Revisiting the Second Law of Thermodynamics: Challenges and Misconceptions

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Article Info

Article history:

Received May 22, 2024
Revised July 15, 2024
Accepted August 10, 2024

Keywords:

Carnot Cycle,
Heat Engine,
Entropy,
Energy Conservation.

ABSTRACT

Since the 1850s, numerous thermodynamic concepts have been proposed. Nicolas Carnot laid the foundation of the second law of thermodynamics in 1824 with insightful work on reversible cycles, well before James Joule's 1843 discovery of the energy conservation law. In 1941, Leonard Bridgman remarked that the second thermodynamic law had been formulated nearly as often as discussed, highlighting its ongoing complexity and intrigue. Despite extensive discussions and formulations, understanding the second law remains challenging, prompting continuous efforts to clarify it, as explored in this paper. The second law of thermodynamics, which addresses irreversible transformations and the direction of natural processes, encompasses a wide range of phenomena across the universe, along with various challenges and misconceptions. The current paper revisits and modifies Carnot's original proposals for reversible heat engines. It emphasizes the difficulty of achieving more efficient reversible processes within the context of irreversible processes, which adds complexity to the second law and its potential violations. However, the concept remains that the entropy of every energy system is always increasing, and entropy cannot be removed, only transferred or altered.

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1. Introduction

Rudolf Clausius formulated the second law of thermodynamics in 1850, which was further refined by Lord Kelvin. It posits that the total entropy of an isolated system cannot diminish with time, indicating that natural processes generally evolve towards a state of maximal chaos (Oliveira, 2024). The second law of thermodynamics is crucial for thermal power plants, gas turbines, and many applications since it dictates the efficiency and viability of energy conversion processes (Ntantis, 2009; Ntantis & Xezonakis, 2024). In thermal power plants and gas turbines, regulations stipulate that not all thermal energy may be converted into useful activity, highlighting the need of waste heat management and efficiency enhancement (Ntantis & Botsaris, 2015; Xezonakis & Ntantis, 2023). Engineers utilise this principle to develop systems that optimise energy production while reducing losses. The second rule encompasses refrigeration, air conditioning, and chemical engineering operations in addition to power plants and gas turbines. It regulates the design of systems for heat transfer, energy storage, material synthesis, and even cosmic phenomena to guarantee compliance with thermodynamic constraints (Mulki & Ntantis, 2024). Understanding and implementing the second rule is crucial for boosting the sustainability and performance of energy systems across a range of industries. Despite its fundamental significance in physics, the law has created misunderstanding and disagreement due to the abstract character of entropy, the statistical base of the law that allows for a rare reduction in entropy, and its implication of a unidirectional flow of time, sometimes known as time's arrow (Carnot, 1824). These aspects lead to various interpretations and philosophical questions about the nature of time and the behavior of physical systems at macroscopic and microscopic levels. This law, which deals with the direction of heat transfer and the efficiency of heat engines, has prompted many discussions and clarifications over the years. In response to ongoing confusion, the *British Association for the Advancement of Science* established a special committee around 1900 to resolve any ambiguities. Despite these efforts, many people still find the second law challenging to understand fully (Orange, 1972). Classical thermodynamics uses a phenomenological approach, focusing on observable quantities and how they change. Early scientists like Sadi Carnot, Lord Kelvin, and Max Planck established the foundational principles of thermodynamics, which laid the groundwork for understanding energy transfer and transformation (Guerra, 2021). Modern physicists continue to acknowledge the significance of thermodynamics. Albert Einstein famously remarked that thermodynamics is the only physical theory of universal content that will never be overthrown. Einstein saw it as a fundamental and unchangeable part of physical science (Reyes-Ayala et al., 2023). From his side, James Maxwell praised thermodynamics for its secure foundations, precise definitions, and clear boundaries. John von Neumann, a mathematician and physicist, humorously pointed out that using the term *entropy* in discussions often gives one an advantage because it is a concept many people find difficult to grasp (Gonzalez-Ayala & Angulo-Brown, 2013; Philippi, 2024). Entropy, a measure of disorder or randomness in a system, is a critical concept in the second law of thermodynamics and often serves as a point of confusion and debate. Overall, while the second law of thermodynamics is a cornerstone of physics, it requires careful explanation and discussion to be fully understood. An introduction to interpreting the Second Thermodynamic law concept is designated below.

2. Reasoning of the Second Thermodynamic Law

In certain situations, processes can be more efficient when they occur without energy dissipation, maintaining the non-equilibrium state of the system (Feidt & Costea, 2024). These processes can be reversed, meaning entropy is conserved and not generated. Reversible processes are the most efficient because they do not lose energy and can return to their original state without any energy loss. However, this argument is trivial and or challenging. In contrast, irreversible processes involve random energy dissipation, converting potential work into heat. The second law of thermodynamics describes how natural processes spontaneously move from non-equilibrium to equilibrium. This law explains that all natural processes tend to spread out their energy. Thus, the systems move towards a state of a more significant disorder. Reversible processes maximize the work potential between these states, while irreversible processes increase entropy and dissipate energy (Kostic, 2011). Anyway, the second law of Thermodynamics presents several challenges and issues to be highlighted in the succeeding section.

3. Challenges and Issues of the Second Thermodynamic Law

The second law of thermodynamics has undergone significant review over recent decades, with numerous research groups worldwide investigating its principles significantly. Several foundational statements have emerged from these investigations (Cápek & Sheehan, 2005). Rudolf Clausius, for instance, stated that heat can pass from a cold to a warmer body only if some other change coincides. Lord Kelvin and Max Planck further asserted that creating a device that operates cyclically and solely absorbs energy from a single thermal reservoir to do equivalent work is impossible, aligning with the broader understanding that the universe's entropy always increases in all natural processes (Xue et al., 2024). It is widely accepted that any scientist who comprehends the second law would not challenge it based on incomplete facts. However, even highly accomplished scientists sometimes struggle to grasp its essence fully. A key aspect of the second law is that the entropy of a closed system or the universe constantly increases. This increase is necessary but not sufficient to describe the second law, as entropy cannot be destroyed locally at any point. This is similar to water flowing uphill in one area while compensating with a greater downhill flow elsewhere (Jaffe, 2024). Local entropy reduction through outflow should not be confused with the destruction of entropy. John von Neumann humorously noted that whoever uses the term entropy in a discussion always wins since no one knows what entropy is. Thus, in a debate, one always has the advantage. This highlights the complexity and sometimes misunderstood nature of entropy. Entropy cannot be decreased globally, and it cannot be destroyed at any scale. This ties into the concept of the thermodynamic arrow of time, representing the direction of time based on thermodynamic irreversibility and entropy's overall increase. Meanwhile, theoretically, the arrow of time might reverse in an ideal, reversible process. Such a case would not violate the second law since entropy would be conserved and not destroyed. Micro-fluctuations at the thermal level, which might seem to violate the second law on a small scale, actually contribute to maintaining macro-equilibrium and maximizing entropy without destroying it. This principle extends to quantum systems, where recent years have seen new implementations that challenge classical thermodynamic views (Li, 2022). For example, splitting a light beam into two via a half-silvered mirror increases the entropy of the system compared to a single beam, illustrating the irreversibility of the process. Furthermore, the adiabatic piston model provided by

Bruno Crosignani and Paolo Di Porto reveals how heat is taken from its surroundings on a mesoscopic scale, which can empirically contradict typical second law predictions. Several thermodynamic gas cycles have also empirically tested the concept by studying molecule scattering on short-distance scales, frequently without reaching extreme thermodynamic regimes (Raman & Ramanathan, 1923). To summarise, while the second law of thermodynamics has been rigorously studied in many scientific domains, it remains a cornerstone in physics. The next part will focus on the key components of Carnot's theory as applied to heat engines.

4. Expanding of the Second Thermodynamic Law Across Science and Technology

While important, the second rule of thermodynamics is not without difficulty, especially when considering the collaboration of thermodynamics and other technical areas. In cosmology, the rule has extensive repercussions for the universe's eventual fate. The theory of heat death postulates that the world will finally approach a condition of maximum entropy, when all energy is consistently dispersed and no work can be achieved, important to a thermodynamic balance. This idea is based on the irreparable nature of entropy growth. This idea has been considerably authorized by apparent evidence, such as the cosmic warm background radiation, which chronicles the universe's thermal antiquity and its development towards increasing entropy states (Allday, 2016). Furthermore, the second law is vital for inventing new resources and energy technologies. Understanding and management entropy is serious for cultivating efficiency in the design of thermoelectric materials, which change temperature alterations into electrical energy. These materials offer a temperature incline across a electrode or semiconductor device, empowering heat to flow from hot to cold locations and generate an electric current. However, the efficiency of this conversion is automatically measured by the second law, as some energy is frequently squandered as waste heat, cumulative the system's overall entropy (Rowe, 2018). In biological systems, the second law propositions a framework for acquisitive the energetics of life processes. Living species continue their entropy levels low in relation to their environments by frequently exchanging energy and material with the environment. This exchange, controlled by the second rule, energies the cultured biological functions vital for life, such as cellular exhalation and photosynthesis, both of which produce an overall increase in the universe's entropy (Prigogine & Hiebert, 1982). Applying the second rule to biological systems provided rise to the notion of entropy generation, a measure of the irreversibility of biochemical processes that has become a hot focus in biophysics and systems biology. The second law's significance extended to scientific philosophy, where it has been considered a metaphor for time's reversibility and progress. Arthur Eddington professionally showed this theory by creating the expression "arrow of time" to define the one-way orientation of time humans feel as a result of entropy's a constant rise. Eddington's arrows of time emerged as an essential issue in contentions on the nature of time and the universe's chronological evolution, integrating thermodynamics to basic questions in physics and philosophy (Eddington, 1968). In recent times, research into quantum thermodynamics has produced interesting difficulties solving the second rule on the quantum scale. Researchers investigated at how quantum unity and entanglement can impact the generation of entropy and dissipating energy in quantum systems. These tests indicate that, while quantum influences might produce alterations from classical thermodynamic behaviour, the second rule remains true when analysing the overall entropy of all involved systems, including the surrounds (Goold et al., 2016). This discovery has enormous implications for the development of quantum technology, such as quantum computers, in which regulating energy and entropy at the quantum level is critical for protecting coherence and preventing decoherence (Nielsen & Chuang, 2010). As previously stated, the second rule of thermodynamics maintains one of science's fundamental and frequently accessible ideas, contacting phenomena ranging from the miniscule size of quantum elements to the macroscale of galaxies. Its significance exceeds beyond sciences, from physics and engineering to biology and philosophy, illustrating its value as a basis for our knowledge of the natural world. As scientific research continues, the second rule is going to be the subject of increased investigation and change as scholars seek fresh perspectives into the fundamental nature of entropy and its role in the cosmos.

5. Carnot's Theory

The second law of thermodynamics, conceived by Rudolf Clausius and other pioneers, consists of two parts. The first validated part has the same efficiency in all engine operations, with the main consequence being that the ratio $\frac{dQ}{T}$ of the infinitesimal heat Q and the temperature T provides the entropy definition S. The second part comprises the law of increase in entropy (Kostic, 2004). Before thermodynamics emerged, the theory of heat included laws related to the behavior of bodies during the adiabatic and thermal expansion of gases and calculations of the specific heat of substances. The study and production of mechanical work from heat began in the early 18th century. Sadi Carnot, a key figure in thermodynamics, argued that the maximum work produced by a heat engine is independent of the working substance. Carnot stated that the motive power of heat is independent of the agents used to realize it, meaning that the ability of heat to do work does not depend on the specific substances or mechanisms employed to harness this work (Kostic, 2004). Instead, the quantity of motive power by means of lost work is determined solely by the temperatures of the bodies involved. Specifically, the temperature difference between the two bodies, through which the heat transfer occurs, ultimately governs the amount of work to be extracted. Essentially, Carnot's principle highlights that the temperature differential fixes the efficiency of converting heat into work and is not influenced by the materials or methods utilized (Kostic, 2018). After extensive investigations, Carnot proved that the maximum performance of a heat engine depends only on the temperature difference between the heat source and the cooling medium, identically to how a water wheel's efficiency depends on the height difference of a waterfall. The heat engine and the water wheel exemplify the principle of converting natural energy into mechanical work (Sheehan, 2008). A heat engine transforms thermal energy from a heat source into mechanical energy using a working fluid, such as steam or gas, which expands and drives pistons or turbines. Similarly, a water wheel converts the potential energy of water, usually from a higher elevation, into mechanical energy as the flowing water exerts force on the blades or buckets of the wheel, causing it to rotate. Both systems are designed to maximize efficiency: the heat engine's efficiency is influenced by the temperature difference between its heat source and sink, while the water wheel's efficiency depends on the height of the waterfall (head) and the flow rate. Despite their different energy sources and mechanisms, the heat engine and the water wheel harness natural energy to produce useful mechanical work. This concept is illustrated in Figure 1, demonstrating that the efficiency of heat engines is determined by temperature differences rather than the specific medium used.

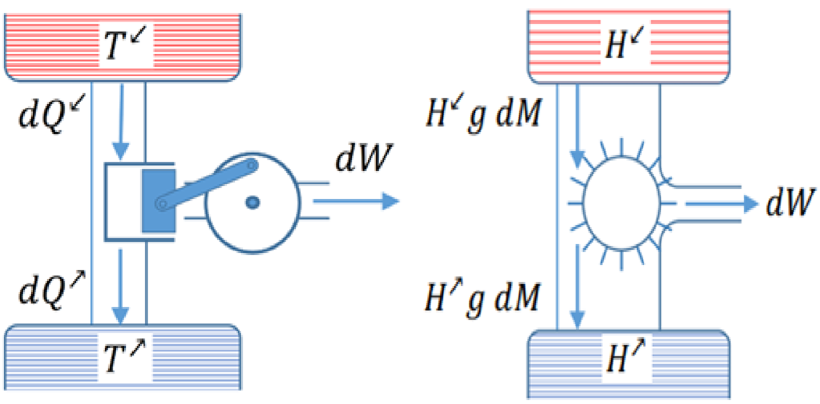

Figure 1. Similarity of the heat engine and the water wheel (Prigogine & Hiebert, 1982).

Therefore, the analogy between the heat engine and the water wheel model depicts the equivalency of the heat added $dQ,$ an energy exchange $dE,$ expressed by the potential energy of the quantity dM of the water entering or exerting at a height *H*. The potential energy is given by:

$$dE = HgdM \tag{1}$$

Whereas g is the gravitational acceleration in $\frac{m}{s^2}$. Hence, the model's performance *n* is provided by:

$$n = \frac{dW}{dE} \tag{2}$$

Carnot (Carnot, 1824), in 1824, introduced the fundamental reversibility concept in thermodynamics, which defines the maximum possible efficiency of a heat engine operating between two thermal reservoirs (Guerra, 2021). It represents an idealized thermodynamic cycle that serves as a benchmark for the performance of real engines. It points out four reversible processes: two isothermal processes, where the working fluid absorbs and rejects heat at constant temperatures, and two adiabatic processes, where the fluid undergoes expansion and compression without heat exchange. The thermal and mechanical fluctuations of a reversible heat transfer on a pressure-volume (P-V) diagram are illustrated in Figure 2 for a performance cycle that can be described as follows:

- Process 1-2: Isothermal heating and expansion work W_H at constant high-temperature T_H.
- Process 2-3: Adiabatic expansion works W_E towards a low-temperature T_L.
- Process 3-4: Isothermal contraction work W_L and cooling at low-temperature T_L.
- Process 4-1: Adiabatic compression work W_C towards a high-temperature $T_{H,}$ including the cycle's completion.

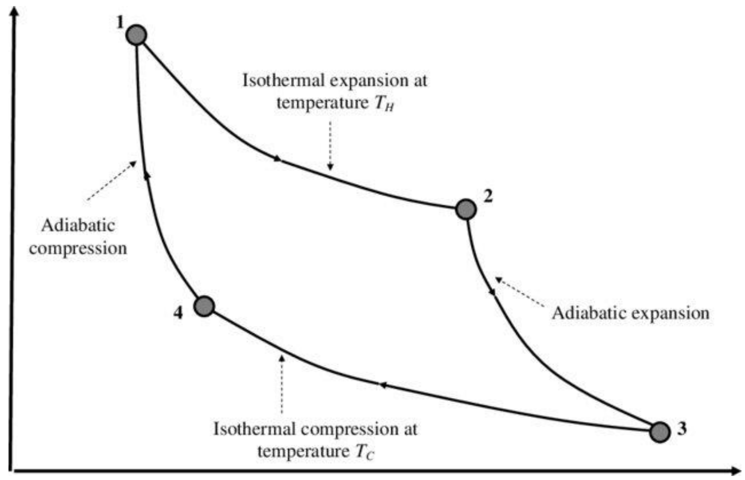

Figure 2. The P-V diagram of a heat engine's ideal Carnot cycle

The efficiency of the Carnot cycle represents the highest possible efficiency for a heat engine operating between two thermal reservoirs. Efficiency is defined by the ratio of the engine's work output to the heat input, and it depends solely on the temperatures of the hot and cold reservoirs (Carnot, 1824). Specifically, the Carnot efficiency is given by the formula:

$$n_c = \frac{W}{Q_H} = \frac{|W_H + W_E| - |W_L + W_C|}{Q_H} = \frac{|Q_H| - |Q_L|}{Q_H} = 1 - \frac{T_L}{T_H} \tag{3}$$

By demonstrating that no engine operating between two heat reservoirs can be more efficient than a Carnot engine, Carnot's work laid the groundwork for the second law of thermodynamics. It provided crucial insights into the limitations and potential of heat engine performance. The Carnot cycle remains a cornerstone in studying thermodynamics, offering a theoretical framework to evaluate and compare the efficiency of actual engines and refrigeration systems. Therefore, these processes are considered reversible. Figure 3 demonstrates this by showing the heat engine cycle and its reverse process, such as refrigeration or heat pump, operating along the same path. In both cases, the quantities of heat and work are equivalent but flow in opposite directions. This illustrates that the same energy transfers and work outputs occur for a reversible process, whether the cycle is running forward or backward.

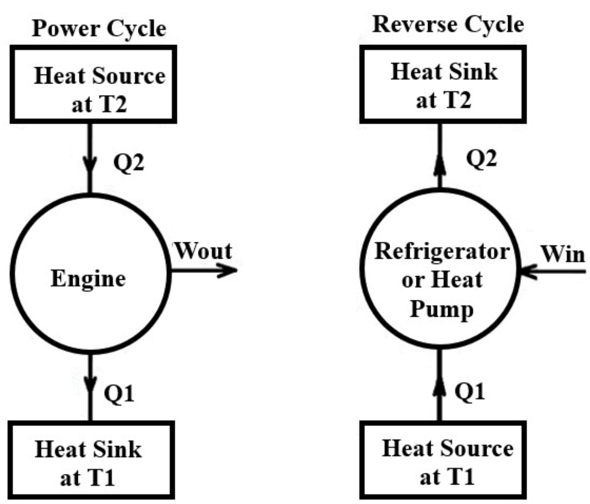

Figure 3. Power cycle and reverse cycle of the Carnot cycle (Goold et al., 2016)

The respective motive heat power is independent of the agents employed to realize it. Its quantity is determined solely by the temperatures of the bodies involved in the process. Ultimately, the transfer of caloric is defined in mathematical terms as:

$$W_{motive} = W_{c(Carnot)} = Q_H\, f_C(t_H, t_L);\;\; n_c = \frac{W_{motive}}{Q_H}\,|_{\text{Max}|Rev.} = f_c\,(t_H, t_L) \tag{4}$$

Where n_c is Carnot efficiency of all the possible reversible cycles. The cycle converts heat Q_H from the high-temperature thermal reservoir at $T_{H,}$ extracting cycle work, $W_{C,}$ and passing heat to a low-temperature thermal reservoir at T_L (Tjiang & Sutanto, 2006). Consequently, the reversibility of a process is considered the most efficient, as illustrated in Figure 4.

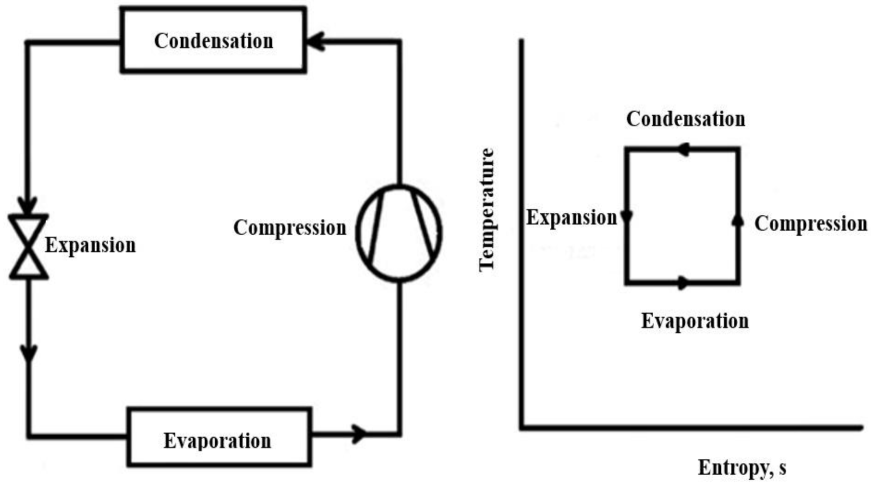

Figure 4. Reversibility process cycle (Nielsen & Chuang, 2010)

According to Carnot's principles, an ideal heat transfer is achieved through the compression or expansion of the working medium. Carnot concluded that all heat engines (HEs) have the same maximum efficiency when operating reversibly. If these processes are reversed, it theoretically leads to an impossible perpetual motion scenario. Consider two reversible heat engines (HE_{R1} and HE_{R2}) in this context. HE_{R1} is less efficient compared to HE_{R2}. If HE_{R1} is reversed and combined with HE_{R2}, it would theoretically produce a network from a single thermal reservoir ($W_{R2}\,|I - W_{R1}$) and transfer heat from a lower to a higher temperature ($QH - QH, R2/\ I_{rr}$). However, in practical terms, irreversible cycles cannot be reversed and have lower efficiency than reversible ones. They may even require external work input, resulting in a net negative work output. This occurs because the work initially converted into heat is dissipated and cannot be recovered, as illustrated by:

$$n_{Irr} < n_{rev} = f_c\ (T_H, T_L) \tag{5}$$

The impact between irreversible and reversible processes is designated in the following section.

6. Practical Implications

Reversible and irreversible processes profoundly impact various fields by shaping system efficiency and performance. Reversible processes, such as those modeled by the Carnot cycle, provide ideal benchmarks for maximum efficiency in heat engines, refrigeration, and energy systems (Hundy, 2016; Kostic, 2020; Lee & Park, 2017). The second law has one of the greatest basic applications in mechanical engineering: heat engine analysis. According to the second rule, no heat engine can function at 100% productivity as some energy is frequently rejected as waste heat, which increases entropy. This idea is illustrated in the Carnot cycle, which gives the maximum effectiveness for any heat engine that functions between two temperature reservoirs. Engineers utilise this theory to evaluate the performance of real-world engines, such as combustion engines and gas turbines, with the goal of decreasing inefficiencies along with improving thermal efficiency (Moran et al., 2010). The second law is equally crucial in refrigeration and air-conditioning systems. These devices capitalise on heat from a low-temperature environment and send it to a higher-temperature reservoir. Because of the growth in the entropy this process needs outside intervention. The coefficient of performance of the refrigeration technique is a crucial metric that engineers tweak to optimum energy efficiency. Understanding the second rule allows engineers to build more efficient refrigeration equipment by reducing entropy development during compression as well, development, and heat exchange (Stoecker & Jones, 1981).The second rule is highly crucial for comprehending thermodynamic cycles used in power plants, such as the Rankine method in steam and the Brayton cycle in gas turbines. These cycles make up many phases of heat addition, work the extraction process, and heat rejection, all of which follow the principles of the second law. Engineers utilise this information to control cycle components such as pressure, temperature, and flow rates, in order help improve energy conversion efficiency from energy to usable work while minimising entropy generation (Cengel, 2011). In materials science and mechanical engineering, the second law effects the design of thermoelectric materials for harvesting energy. These materials translate variations in temperature directly into electrical energy, making them possibly beneficial in systems that apply waste heat in industrial operations and automotive engines. Engineers attempt to produce materials with high thermoelectric efficiency, which involves a comprehensive knowledge of how to limit entropy creation while enhancing electrical power output (Snyder, 2008). The second rule is particularly crucial for building unique combustion technology (Mulki & Ntantis, 2024; Ntantis, 2009; Ntantis & Botsaris, 2015; Ntantis & Xezonakis, 2024; Xezonakis & Ntantis, 2023). In internal combustion engines, for example, incomplete combustion can result in unburned fuel, lowering efficiency and increasing the entropy of exhaust gases.

To solve this, engineers are developing technologies such as lean-burn combustion, exhaust gas recirculation, and turbocharging, which enhance combustion efficiency and minimise entropy generation, resulting in higher fuel economy and fewer emissions (Heywood, 1988). Furthermore, the second law offers suggestions for lowering entropy generation during heat transfer activities in the design of heat exchangers, which are crucial components in many mechanical systems. Engineers apply principles like limiting temperature differences between hot and cold fluids, refining flow patterns, and choosing appropriate materials to maximise heat exchanger performance. This resulted in more effective thermal management in a number of applications, including power generation and HVAC systems (Shah & Sekulic, 2003). Finally, the second law guides the design of energy conversion processes in renewable energy systems like solar thermal power plants. Concentrating solar power systems, for example, employ mirrors to focus sunlight onto a receiver, resulting in high temperatures that power a thermodynamic cycle, often a Rankine or Brayton cycle. Engineers tweak these systems to limit entropy production, which boosts total solar energy conversion to electricity efficiency (Behar et al., 2013; Haleem et al., 2024). These approaches help engineers develop systems that approach theoretical restrictions, culminating in fuel efficiency and energy consumption improvements. Conversely, irreversible processes have an impact on real-world systems, causing inefficiencies owing to friction and heat dissipation. This needs scientific methods to lower energy losses while increasing performance, such as boosting insulation in refrigeration systems or optimising industrial operations to increase production (De Hemptinne et al., 2022). Understanding these principles also informs sustainability initiatives, which strive to eliminate waste and environmental damage. In computing systems, reversible methods aid generate low-power technologies, but irreversible procedures emphasise energy usage and heat creating challenges (de Hemptinne et al., 2023). Ultimately, while reversible processes offer a theoretical ideal, managing the practical effects of irreversibility is crucial for advancing technology and addressing environmental challenges (Kostic, 2014). Concluding remarks are envisaged in the following section.

7. Conclusion

Since non-equilibrium cannot be created or increased without interacting with the surrounding environment, all reversible processes must be equally efficient. If they were not, creating non-equilibrium by reversing and coupling processes with different efficiencies would be possible. However, irreversible processes inevitably lose work potential as they are converted into thermal energy, increasing entropy and resulting in lower efficiency than reversible processes. The concept of reversibility provides a benchmark for efficiency. According to this principle, a heat engine operating reversibly is as efficient as or more efficient than the ideal Carnot engine. It matches heat transfer efficiency from a low to a high temperature or heat pumping from a single reservoir into a warmer system. Any deviation from this ideal efficiency would challenge the validity of the second law of thermodynamics, which remains a fundamental aspect of thermodynamic theory. Efforts to create hyper-reversible processes that could generate non-equilibrium or destroy entropy across any time or space scales are deemed impossible. Entropy transfer may be localized, but it cannot be destroyed. Therefore, entropy is always produced or increased, adhering to the second law's principle.

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