Ozone Degradation Potential (ODP) and low Global Warming Potential (GWP). Compared with steam compression systems, adsorption heat pumps have the advantage of being able to obtain greater energy savings, because they are powered by waste heat or solar energy, and they also have simpler control, absence of vibrations, and lower operating costs [5]. It is stated that the adsorption cycle can be powered by a wide range of temperatures, starting from 50 up to 600 °C. Adsorption systems are suitable for any applications, since the adsorbents are always in the solid-state [6]. There are various adsorbent-adsorbed working fluids: silica gel–water, activated carbon–ammonia, and activated carbon–methanol; however, the most common is the zeolite–water pair. Zeolite is a mineral that produces heat up to 80 °C upon simple contact with water, and then quickly returns to its original state. In general, the Coefficient
of Performance (COP) is still below 0.4 due to the irreversibility of the thermal coupling; it is necessary to identify new cycles able to increase the COP, new working fluids, and improvements for the absorber bed, to guarantee a greater heat exchange [6–8].

The main characteristic of the chemical heat pump is its ability to store thermal energy in the form of chemical energy during a fully reversible reaction [9]. The thermal accumulator consists of a reactor and a condenser/evaporator, connected by a shut-off device that allows them to be isolated from each other. The operating process is divided into four stages: pre-charge, charge, pre-discharge, and discharge. The absorption/release of energy by the reactor in the charging and discharging phases is possible thanks to the temperature difference between the warmer reactor and the condenser/evaporator ($\Delta T_{\text{drive}}$) in the process charge and between the condenser/evaporator and the colder reactor ($\Delta T_{\text{lift}}$) in the discharge process, which are set up in the design stage [10]. For a chemical heat pump, heat for dehydration is supplied at 673 K, and the vapor condenses at 290 K. During the hydration process, the heat required for water evaporation is supplied at 290 K, and consequently, the heat given up by salt hydration is transferred to 353 K [11].

The refrigerators and thermo-acoustic heat pumps can reach 41% efficiency. The operation of a thermo-acoustic heat pump is achieved by the rapid movement of a surface, which generates a pressure wave that is transmitted into the gas at the speed of sound. Inside the hermetic container, there is a septum (stack) with longitudinal channels. The gas in the channels, subject to acoustic waves, moves to the right compressing itself, increasing both pressure and temperature. Then the sound waves force the gas to move back and forth through the septum openings. When the volume of gas is compressed, it transfers heat to the solid walls that contain it, while when it is expanded, it absorbs heat from the adjacent surfaces. To obtain a useful effect from this device, it is necessary to ensure that the gas itself gives off heat or absorbs it from the walls of the septum by means of heat exchangers located, respectively, to the right and left of the septum. The ideal conditions to be achieved would be those in which the compressed volume, at its maximum pressure and temperature, came into contact with the hot exchanger, while the same expanded volume, at its minimum pressure and temperature, came into contact with the cold exchanger. In this way, the heat, available to the right of the septum, can be removed by means of a compact heat exchanger, thus creating a thermoacoustic heat pump. On the opposite side of the septum, the other exchanger removes heat from the user fluid, thus creating a thermo-acoustic refrigerator. It was estimated that for sound pressure levels of 74 dB, the temperature fluctuation is 0.0001 K; for sound pressure levels of 120 dB, the temperature fluctuation is about 0.02 K. For fluctuations over $20 \div 30$ K, the sound pressure level needs to be increased over 170 dB. In some prototypes, as much as 194 dB has been detected [12].

1.2. Magnetocaloric Technology

Thermomagnetic machines exploit the Magneto-Caloric Effect (MCE) of magnetic materials; the magneto-thermodynamic process relies on the variation of the magnetic field to produce a reversible change in temperature. Unlike conventional cycles, pressure variation has no influence. The magnetocaloric material is placed within a magnetic field, which leads to simultaneous heating of the material. The heat of the material is extracted using a utilization fluid (usually water) and introduced into the environment to be heated. In this way, the magnetocaloric alloy is cooled. Its temperature further decreases due to demagnetization or removal of the external magnetic field. At this point, the cycle ends with the heating of the magnetocaloric alloy thanks to the passage of another user fluid that transfers its heat, extracted from the environment to be cooled, to the alloy. If the hot fluid obtained at the beginning of the process is used for air conditioning, the machine operates as a heat pump; on the other hand, if the useful effect is on the cold fluid, the machine operates as a refrigerator. This technology has been successfully applied in low-temperature physics to cool samples from many hundreds of degrees kelvin to temperatures near absolute zero [13].
The thermal response of ferromagnetic materials subjected to a change in a magnetic field can be quantified in the reversible change in temperature ($\Delta T_{ad}$) when the magnetic field change occurs in an adiabatic process, or in magnetic entropy ($\Delta S_m$) if the field change occurs during an isothermal process. Both are characteristic terms of the magnetocaloric effect, for a fixed temperature $T_0$ and a variation of the magnetic field [14].

The relationship between the two properties is schematized in the T-S diagram in Figure 1.

![Figure 1](image)

**Figure 1.** Temperature and entropy as a function of the external magnetic field applied to the material [14].

The existence of the MCE phenomenon at temperature $T_0$ can cause an adiabatic variation of the temperature $\Delta T_{ad} = T_1 - T_0$, or a variation of magnetic entropy at constant temperature $\Delta S_m = S_1 - S_0$. Both are characteristic terms of the magnetocaloric effect, for a fixed temperature $T_0$ and a variation of the magnetic field.

A ferromagnetic material is divided into regions, called magnetic domains. Each region is characterized by atoms with uniform magnetization but with a different orientation to nearby regions [15]. Increasing the intensity of the externally applied magnetic field results in increasing magnetic spins and decreasing magnetic entropy. The total entropy ($S_{tot}$) of a ferromagnetic material, at constant pressure, can be determined by the following equation:

$$S_{tot}(H, T) = S_m(H, T) + S_r(T) + S_e(T) \quad (1)$$

where $S_m$ is the magnetic entropy resulting from the magnetization of the material, $S_r$ is the reticular entropy of the material due to its vibration, and $S_e$ is the entropy of the free electrons of the material. $S_r$ and $S_e$ are independent of the magnetic field $H$ and function of the material temperature $T$, while $S_m$ is highly dependent on both quantities [14].

When a magnetic field is applied to a sample of ferromagnetic material, in adiabatic conditions, the total entropy remains constant during the magnetization process. This is due to a decrease in magnetic entropy and, therefore, by compensation, an increase in reticular and electronic entropy. This causes an increase in $\Delta T_{ad}$, directly related to the extent of the external magnetic field. In other words, when a magnetic field is applied to the magnetocaloric alloy, the magnetic domains tend to conform in a single larger domain where the magnetic moments of the atoms are all equal. This leads to greater molecular agitation and, consequently, heating of the material. A decrease in the previously applied magnetic field corresponds to a tendency towards the free reorientation of the individual atoms.
magnetic domains. This reorientation takes place with the absorption of thermal energy, and the material, which is in an isolated environment, cools down. The moment the external magnetic field is completely removed, the system returns to the original disorder conditions. The particles of the material are no longer forced by the magnetic field lines, and the terms of entropy and temperature return to the initial values. In the event that the magnetization of the material occurs under isothermal conditions, the total entropy of the system is directly linked to the term magnetic entropy (which follows the variation of the magnetic field itself); the entropy terms related to temperature, on the other hand, remain unchanged [14,15].

Magnetic technology, thanks to the presence of a solid refrigerant (magnetocaloric material), allows us to totally avoid the use of fluorinated refrigerant gases with all the risks and environmental damages that they cause. This is also guaranteed using water-based fluids for the transmission of heat from the machine to the surrounding environments and the other way around.

The refrigerant material can be moved inside and outside of the magnetic field by means of a simple electric machine with low energy consumption, which entails less maintenance, longer life of the longest machine, absence of noise, and excessive vibration. If the purchase or transfer of heat in a gaseous refrigerant is a rather rapid process, since the turbulences that are created allow rapid and efficient transmission of heat, the same cannot be said for solid materials, where the heat transport mechanism occurs thanks to slow molecular propagation. For this reason, it is currently believed that the best solution to overcome the problem is the use of porous conformations which, allowing a greater contact surface between the solid and the user fluid, make the process faster [13].

Magnetocaloric devices have not yet fully replaced the traditional ones, as this technology requires intense magnetic fields, complex systems that are too expensive from an energy point of view. In fact, to obtain a temperature variation from 0.5 to 2 °C at room temperature, a change in the magnetic field of 1 Tesla is required. Research is moving towards the use of permanent, less bulky magnets that consume less energy but produce weaker electromagnetic fields, drastically reducing the performance of the process [16].

1.3. Magnetocaloric Materials

Magnetocaloric materials can be first-order or second-order phase transition materials. Materials with a first-order phase transition have a magnetic-structural change in the crystal lattice. During the transition, the two phases are in equilibrium, making the transformation non-instantaneous. This structural change is affected by a strong change in magnetic entropy; the lattice structure changes, while its temperature is kept constant. The process is isothermal, and the heat involved is latent. Ferromagnetic materials show a good aptitude to be used in refrigeration/heat pump systems with magnetocaloric technology. The second-order phase transition proceeds continuously from one phase to another without reaching the equilibrium condition, and it is not associated with latent heat. The phase transition temperature is called the Curie Temperature ($T_C$).

Good entropy ($\Delta S_m$) and temperature ($\Delta T_{ad}$) variations are required for a magnetocaloric material suitable for a reverse cycle magnetic machine, as well as $T_C$ close to the working temperature for greater entropy variation over the entire temperature range of the cycle. High specific heat and high thermal conductivity are required to facilitate the heat transfer process by allowing wide temperature variation and higher efficiency, and high electrical resistance is needed to limit eddy currents during rapid magnetic field changes. In addition, these materials should be non-toxic, with high corrosion resistance; good mechanical properties, characterized by low production costs required for commercial use; and with low environmental impact. However, solid magnetocaloric materials lead to some drawbacks, such as hysteresis loops, low kinetics, and a reduced temperature range for machine operation.

The technical feasibility of using ferrofluids critically depends on the possibility of reaching high concentrations of magnetic particles, having low sliding thresholds when
they are magnetized, and on the resolution of problems associated with heat transmission during the process. Compounds containing Gadolinium (Gd) are well suited as they meet many requirements [14].

1.4. Thermodynamic Cycles of Magnetocaloric Systems

A magnetic refrigeration/heating system consists of ferromagnetic material, magnetization/demagnetization system, heat exchangers (hot and cold), and a circuit that allows the passage of the heat exchange carrier fluid and to transfer heat from the ferromagnetic material to the exchanger and vice versa. The operating principle consists of the absorption of the heat load, by the cooling material, from the cold source and the transfer of the same to the heat exchanger. This step, performed cyclically, leads to the removal of heat from the environment to be cooled or the introduction of heat into the environment to be heated. In these systems, the material changes its temperature due to the external magnetic field [14].

There are numerous advantages of the magnetic cycle of Ericsson and Brayton compared to the gas cycle. By replacing the compression phase of gas with magnetization, there is a significant reduction in energy demand. The expansion is replaced by the demagnetization phase, leading to a reduction in the irreversibility phenomenon characteristic of steam compression systems. A further advantage is the absence of environmentally harmful refrigerant gases; the refrigerants used are solid substances with zero environmental impact. However, in the reverse magnetic cycles of Ericsson and Brayton without regeneration, the difference in temperature between the hot and cold source is less than the variation in adiabatic temperature typical of the refrigerant substance used. These machines have lower thermal jumps than those of refrigeration machines operating with vapor compression cycles, since at room temperature the cooling magnetic substances reach modest values of $\Delta T_{ad}$ (about 3 K). Magnetic cycles with regeneration are one viable solution. In both the Ericsson and Brayton cycles, regeneration is only possible if there is a temperature difference that allows heat transfer, meaning that the processes are not reversible and the efficiency of the machine decreases. When the magnetocaloric machine operates as a refrigerator, the reticular entropy at room temperature is too large to be neglected, and part of the cooling capacity is consumed to cool the heat load of the reticular system. This involves a decrease in the net cooling capacity of the magnetocaloric material. By adding a regenerator to the magnetic refrigerator, the heat expelled by the reticular system in one stage of the cycle, thanks to the regenerator, is recovered and returned to the reticular system in another stage. In this way, the cooling capacity is not wasted to cool the reticular system of the material but can be used for the effective increase in $\Delta S_m$ and $\Delta T_{ad}$. The regeneration permits to work with a wider temperature range independent of the cycle used.

Active Magnetic Regenerator (AMR) Cycle

In the AMR cycle, the magnetic substance acts as a refrigerant and regenerant for a fluid, transferring thermal energy. These systems consist of a solid ferromagnetic material that is cyclically crossed by the regenerating fluid, driven by a pumping system. The AMR system includes the magnet (which magnetizes and demagnetizes the refrigerant), the regenerator, the cold side heat exchanger (in which heat is transferred to the regenerating fluid from an external source at a higher temperature), the hot side heat exchanger (which dissipates the thermal energy carried by the regenerating fluid into an external source at a lower temperature), and the displacer (as the pumping system allows the regenerating fluid to pass through the regenerator).

The four stages that describe the operation of the system are [14]:

1. A magnetization process that leads to heating the ferromagnetic material of the regenerator, which heats the carrier fluid flowing inside it.
2. A regenerator cooling process with a constant applied magnetic field. The pumping system allows the passage of the regenerating fluid which, being at a lower tempera-
ture than the magnetic substance, heats up and is sent to the lateral heat exchanger taking thermal energy from the magnetic substance, which cools down.

3. A demagnetization process that leads to further lowering of the regenerator temperature. The magnetic field affecting the regenerator is removed, causing a lowering of the regenerator temperature profile due to the magnetocaloric effect.

4. A regenerator heating process. In the absence of an external magnetic field, the regenerator is passed through the regenerating fluid leaving the heat source exchanger which, being at a higher temperature than the extreme heat of the magnetic substance, will release energy by cooling to be sent to the cold side exchanger as the temperature profile of the regenerator increases.

A different temperature characterizes each section of the regenerator; it is possible to place along with the AMR different magnetocaloric materials that have a $T_C$ close to that present at that point of the regenerator so that they express the maximum effect magnetocaloric. For the AMR refrigerator, there will be infinite cycles corresponding to each elemental portion of the magnetic refrigerant. In the AMR cycle, all particles absorb or transfer heat simultaneously to the heat transfer fluid. The temperature difference obtainable from a refrigerator operating according to this cycle is greater than the adiabatic temperature variation, characteristic of magnetocaloric material, and therefore, much higher than that allowed by the non-regenerative cycle.

2. Methodology—Mathematical Models and Experimental Comparison

The aim was to carry out a mathematical approach to the study of the Ericsson cycle to define the COP, and thus the performance of a thermomagnetic system operating in refrigeration mode. The analysis is also valid for materials with second-order phase transition, such as gadolinium. The results of the mathematical model were compared with the experimental data presented in the literature [17].

2.1. The Curie-Weiss Law Applied to the Ericsson cycle

The generic magnetic cycle consists of magnetization and demagnetization, where heat is expelled and absorbed, respectively, and two intermediate generic processes. The COP of a refrigeration unit is defined as:

$$\text{COP} = \frac{Q_1}{L}$$  \hspace{1cm} (2)

where:

$$Q_1 = T_1 \Delta S_{m|T_1} = T_1 \left( \frac{\partial S_m}{\partial H} \right)_{T_1} \Delta H_1$$  \hspace{1cm} (3)

The term $Q_1$ and $T_1$ are the heat subtracted from the cold source due to the magnetocaloric effect and the temperature of the cold source; $\Delta S_{m|T_1}$ and $\Delta H_1$ are, respectively, the change in entropy and magnetic field at temperature $T_1$. The work $L$ supplied to the system is:

$$L = T_1 \Delta S_{m|T_1} - T_2 \Delta S_{m|T_2} = T_1 \left( \frac{\partial S_m}{\partial H} \right)_{T_1} \Delta H_1 - T_2 \left( \frac{\partial S_m}{\partial H} \right)_{T_2} \Delta H_2$$  \hspace{1cm} (4)

$T_2$ is the temperature of the hot source where the heat must be introduced; $\Delta S_{m|T_2}$ and $\Delta H_2$ are, respectively, the change in entropy and magnetic field at that temperature. In Equations (3) and (4), magnetic entropy is considered as only it can be controlled by changing the external magnetic field. Consequently, COP becomes:

$$\text{COP} = \frac{T_1 \left( \frac{\partial S_m}{\partial H} \right)_{T_1} \Delta H_1}{T_1 \left( \frac{\partial S_m}{\partial H} \right)_{T_1} \Delta H_1 - T_2 \left( \frac{\partial S_m}{\partial H} \right)_{T_2} \Delta H_2} = \left[ 1 - \frac{T_2 \left( \frac{\partial S_m}{\partial H} \right)_{T_2} \Delta H_2}{T_1 \left( \frac{\partial S_m}{\partial H} \right)_{T_1} \Delta H_1} \right]^{-1}$$  \hspace{1cm} (5)
The magnetization $M$ is:

$$M = \chi (H + H_{\text{ext}}) \tag{6}$$

$H$ and $H_{\text{ext}}$ are the internal and external magnetic field, while $\chi$, according to the Curie-Weiss law, is the magnetic susceptibility defined as:

$$\chi = \frac{C}{(T - C\lambda)} \tag{7}$$

where $C$ is the Curie constant, $T$ is the temperature and $\lambda$ is a constant, independent of the temperature, defined as:

$$\lambda = \frac{3kT_C}{N_mS^2N_S(N_S + 1)\mu_B^2} \tag{8}$$

in which $T_C$ is the Curie temperature [K], $k$ is the Boltzmann constant (equal to $1.38 \times 10^{-23}$ J/K), $N_S$ is the quantum number of spins, $g$ is the Landé factor, $N_m$ is the number of atoms or molecules, and $\mu_B$ is the Bohr magneton (equal to $9.27 \times 10^{-21}$ J/K). The Landé factor $g$ is defined as:

$$g = 1 + \frac{[J_A(J_A + 1) + N_S(N_S + 1) - J_O(J_O + 1)]}{2J_A(J_A + 1)} \tag{9}$$

where $J_A$ is the quantum number of the total angular momentum, and $J_O$ is the quantum number of the orbital moment. Replacing Equation (7) with Equation (6), the following is obtained:

$$M = \frac{C(H + H_{\text{ext}})}{(T - C\lambda)} \tag{10}$$

Deriving Equation (10) with respect to $T$ while keeping $H$ constant:

$$\left(\frac{\partial M}{\partial T}\right)_H = -\frac{C(H + H_{\text{ext}})}{(T - C\lambda)^2} \tag{11}$$

Using Maxwell’s relation, the following is obtained:

$$\left(\frac{\partial S_m}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H = -\frac{C(H + H_{\text{ext}})}{(T - C\lambda)^2} \tag{12}$$

Considering Equations (8) and (9), Equation (12) becomes:

$$\left(\frac{\partial S_m}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H = -C(H + H_{\text{ext}}) \cdot \left[\frac{12CkT_CJ_A^2(J_A + 1)^2}{N_mN_S(N_S + 1)\mu_B^2[3J_A(J_A + 1) + N_S(N_S + 1) - J_O(J_O + 1)]^2}\right]^{-2} \tag{13}$$

Hence, Equation (5) of the COP becomes:

$$\text{COP} = \left[1 - \frac{T_2\Delta H_2}{T_1\Delta H_1} \left(\frac{T_1 - \Gamma}{T_2 - \Gamma}\right)^2\right]^{-1} \tag{14}$$

where:

$$\Gamma = \frac{12CkT_CJ_A^2(J_A + 1)^2}{N_mN_S(N_S + 1)\mu_B^2[3J_A(J_A + 1) + N_S(N_S + 1) - J_O(J_O + 1)]^2} \tag{15}$$

Thus, through a general theoretical approach, the expression of the COP for a magnetic refrigerator that evolves according to an ideal cycle was obtained. The COP is correlated to the magnetic properties through the factor $\Gamma$, which depends solely on the magnetocaloric material considered, with reference to its magnetic properties, on the temperature of the initial and final state considered and on the variation of the magnetic field at the
temperature of the cycle considered [18]. From Equation (14), it is evident that the COP depends on temperature in a non-linear way, does not depend on the value of the applied magnetic field but on its variation $\Delta H_1$ and $\Delta H_2$, and is expressed in terms of the ratio between the two magnetic variations $\Delta H_2 / \Delta H_1$. Considering the Ericsson cycle (Figure 2), the relations of the thermal powers exchanged at the sources and the final relation of the COP are expressed. From Equations (13) and (15):

\[
\left( \frac{\partial S_m}{\partial H} \right)_{T} = -C(H + H_{ext})[T - \Gamma]^{-2}
\]

(16)

**Figure 2.** Ericsson cycle with regeneration.

It follows that:

\[
Q_h = T_h(S_2 - S_1) = -C \frac{T_h}{(T_h - \Gamma)^2}(H_1 - H_0)
\]

(17)

\[
Q_c = T_{cold}(S_4 - S_3) = C \frac{T_{cold}}{(T_{cold} - \Gamma)^2}(H_1 - H_0)
\]

(18)

\[
L = Q_h - Q_c = -C(H_1 - H_0) \left[ \frac{T_h}{(T_h - \Gamma)^2} + \frac{T_{cold}}{(T_{cold} - \Gamma)^2} \right]
\]

(19)

\[
COP = \frac{Q_c}{L} = \frac{T_h}{T_{cold}} \left( \frac{T_{cold} - \Gamma}{T_h - \Gamma} \right)^2 + 1
\]

(20)

**2.2. Effect of Regeneration**

The regeneration process of magnetic cycles cannot be perfectly ideal, leading to a decrease in COP. The cycle is composed of two isothermal transformations and two transformations with a constant magnetic field. During the isothermal magnetization phase (A→B) at temperature $T_{hot}$, the heat released is:

\[
Q_h = \int_A^B TdS = T_{hot}\Delta S(\Delta H, T_{hot})
\]

(21)
During the isothermal demagnetization phase (C→D) at \( T_{\text{cold}} \) temperature, the absorbed heat is:

\[
Q_c = \int_C^D T \, ds = T_{\text{cold}} \Delta S(\Delta H, T_{\text{cold}})
\]

(22)

where the change in entropy is defined as follows:

\[
\Delta S(\Delta H, T) = S(H_1, T) - S(H_0, T)
\]

(23)

The heat absorbed by the operating fluid by the regenerator during the transformation D→A (heating with constant magnetic field \( H_0 \)) is:

\[
Q_{rs} = \int_D^A T \, ds = \int_{T_{\text{cold}}}^{T_{\text{hot}}} C_H(H_0, T) \, dT
\]

(24)

While during the transformation B→C (cooling with constant magnetic field \( H_1 \)), the operating fluid releases heat to the regenerator equal to:

\[
Q_{sr} = \int_B^C T \, ds = \int_{T_{\text{hot}}}^{T_{\text{cold}}} C_H(H_1, T) \, dT
\]

(25)

\( C_H(H_1, T) \) and \( C_H(H_0, T) \) are the thermal capacities in constant magnetic field transformations, respectively, \( H_1 \) and \( H_0 \).

For most magnetocaloric materials, for \( T \geq T_0 \), it turns out that \( C_H(H_0, T) \leq C_H(H_1, T) \). Otherwise, for \( T \leq T_0 \), \( C_H(H_0, T) \geq C_H(H_1, T) \).

It can be deduced that \( T_0 \) is the temperature at which there are the maximum entropy variations. It represents the \( T_c \) and plays a very important role in inverse regenerative cycles, as it affects their performance. Based on the previous analysis, it is possible to obtain a quantity of heat from a non-perfect regeneration:

\[
\Delta Q = -(Q_{rs} + Q_{sr}) = \int_{T_{\text{cold}}}^{T_{\text{hot}}} [C_H(H_1, T) - C_H(H_0, T)] \, dT
\]

(26)

For \( T_0 > T_{\text{hot}} > T_{\text{cold}} \), the \( \Delta Q < 0 \); otherwise, for \( T_{\text{hot}} > T_{\text{cold}} > T_0 \), the \( \Delta Q > 0 \).

If the heat transferred from the working substance to the regenerator is greater than that transferred from the regenerator to the working substance, the case where \( \Delta Q > 0 \), the excess redundant heat must be released to the cold source in order to avoid the temperature change of the regenerator which, consequently, would no longer be in good operating conditions. In this case, the net heating quantity is \( Q_L = Q_c - \Delta Q \).

Similarly, if the heat transferred from the working substance to the regenerator is smaller than that transferred from the regenerator to the working substance, the case where \( \Delta Q < 0 \), insufficient regenerative heat can only be compensated for by the hot source. Therefore, the net cooling quantity is \( Q_H = Q_h - \Delta Q \), while \( Q_L = Q_c \) remains unchanged.

More complex is the case \( T_{\text{hot}} > T_0 > T_{\text{cold}} \); there are two sub-cases:

1. From \( T_{\text{cold}} \) to \( T_0 \), \( C_H(H_0, T) \geq C_H(H_1, T) \), \( \Delta Q^- \);
2. From \( T_0 \) to \( T_{\text{hot}} \), \( C_H(H_0, T) \leq C_H(H_1, T) \), \( \Delta Q^+ \).

\( \Delta Q^+ \) must be yielded to the cold source, while \( \Delta Q^- \) must be compensated by the hot source. These two quantities of heat are not released simultaneously and, therefore, cannot be eliminated. Then it is \( Q_L = Q_c - \Delta Q^+ \) and \( Q_H = Q_h - \Delta Q^- \).

From this, it can be deduced that, in any case, perfect regeneration never exists.

For all three analyzed cases, the net cooling quantity can be defined as:

\[
Q_L = Q_c - Q_r
\]

(27)
where $Q_r$ is insufficient regenerative heat:

$$Q_r = \int_{\text{max}(T_{\text{cold}}, T_0)}^{\text{max}(T_{\text{hot}}, T_0)} [C_H(H_1, T) - C_H(H_0, T)]dT$$

(28)

and

- If $T_0 > T_{\text{hot}} > T_{\text{cold}}$, the integral of $Q_r$ would be between $T_0$ and $T_0$ and, therefore, equal to 0;
- If $T_{\text{hot}} > T_{\text{cold}} > T_0$, the integral of $Q_r$ would be between $T_{\text{cold}}$ and $T_{\text{hot}}$ and, therefore, it would be $Q_r = \Delta Q$;
- If $T_{\text{hot}} > T_0 > T_{\text{cold}}$, the integral of $Q_r$ would be between $T_0$ and $T_{\text{hot}}$ and, therefore, it would be $Q_r = \Delta Q^+$.

2.3. Definition of the COP through Langevin’s Theory

One more theory was investigated [19]; Langevin’s theory was applied to Ericsson and Brayton cycles. The magnetic system adopted in this study consists of $N_D$ identical, localized, mutually non-interacting, and freely orientable dipoles, each having a magnetic moment $\mu$. The mean magnetic moment $M$ of the system results:

$$M = \mu N_D L(x)$$

(29)

The effective spin magnetic moment $\mu$ is calculated as:

$$\mu = g \mu_B \sqrt{J_A (J_A + 1)}$$

(30)

in which $g$ is the Landé factor, $\mu_B$ is the Bohr magneton, and $J_A$ is the quantum number of the total angular momentum.

In Equation (29), $L(x)$ is the Langevin function, defined as:

$$L(x) = \coth (x) - \frac{1}{x}$$

(31)

where:

$$x = \beta \mu (H + \lambda M)$$

(32)

In Equation (32), $\lambda$ is a parameter concerning the molecular magnetic field and is obtained through Equation (8) and

$$\beta = \frac{1}{kT}$$

(33)

where $k$ always indicates the Boltzmann constant.

By applying the Helmholtz free energy equations to the magnetic system, the expression of the magnetic entropy $S_m$ is:

$$s_m = N_D k \left[ 1 - x \coth (x) + \ln \frac{4\pi \sinh (x)}{x} \right]$$

(34)

While the specific heat with a constant magnetic field $c_m$ is:

$$c_m = T \left( \frac{\partial s_m}{\partial T} \right)_H = T N k x' \left( x \left( \sinh^{-1} \right)^2 (x) - \frac{1}{x} \right)$$

(35)

where:

$$x' = \frac{\mu \lambda T \left( \frac{\partial M}{\partial T} \right)_H - \mu (H + \lambda M)}{k T^2}$$

(36)
Deriving Equation (29) with respect to the temperature $T$, while keeping the magnetic field $H$ constant, the following is obtained:

$$\left( \frac{\partial M}{\partial T} \right)_H = \mu N \frac{\partial \xi(x)}{\partial T} = \mu N \left( \frac{1}{x^2} - \left( \sinh^{-1} \right)^2(x) \right) \frac{\partial x}{\partial T} = \mu N \left( \frac{1}{x^2} - \left( \sinh^{-1} \right)^2(x) \right) \frac{\mu \lambda T}{kT} \frac{\partial M}{\partial T} - \mu \left( H + \lambda M \right)$$  \hspace{1cm} (37)

Multiplying the first and second sides by $T$ and isolating $\frac{\partial M}{\partial T}$, the following is obtained:

$$\left( \frac{\partial M}{\partial T} \right)_H = H + \lambda M \frac{T}{\xi(x)} \left[ \frac{kT}{N\mu^2} + \lambda \xi(x) \right]$$  \hspace{1cm} (38)

in which:

$$\xi(x) = \left( \sinh^{-1} \right)^2(x) - \frac{1}{x^2}$$  \hspace{1cm} (39)

### 2.4. Performance Analysis of the Brayton Cycle

Theoretical calculations on the Brayton cycle are more complex than those made on the Ericsson cycle, because the heat removed from the cold source and that transferred to the hot source are exchanged when the material is operating at a constant magnetic field; therefore, their value cannot be associated, as in the Ericsson cycle, to a simple expression $T \Delta S$, but to a more complex relationship, of the type $\int TdS$, which can only be calculated by determining the function of the entire iso-field curve, which is a peculiar characteristic of each individual magnetocaloric material.

The analysis taken into consideration starts, also for the Brayton cycle, from the theory of statistical mechanics and the Helmholtz free energy Equation [20].

Entropy $S$ results:

$$S = N_D k \left[ \ln \sinh \left( \frac{2J_A + 1}{2J_A} x \right) - \ln \sinh \left( \frac{x}{2J_A} \right) - x B_j(x) \right]$$  \hspace{1cm} (40)

where $N_D$ is the number of magnetic moments, $k$ is the Boltzmann constant, and $J_A$ is the quantum number of the total angular momentum. The $x$ is defined as follows:

$$x = \frac{8 \mu_B J_A H}{k T}$$  \hspace{1cm} (41)

in which $g$ is the Landé factor, $\mu_B$ is the Bohr magneton, $H$ is the magnetic field applied, and $T$ is the absolute temperature. In Equation (40), $B_j(x)$ is the Brillouin function defined as:

$$B_j(x) = \frac{2J_A + 1}{2J_A} \coth \left( \frac{2J_A + 1}{2J_A} x \right) - \frac{1}{2J_A} \coth \left( \frac{1}{2J_A} x \right)$$  \hspace{1cm} (42)

As for the magnetization $M$, it results in:

$$M = N_D \mu_B J_A B_j(x)$$  \hspace{1cm} (43)

While the specific heat with a constant magnetic field $C_H$ is:

$$C_H = -N_D k x^2 \left[ \left( \frac{2J_A + 1}{2J_A} \right)^2 \left( \sinh^{-1} \right)^2 \left( \frac{2J_A + 1}{2J_A} x \right) - \left( \frac{1}{2J_A} \right)^2 \left( \sinh^{-1} \right)^2 \left( \frac{1}{2J_A} x \right) \right]$$  \hspace{1cm} (44)

with high temperatures or weak magnetic fields, $x << 1$ and Equation (43) becomes:

$$M = \frac{C H}{T}$$  \hspace{1cm} (45)

where $C$ is the Curie constant.
Consequently, Equations (40) and (44) are simplified as follows:

\[ S = Nk \ln (2J_A + 1) - \frac{CH^2}{2T^2} \]  

(46)

\[ C_H = \frac{CH^2}{T^2} \]  

(47)

Considering the irreversible Brayton magnetic cycle with regeneration reported in Figure 3 [20], the cycle is composed of two adiabatic transformations and two transformations with a constant magnetic field, more precisely:

- From point 1 to point 2s, an isentropic adiabatic magnetization from the \( H_2 \) field to the field \( H_1 \) is represented. The real process that is carried out is, however, adiabatic and irreversible and goes from 1 to 2; the material temperature rises from \( T_1 \) to \( T_2 \).
- From point 2 to point 3, the material, with a constant magnetic field \( H_1 \), releases heat \( Q_h \) to the hot source, decreasing its temperature up to \( T_3 \). This temperature, assuming an ideal heat exchange, is equal to \( T_h \) of the hot source.
- From point 3 to point 4, the material cools down to \( T_4 \) giving \( Q_R \) heat to the regenerator.
- From point 4 to point 5s, the material is subjected to an isentropic adiabatic demagnetization from the \( H_1 \) field to the field \( H_2 \). The real process that is performed is, however, adiabatic and irreversible and ranges from 4 to 5; the material temperature drops from \( T_4 \) to \( T_5 \).
- From point 5 to point 6 the material, with constant magnetic field \( H_2 \), absorbs heat \( Q_l \) from the cold source, rising to the temperature \( T_6 \). This temperature, assuming an ideal heat exchange, is equal to \( T_l \) of the cold source.
- From point 6 to point 1, the regenerator transfers the \( Q_R \) heat to the magnetocaloric material, making it return to the starting temperature \( T_1 \).

Using Equation (47), the thermal energies \( Q_R \), \( Q_h \) and \( Q_l \) can be expressed as:

\[ Q_R = CH_1^2 \left( T_4^{-1} - T_h^{-1} \right) = CH_1^2 \left( T_1^{-1} - T_4^{-1} \right) \]  

(48)

\[ Q_h = CH_2 \beta^2 \left( T_h^{-1} - T_2^{-1} \right) \]  

(49)
\[ Q_l = CH_2^2 \left( T_{5}^{-1} - T_{1}^{-1} \right) \]  

where \( \beta = H_1 / H_2 \), with \( H_1 > H_2 \), is the relationship between the two magnetic fields.

When the two adiabatic are reversible and isentropic (ideal process), from Equation (46), the following is obtained:

\[ \frac{T_{2s}}{T_1} = \frac{T_4}{T_{5s}} = \frac{H_1}{H_2} \]  

When the process is real, and therefore, the two adiabatic processes are irreversible, the isentropic performance can be used to describe the degree of irreversibility of the transformations:

\[ \eta_e = \frac{T_4 - T_3}{T_4 - T_{5s}} \]  
\[ \eta_c = \frac{T_{2s} - T_1}{T_2 - T_1} \]

Other parameters useful for the analysis are the relationship \( \tau \) between the temperatures of the sources and the regeneration factor \( \alpha \):

\[ \tau = \frac{T_i}{T_h} \]  
\[ \alpha = \frac{T_1}{T_h} \]

When \( \alpha = 1 \), the cycle operates with maximum regeneration, and in this case, \( Q_R = CH_2^2 \left( T_1^{-1} - T_h^{-1} \right) \);

When \( \alpha = \tau \), the cycle operates without regeneration. So, the range of variation of \( \alpha \) is \( \tau \leq \alpha \leq 1 \).

Using Equations (51)–(53) and \( \alpha \) and \( \tau \), the temperatures assumed by the magnetocaloric material during the cycle can be expressed as:

\[ T_1 = aT_h = \frac{\alpha T_i}{\tau} \]  
\[ T_2 = \frac{aT_i(\beta + \eta_c - 1)}{\eta_c \tau} \]  
\[ T_4 = \frac{a\beta^2 T_i}{\alpha + (a\beta^2 - 1) \tau} \]  
\[ T_5 = \frac{a\beta T_i(\eta_e + \beta - \beta \eta_c)}{\alpha + (a\beta^2 - 1) \tau} \]

Substituting these last four equations in Equations (49) and (50), the following is obtained:

\[ Q_h = CH_2^2 \left\{ \frac{\tau \beta^2 [a(\beta + \eta_c - 1) - \eta_c]}{\alpha T_i (\beta + \eta_c - 1)} \right\} \]  
\[ Q_l = CH_2^2 \left[ \frac{\alpha + (a\beta^2 - 1) \tau - a\beta (\eta_e - \beta \eta_c + \beta)}{a\beta T_i (\eta_e - \beta \eta_c + \beta)} \right] \]

with the equations just obtained, we can derive the relations of the work and the COP of the cycle:

\[ W = Q_h - Q_l = CH_2^2 \left\{ \frac{\tau \beta^2 [a(\beta + \eta_c - 1) - \eta_c]}{\alpha T_i (\beta + \eta_c - 1)} - \frac{\alpha + (a\beta^2 - 1) \tau - a\beta (\eta_e - \beta \eta_c + \beta)}{a\beta T_i (\eta_e - \beta \eta_c + \beta)} \right\} \]
\[
\text{COP} = \frac{Q_l}{Q_h - Q_l} = \left\{\frac{\tau \beta}{(\beta + \eta_c - 1) \left[ \alpha + (\alpha \beta - 1) \right] (\eta_c - \beta \eta_c + \beta)} - 1 \right\}^{-1}
\] (63)

Even considering this type of cycle, the conditions \(\text{COP} > 0\) and \(Q_l > 0\) must be met for normal refrigerator operation to be ensured. These conditions are met only if the ratio of magnetic fields is greater than a minimum value, that is, with \(\beta > \beta_{\text{min}}\), where

\[
\beta_{\text{min}} = \left( \frac{H_1}{H_2} \right)_{\text{min}} = \frac{\eta_c + \sqrt{\eta_e^2 + 4 \left( \frac{1}{\alpha} - 1 \right) (\tau + \eta_e - 1)}}{2 (\tau + \eta_e - 1)}
\] (64)

Equation (64) defines that \(\beta_{\text{min}}\) is a decreasing monotone function with respect to \(\alpha\), \(\tau\), and \(\eta_e\).

The minimum ratio between the magnetic fields \(\beta_{\text{min}}\) is an important parameter to determine the operability limits of the cycle. When the cycle operates with \(\beta > \beta_{\text{min}}\), the COP is not a monotone function of \(\beta\), while the thermal load removed by the cold source \(Q_l\) is an increasing monotonous function of \(\beta\); see Figures 4–7.

Figure 4. Correlation of the Coefficient of Performance (COP) with the ratio of the magnetic fields \(\beta\) for various values of \(\alpha\), by fixing \(\tau = 0.7\) and \(\eta_e = \eta_c = 0.98\).

In Figures 4 and 5, the COP reaches the maximum peak for a given value of the ratio of magnetic fields that we will call \(\beta_m\). By simultaneously observing the trend of the COP (Figures 4 and 5) and the trend of the dimensionless thermal load removed \(Q_l = Q_l / (CH_2^2)\) (Figures 6 and 7), it can be seen that when \(\beta < \beta_m\), the COP decreases very quickly as the load removed from the cold source decreases. Therefore, in the range \(\beta_{\text{min}} < \beta < \beta_m\), the refrigeration unit works but not optimally (this is the area of the graph where the COP curve is very steep). Instead, when \(\beta > \beta_m\), the COP increases as the load removed by the cold source decreases and the other way around.
Figure 5. Correlation of the COP with the ratio of the magnetic fields $\beta$ for various values of $\eta_e = \eta_c$, by fixing $\tau = 0.7$ and $\alpha = 0.8$.

Figure 6. Correlation of the dimensionless refrigeration load $Q_l$ with the ratio between the magnetic fields $\beta$ for various values of $\eta_e = \eta_c$, by fixing $\tau = 0.7$, $\alpha = 0.8$ and $T_l = 200$ K.

Furthermore, it can be noted that when operating in the range $\beta \geq \beta_m$, as the regeneration factor $\alpha$ increases, the load absorbed by the cold source increases, while the COP decreases. Therefore, the more it regenerates, the greater the load removed, but the smaller the COP. This makes regeneration more convenient and effective because absorbing more heat from the cold source makes it possible to use a lower ratio between magnetic fields (therefore, the system would be more economical from an energy point of view) and allows it to operate with a temperature difference between the highest sources.

Finally, as regards the isentropic performance $\eta_e = \eta_c$, as the degree of irreversibility of the adiabatic processes increases, there is a natural reduction in both the COP and the load removed by the cold source.
Figure 7. Correlation of the dimensionless refrigeration load $Q_l$ with the ratio between the magnetic fields $\beta$ for various values of $\alpha$, by fixing $\tau = 0.7$, $\eta_e = \eta_c = 0.98$ and $T_i = 200$ K.

In order to have a performing machine, COP and $Q_l$ should have simultaneously very high values. This is the reason why the optimal working range of the relationship between the two magnetic fields is $\beta \geq \beta_m$. The $\beta_m$ is a very important parameter in the Brayton magnetic refrigeration cycle, because it determines the minimum admissible value for optimal operation of the machine. In conclusion, $\beta \geq \beta_m$ is a valid optimization criterion for a magnetic Brayton cycle.

3. Results

3.1. Ericsson Cycle Experimental Data

Results of the hypothetical mathematical models and those derived from a real experiment [17] were compared to deduce which mathematical model best describes the Ericsson cycle. An evaluation was made of the performance of the Ericsson cycle based on the experimental data of the entropy change in the iso-field transformations with the change in temperature. Table 1 shows experimental data and results of gadolinium and the alloy La (Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_1$.

Table 1. Experimental data and results of both magnetocaloric materials.

| Mass | $Q_{c,\text{max}}$ at $T_{\text{cold}} = 294.4$ K | $\Delta S_m$ at $T_{\text{cold}} = 294.4$ K | $T_c$ | $\Delta H$ | $Q_{c,\text{max}}$ at $T_{\text{cold}} = 277.3$ K | $\Delta S_m$ at $T_{\text{cold}} = 277.3$ K | $T_c$ | $\Delta H$ |
|------|----------------------------------|----------------------------------|------|---------|----------------------------------|----------------------------------|------|---------|
| Gadolinium (Gd) | 1 kg | 1257 J/kg | 4.27551 J/kg | 294 K | 2 T | 1 kg | 5830 J/kg | 21.02416 J/kg | 277.3 K | 2 T |
| La (Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_1$ | |

$T_0$ indicates the temperature $T_{\text{cold}}$ at which there is the greatest absorption of heat $Q_c$; in other words, $T_0$ is the Curie temperature ($T_c$). Considering the imperfect regeneration, the $\Delta Q$ is measured and, therefore, also the net heat removed by the cold load (net cooling quantity) $Q_L$. In [17], the relation of the $T_{\text{cold}}$ and the $T_{\text{hot}}$ for the gadolinium is presented.

When $T_{\text{hot}} = T_0 - 3K = 291$ K (case $T_0 > T_{\text{hot}} > T_{\text{cold}}$), $Q_L$ coincides with $Q_c$ since $C_{H_1}(H_0, T) \geq C_{H_1}(H_1, T)$ and, therefore, $\Delta Q$ represents the compensated heat absorbed by the hot source. All this allows the cooling power to remain unchanged.

When, on the other hand, $T_{\text{hot}} > T_{\text{cold}} > T_0$, the heat $\Delta Q$ must be transferred to the cold source by decreasing the net cooling quantity $Q_L$. After the $T_c$, in addition to the fact
that $Q_L$ is always less than $Q_c$, the slope of the $Q_L$ curve, equal to $T_{hot}$ and increasing $T_{cold}$, abruptly decreases. On the other hand, slightly before the $T_c$, when $T_{hot} > T_0 > T_{cold}$, only a small part of the heat exchanged for imperfect regeneration is transferred to the cold source so that, as the $T_{cold}$ increases, $Q_L$ increases much more than the part in which $T_{hot} > T_{cold} > T_0$.

Moreover, it can be noted that, with $T_{cold}$ equal and $T_{hot}$ increase, $Q_L$ decreases. This is because the higher the temperature range, the more difficult it is to absorb heat from the cold source and transfer it to the hot source.

Finally, the COP values were calculated as the $T_{cold}$ varies for different $T_{hot}$, the trend of which is reported in Figure 8.

![Figure 8. COP trends of an Ericsson cycle with gadolinium [17].](image)

The COP increases monotonously with the increase in the $T_{cold}$ while keeping the $T_{hot}$ fixed. This is because the range between the two temperatures narrows increasingly, increasing the efficiency of the system.

### 3.2. Ericsson Cycle Results through Curie-Weiss Theory

A comparison was made between the COPs calculated using the Curie-Weiss law and that obtained experimentally. Using Equation (20), the graph of Figure 9 shows the trend of the COP as the $T_{cold}$ changes, keeping the $T_{hot}$ fixed and considering gadolinium as a magnetocaloric material. The $\Gamma$ value was deduced. As reported in Equation (15), it is necessary to know many terms, including the quantum numbers $J_O$, $N_S$ and $J_A$ of the material. Through Equation (9), the Landé factor $g$ was obtained. Knowing the mass $m$, in kg, of gadolinium and its molar mass $M_m$, it is possible to calculate the number of moles $n$ as:

$$n = \frac{m}{M_m} \quad (65)$$

The Avogadro number $N_A$ is equal to $6.022 \cdot 10^{23}$; the number $N_g$ of atoms in 1 kg of gadolinium is:

$$N_g = n \cdot N_A \quad (66)$$

Knowing Bohr magneton $\mu_B$ and Boltzmann constant $k$, the Curie constant $C$ is:

$$C = \frac{N_g g^2 N_S (N_S + 1) \mu_B^2}{3k} \quad (67)$$
The same value used in the experimental case is assumed as the $T_C$. It is possible to calculate the value of $\Gamma$ with Equation (15). Table 2 shows data for the COP calculation considering gadolinium as magnetocaloric material.

![COP trend of the Ericsson cycle according to the Curie-Weiss law](Image)

**Figure 9.** Trend of the COP of the Ericsson cycle according to the Curie-Weiss law as the variation of $T_{\text{cold}}$ for two fixed $T_{\text{hot}}$ values.

**Table 2.** Data used for the COP calculation considering gadolinium as magnetocaloric material.

| Property                  | Value                  |
|---------------------------|------------------------|
| External electronic config | $4f^7 5d^1 6s^2$      |
| Quantum number of spins $N_S$ | 3.5                   |
| Quantum orbital number $J_Q$ | 0                     |
| Quantum number of the total angular momentum $J_A$ | 3.5                   |
| Landé factor $g$           | 2                      |
| Mass $m$                  | 1                      |
| Molar mass $M$            | 157.25                 |
| Number of moles $n$       | 6.36                   |
| Avogadro number $N_A$     | $6.02 \times 10^{23}$  |
| Number of atoms in 1kg of gadolinium $N_g$ | $3.83 \times 10^{24}$ |
| Bohr magneton $\mu_B$     | $9.27 \times 10^{-24}$ |
| Boltzmann constant $k$    | $1.38 \times 10^{-23}$ |
| Curie constant $C$        | 501.23                 |
| Curie Temperature $T_C$   | 294.4                  |
| $\Gamma$                 | 294.40                 |

COP of Figure 9 never exceeds unity, differing from what is deduced from the experimental results, which showed much higher values. However, the COP obtained through the Curie-Weiss law, not considering the losses due to an imperfect regeneration, should always show higher values.

1. When $T_{\text{cold}} > T_C$, the curve decreases for any $T_{\text{hot}}$, while in the experimental graph (Figure 8), even after 294.4 K, the curves with $T_{\text{hot}} = T_C + 6$ K and $T_{\text{hot}} = T_C + 9$ K do not change curvature.
2. The orange curve, calculated with a larger $T_{\text{hot}}$, should not be higher than the blue one, calculated with a smaller $T_{\text{hot}}$, this is because the COP decreases when operating with a higher temperature range.
In conclusion, the results derived from the mathematical model based on the Curie-Weiss law for a magnetic Ericsson cycle do not seem to be in agreement with the experimental results.

3.3. Ericsson Cycle Results through Langevin’s Theory

To verify the correctness of this mathematical model, the relations obtained were used to calculate the values of the magnetic entropy change \( \Delta s_m \) at a constant temperature of the gadolinium when it is subjected to a magnetic field variation equal to 5 T. These values, then, were compared with the experimental correspondents (Figure 10). Figure 11 shows the iso-field curves of entropy trend as the temperature varies. These represent the curves on which the thermodynamic cycle of a refrigeration machine whose operation is based on the magnetocaloric effect is plotted.

**Figure 10.** Comparison between theoretical and experimental values of the isothermal variation of magnetic entropy as the temperature varies considering a magnetic field variation of 5T.

From Figure 10, it is evident that the curve deduced from the mathematical model is close to the experimental one, showing approximately the same value of the maximum variation of magnetic entropy at the Curie temperature, making the theoretical approach suitable for describing the physics of the problem.

The theoretical data are not perfectly consistent with the experimental data; there is a maximum deviation of about 30%. The main causes of this deviation arise from the fact that Langevin’s theory of statistical mechanics can only approximate the microscopic characteristics of magnetic materials in a macroscopic setting; in addition, the physical properties adopted for the mathematical analysis are theoretical values of pure gadolinium, while the physical properties of the real magnetic materials may be slightly different. However, considering globally the results of \( \Delta s_m \) at temperatures close to ambient, it can be concluded that Langevin’s theory of statistical mechanics can estimate magnetocaloric effects with some precision.
Figure 11. Theoretical values of 0T and 5T iso-field curves representing the entropy trend as a function of temperature.

It is possible to use the equations of this model in order to derive the expression of the COP for the Ericsson cycle with imperfect regeneration. Therefore, considering the Ericsson cycle diagram with regeneration on the s-T diagram of \[19\], to derive the theoretical expressions, the following hypotheses can be carried out:

1. \(Q_{hr}, Q_{lr}, Q_{bcr}\), and \(Q_{dna}\) are all positive;
2. The Ericsson magnetic cycle is stable;
3. The temporal characteristics of demagnetization, magnetization, the magnetocaloric effect, and heat transfer are neglected;
4. Gadolinium is assumed to be an ideal magnetic material;
5. Other irreversibility factors are neglected, except for imperfect regeneration;
6. There is no difference in temperature, during the heat transfer, between the magnetic material and the sources.

The entropy of a magnetic system is given by the sum of a contribution of magnetic entropy, one of reticular entropy and one of entropy linked to free electrons.

\[
(s(H, T) = s_m(H, T) + s_r(T) + s_e(T))
\] (68)

The reticular entropy, a function of temperature alone, cannot be neglected at temperatures close to the ambient one, while the entropy linked to free electronics is small enough to be neglected.

As for the specific heat of the magnetic system, it will be similarly:

\[
c = c_m(H, T) + c_r(T) + c_e(T)
\] (69)

Here, the third term is also neglected. The analyses of the heat exchanged are:

1. For the process a–b, the thermal energy supply to the environment to be heated \((T_{hi} = T_{hot})\):

\[
Q_{h} = T_{h}(s_a - s_b) = T_{h}[s_m(H_0, T_{h}) - s_m(H_1, T_{h})]
\] (70)
2. For the process $c \rightarrow d$, the absorption of thermal energy from the environment to be cooled ($T_l = T_{cold}$):

$$Q_l = T_l(s_d - s_c) = T_l[s_m(H_0, T_l) - s_m(H_1, T_l)]$$  \hfill (71)

3. For the process $b \rightarrow c$, the thermal energy supply to the regenerator:

$$Q_{bc} = \int_{T_i}^{T_h} c_H(H_1, T) \, dT = \int_{T_i}^{T_h} [c_m(H_1, T) + c_r(T)] \, dT$$  \hfill (72)

4. For the process $d \rightarrow a$, the absorption of thermal energy from the regenerator:

$$Q_{da} = \int_{T_i}^{T_h} c_H(H_0, T) \, dT = \int_{T_i}^{T_h} [c_m(H_0, T) + c_r(T)] \, dT$$  \hfill (73)

The difference between the heat transferred to the regenerator and that absorbed by is:

$$\Delta Q = Q_{bc} - Q_{da} = \int_{T_i}^{T_h} [c_m(H_1, T) - c_m(H_0, T)] \, dT$$  \hfill (74)

As already mentioned in Section 2.2, when $\Delta Q > 0$, the net heat removed from the cold source results in $Q_l = Q_l - \Delta Q$, while when $\Delta Q < 0$, $Q_l = Q_i$. The overall work of the system is $W = Q_h - Q_l + \Delta Q$.

Therefore, the COP relationship is:

$$\Delta Q > 0 \Rightarrow COP = \frac{Q_l}{W} = \frac{Q_l - \Delta Q}{Q_h - Q_l + \Delta Q}$$  \hfill (75)

$$\Delta Q < 0 \Rightarrow COP = \frac{Q_l}{W} = \frac{Q_l}{Q_h - Q_l + \Delta Q}$$  \hfill (76)

The net cooling quantity could be zero or even become negative under the influence of imperfect regeneration; in this case, the machine would not work. Therefore, the conditions $\text{COP} > 0$ and $Q_l > 0$ must be met to ensure the normal operation of the refrigeration unit operating with the Ericsson cycle.

Finally, the COP values calculated with Langevin’s theory of statistical mechanics were examined. Figure 12 shows the trend of the COP with the variation of $T_h$ for two temperatures $T_i$, Figure 13 the correlation of COP values with the variation of $T_h$ for two magnetic fields.

In Figure 12, it is observed that the closer the $T_h$ is to $T_i$, therefore, with $\Delta T$ resulting in zero, the higher the COP is. In the same way, when fixing $T_h$ and increasing $T_i$, we see that the COP increases more and more. In Figure 13, it is observed that the COP of the Ericsson cycle increases with the increase in magnetic fields; this is mainly due to the increase in the variation of magnetic entropy, which results in a larger magnetocaloric effect.

In Figure 14, the comparison between numerical and experimental COPs, as a function of $T_{hot}$ by varying the $T_{cold}$, are shown. With a lower $T_{cold}$, there is a better correspondence between numerical and experimental data. Numerical and experimental data confirm that very high COP values of more than 20 can be achieved. Therefore, for the COP, the results are also in line with the values obtained starting from the experimental data. However, the COP values obtained, with the same $T_i$, $T_h$, and $H$, are higher than those obtained experimentally since, in the hypotheses underlying the analytical calculation, some irreversibility was neglected.
Figure 12. Theoretical COP, calculated with Langevin’s theory of statistical mechanics, as the temperature of the hot source $T_h$ varies for two different temperatures of the cold source and with $H = 5 \, \text{T}$.

Figure 13. Theoretical COP, calculated with Langevin’s theory of statistical mechanics, as the temperature of the hot source $T_h$ varies for two different magnetic fields and with $T_l = 298 \, \text{K}$.
4. Conclusions

Heating and refrigeration systems have undergone significant development in recent decades; this is due to the growing demand for residential and non-residential air conditioning, as well as the growing need for food preservation. To date, these systems account for about 20–30% of household consumption.

The most widespread refrigeration technology is steam compression, a mature and established technology that uses fluorinated gases or hydrocarbons as refrigerants and noisy compressors as the source of motion. Magnetic refrigeration systems are a viable alternative to conventional systems, being innovative systems that use a solid as a refrigerant and a fluid as a regenerant. They guarantee high efficiency, no direct impact on global warming, use of non-harmful substances, and minimal noise from motion sources.

This study aimed to perform a critical analysis of the literature on this promising new technology, with the aim of making a first comparison between the numerical and mathematical models found in the literature.

The main aspect addressed in this study concerns the use of mathematical models needed to analyze the thermodynamic cycles that describe the operation of a thermomagnetic refrigeration unit.

The comparison of mathematical models showed that the model based on Langevin’s theory of statistical mechanics most closely represents the correct functionality of a refrigerator operating according to an Ericsson cycle. The theoretical data are not perfectly consistent with the experimental data; there is a maximum deviation of about 30%. Numerical and experimental data confirm that very high COP values of more than 20 can be achieved.

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**Nomenclature**

- $B_j(x)$: Brillouin function
- $c$: Specific heat capacity $\text{J/kgK}$
- $C$: Curie constant
- $C_H$: Heat capacity the constant magnetic field $\text{J/K}$
- $g$: Landé factor
- $H$: Magnetic field $\text{T}$
- $H_{\text{ext}}$: External magnetic field $\text{T}$
- $J_A$: Quantum number of the total angular momentum
- $J_O$: Quantum number of the orbital moment
- $L$: Work supplied to the system $\text{J}$
- $L(x)$: Langevin function
- $m$: Mass $\text{kg}$
- $M$: Magnetization intensity $\text{A/m}$
- $M_m$: Molar mass $\text{g/mol}$
- $n$: Number of moles $\text{mol}$
- $N_A$: Avogadro number
- $N_D$: Number of magnetic moments
- $N_G$: Number of atoms in 1kg of gadolinium $\text{atoms/kg}$
- $N_m$: Number of atoms or molecules
- $N_s$: Quantum number of spins
- $Q_{\text{cold}}, Q_h$: Cold source heat $\text{J}$
- $Q_H$: Hot source heat $\text{J}$
- $Q_{\text{H}}$: Net heating quantity $\text{J/K}$
- $Q_L$: Net cooling quantity $\text{J/K}$
- $Q_r$: Insufficient regenerative heat $\text{J/K}$
- $s$: Specific entropy $\text{J/kgK}$
- $S$: Entropy $\text{J/K}$
- $S_e$: Entropy of free electrons of the material $\text{J/K}$
- $S_m$: Magnetic entropy $\text{J/K}$
- $S_r$: Reticular entropy $\text{J/K}$
- $S_{\text{tot}}$: Total entropy $\text{J/K}$
- $T$: Temperature of material $\text{K}$
- $T_0$: Working temperature $\text{K}$
- $T_C$: Curie temperature $\text{K}$
- $T_{\text{h}}, T_{\text{hot}}, T_2$: Hot source temperature $\text{K}$
- $T_{\text{c}}, T_{\text{cold}}$: Cold source temperature $\text{K}$
- $W$: Overall work of the system $\text{J/K}$

**Greek Letters**

- $\alpha$: Regenerative degree
- $\Delta T_{\text{ad}}$: Adiabatic temperature change $\text{K}$
- $\Delta S_m$: Isothermal entropy change $\text{J/K}$
- $\beta$: Ratio of two magnetic fields $\text{J/K}$
- $k$: Boltzmann constant $\text{J/K}$
- $\chi$: Magnetic susceptibility
- $\lambda$: Molecular magnetic field
- $\mu_B$: Bohr magneton $\text{J/K}$
- $\Gamma$: Factor
- $\mu$: Spin magnetic moment $\text{J/T}$
- $\eta_e$: Adiabatic irreversibility
- $\tau$: Ratio of temperatures of two heat reservoirs
Abbreviations

AMR  Active Magnetic Regenerator
COP  Coefficient of Performance
GWP  Global Warming Potential
MCE  Magneto-Caloric Effect
ODP  Ozone Destruction Potential

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