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Toward an Integrated Forcing, Exergetic and Constructal Analysis of Climate Change and Definition of the Possible Mitigation Measures

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ABSTRACT

The authors approach the scientific evidence for global warming from different points of view. It initially discussed the forcing methods adopted by IPCC and a large part of the scientific community to provide valuable tools for understanding the factors driving climate evolution. It evidences the main limit of the forcing method, which limits radiative heat exchanges according to the first law of thermodynamics. A more exhaustive thermodynamic analysis of the Earth system, considering both the first and second laws of thermodynamics, could offer insights into the energy fluxes and entropy generation associated with climate-related phenomena and better describe the Earth's heat engine. The exergy analysis is a promising tool for assessing the quality and efficiency of energy utilization and identifying the directions and opportunities for sustainable energy development. It provides a complete evaluation of natural and human-induced climate change phenomena. The results have been analyzed in the light of constructal law, observing that human impacts and the fast-growing GHGs in the atmosphere are moving the planet's development against this law.

1. INTRODUCTION

Earth is a limited physical domain characterized by fluxes, namely incoming solar radiation, outcoming dissipation, internal atmospheric and oceanic motion, water, carbon dioxide, and oxygen cycles. Their unstable equilibrium generates the climate [1], the thermal conditions on Earth, and the atmosphere that allows for life to be kept. The Industrial Revolution started atmospheric heating. Globalized economy [2, 3] after WWII evidenced that human activities influence Earth's energy balance and warm the climate. The myth of unlimited resources, abuse of fossil fuels, industrial and agricultural processes, and deforestation appear to cause increased greenhouse gas emissions and global warming [4]. The UN established the IPCC in 1988 to study and predict human-induced climate change [5]. IPCC reports are the most authoritative sources of climate information [6, 7]. The data included is one of the sources for the calculations in this paper. The IPCC states that the change in atmospheric net radiation is due to multiple drivers, especially the concentration of greenhouse gases [8].

Radiative forcing analysis increases awareness of climate change and correlations between changes in atmospheric composition, radiative transparency and temperature. It does not fully capture the thermodynamic processes that influence climate evolution [9, 10] and can be improved despite experimental evidence [11, 12]. Radiative forcing relies on the first law of thermodynamics, which cannot properly describe the evolution of systems far from equilibrium. Therefore, it is intrinsically static, describes climate evolution as a succession of equilibrium states, and may be improved by the second law of thermodynamics [13, 14] and constructal law [15, 16], which describes irreversible systems (as shown in Figure 1).

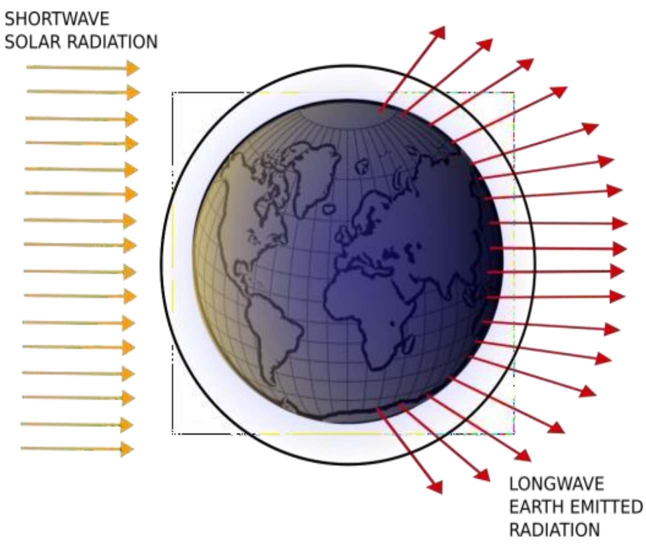

Figure 1. Radiative energies related to the Earth system

Atmosphere models include the second law of thermodynamics to describe the evolution of the climate [17, 18]. In addition, a holistic approach, such as the constructal law, helps to gain a deeper knowledge of the interactions between the biosphere and the atmosphere and the processes driving global warming. It allows for the development of mitigation strategies for climate change and the reduction of the frequency of extreme weather events [19].

2. FUNDAMENTALS OF RADIATIVE FORCING

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2.1 Earth's radiative energy exchanges

Earth's energy exchanges are based on the following radiative energy parameters. The Sun has a temperature of about 5,772 K and peak radiation in visible and near-infrared wavelengths [20]. According to measures by NASA [21], the average distance between the Sun and Earth of about 150 10^6 km produces solar energy around 1,358 W/m^2 reaching the top of the atmosphere facing the Sun. The atmospheric radiative temperature is about 253 K. Therefore, radiative energy dissipation has thermal infrared wavelengths. Hotter matter emits radiation with a shorter peak wavelength of radiated energy.

The total solar irradiance is the maximum power the Sun can deliver to a surface perpendicular to the path of incoming light [22]. Earth is a spherical body.

Only half the planet receives sunlight at one time and halves solar irradiance. The other hemisphere is exposed to Space and irradiates energy. Areas near the equator are nearly perpendicular to the incoming radiation at midday [23]. Everywhere else, the sunlight comes at an angle that increases with the latitude and reduces solar irradiance (Figure 2). The average sunlight reaching the top of the atmosphere is only around one-fourth of solar irradiance (around 340 W/m^2).

2.2 Earth heating imbalances

Incoming solar power has a global average of 340 W/m^2. Solar radiation varies in Space and time, from the tropics to the poles. Earth's axis is tilted off by about 23° (Figure 3). While Earth orbits the Sun, the tilt causes the seasons. One hemisphere, then the other, receives more direct sunlight and has longer days. The difference is extreme at the poles. Even if light increases, solar heating does not grow during summer because of the reflection of snow and ice and their melting.

Illumination and reflectiveness change with latitude and cause net heating imbalances throughout the Earth [24].

Local heating is the difference between incoming sunlight and outcoming heat radiation to Space. Tropical regions present an energy surplus because absorbed sunlight is higher than the heat radiated. Polar regions have an annual energy deficit because radiated heat is higher than absorbed sunlight [25]. The net heating imbalance between the equator and the poles acts as a terrestrial heat engine, generating atmospheric and oceanic circulation, evaporation, convection, and rainfall.

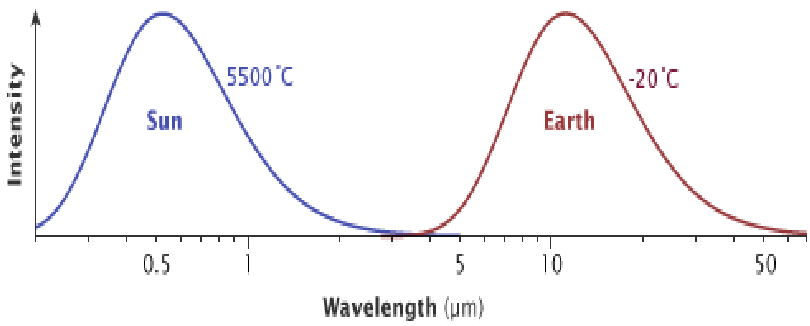

Figure 2. Intensity and wavelengths of solar radiation and Earth's dissipated radiative emissions (adapted from NASA)

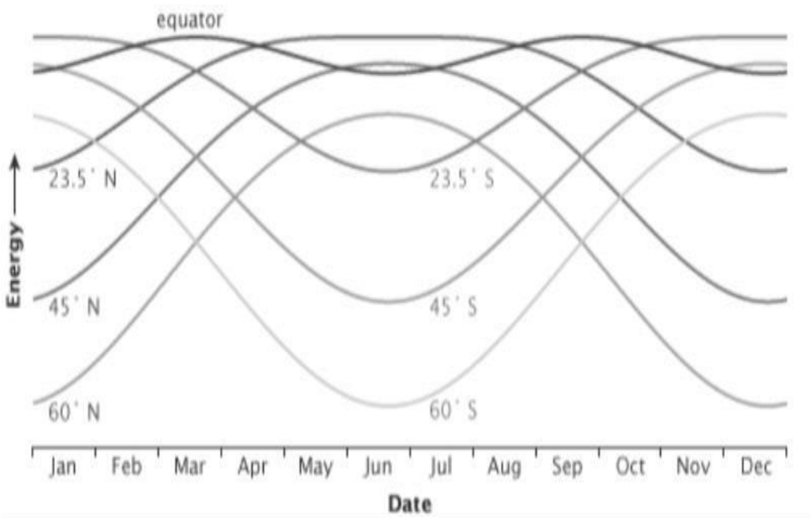

Figure 3. Solar peak energy at local noon each day of the year throughout the year at different latitudes

2.3 Earth's energy budget

Earth's heat engine transfers heat from one part of the surface to another. It moves heat from the surface to the atmosphere and Space. The flow of incoming and outgoing radiant energy stabilizes temperature on Earth's surface over long periods. About 29% of solar energy reaching the atmosphere has no role in the climate system, being directly reflected in Space by bright Earth's surfaces like sea, ice and snow, clouds, and atmospheric particles. About 71% of incoming solar energy is absorbed. Atmospheric water vapour, particulate, and ozone layer absorb about 23% of radiation. The remaining 48% crosses the atmosphere to be absorbed by the planet's surface.

When matter absorbs energy, atoms and molecules get excited. They move faster and increase their temperature, but the temperature does not indefinitely rise because they emit infrared radiation and exchange heat. The Stefan-Boltzmann law estimates emissive power from a black body as follows:

$$P = \sigma\, A\, T^4 \tag{1}$$

The wavelength of the radiative peak from a surface at temperature T can be determined by Wiens displacement law.

$$\lambda = \beta / T \tag{2}$$

The emission of a grey surface (not a black body) depends on the emissivity factor ε that depends on the surface material, quality and colour according to Eq. (3).

$$P = \sigma\, \varepsilon\, A\, T^4 \tag{3}$$

The heat irradiated from a surface is proportional to the fourth temperature power. When the temperature of the whole or a portion of the planet rises, the heat emitted to the atmosphere increases. Radiated heat in response to increasing temperatures is the primary mechanism that limits heating (Figure 4).

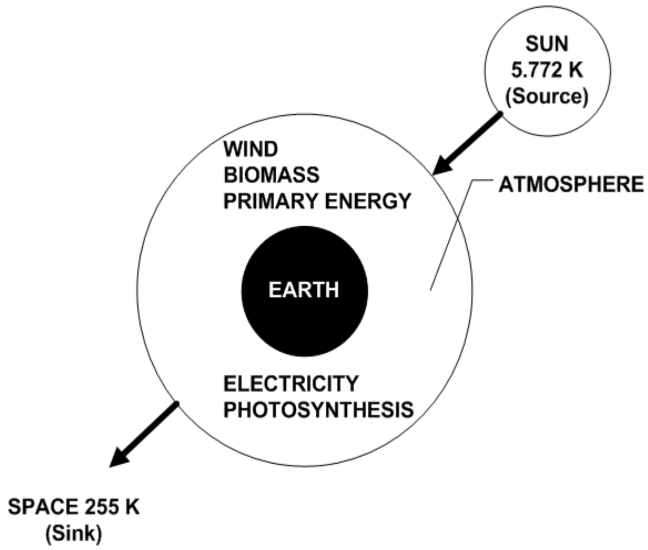

Figure 4. Model of Earth as a closed domain

The atmosphere and Earth's surface absorb 71% of the incoming solar radiation. To keep the average temperature of Earth and its atmosphere stable, they must radiate the same amount of energy to Space. Considering relative contributions by the atmosphere (23%) and surface (48%), the radiation absorbed from the Sun and emitted into Space is asymmetric. The atmosphere radiates 59% of the heat, and the surface radiates only 12% of incoming sunlight. Solar heating on the surface is dominant; radiative cooling happens in the atmosphere.

2.4 Understanding earth's climate

Earth's climate influences the energy budget through processes that take place at three different levels [26, 27]:

- Heart's surface, where most of the solar heating is absorbed;
- The top boundary of the atmosphere, from which sunlight enters and heat radiation exits the Heart's system;
- The atmosphere in between in which heat is both absorbed and transformed into work;
- Atmospheric particles, clouds, and bright ground surfaces reflect about 29% of incoming solar radiation back to Space. The remaining 71% is absorbed by the atmosphere (23%) and ocean and land surfaces (48%). Energy leaves the surface through three processes: evaporation (25%), convection (5%), and emission of thermal infrared energy (17%).

Evaporation is the primary driver of the atmospheric heat engine. The latent heat of evaporation is absorbed, allowing the water to evaporate and spread through the atmosphere. The latent heat is released into the atmosphere when the water vapour condenses to form rain, ice, or snow.

Convective heat exchanges, which heat air in contact with the sun-warmed ground, can be estimated at around 5% (Figure 5).

The air in contact with sun-warmed ground increases temperature and buoyancy through convective exchanges (5%). The low atmosphere (troposphere and Stratosphere) is warmer near the Earth's surface and colder at higher altitudes, producing a rise of warmer air and subtracting heat from the surface. A net radiant emission (about 17% of incoming solar energy) leaves the surface as thermal infrared energy (heat) radiated by the Earth's surface. This net flux is the result of two large fluxes with opposite directions:

- Upward flux from surface to atmosphere (117%);
- Downward flux from the atmosphere to the ground (100%).

The peak wavelength depends on its temperature. The Sun's peak radiation is in the visible and near-infrared wavelengths. The Earth's surface is much cooler, with an average value of about 15°C. The peak radiation from the surface is in the region of wavelengths around 12.5 µm.

2.5 The natural greenhouse effect

Most atmospheric gases (i.e., O_2 and N_2) are transparent to incoming sunlight and outgoing thermal infrared radiation. Therefore, the atmosphere also includes gasses (e.g. water vapour, CO_2, CH_4, and other trace gases), which are opaque to specific infrared wavelengths (as shown in Figure 6). Earth's surface emits around 17% of incoming energy through thermal infrared radiation. However, the energy directly radiated to Space is about 12% of incoming solar energy. The remaining fraction (5-6%) is transferred to the atmosphere because greenhouse gasses absorb thermal infrared energy.

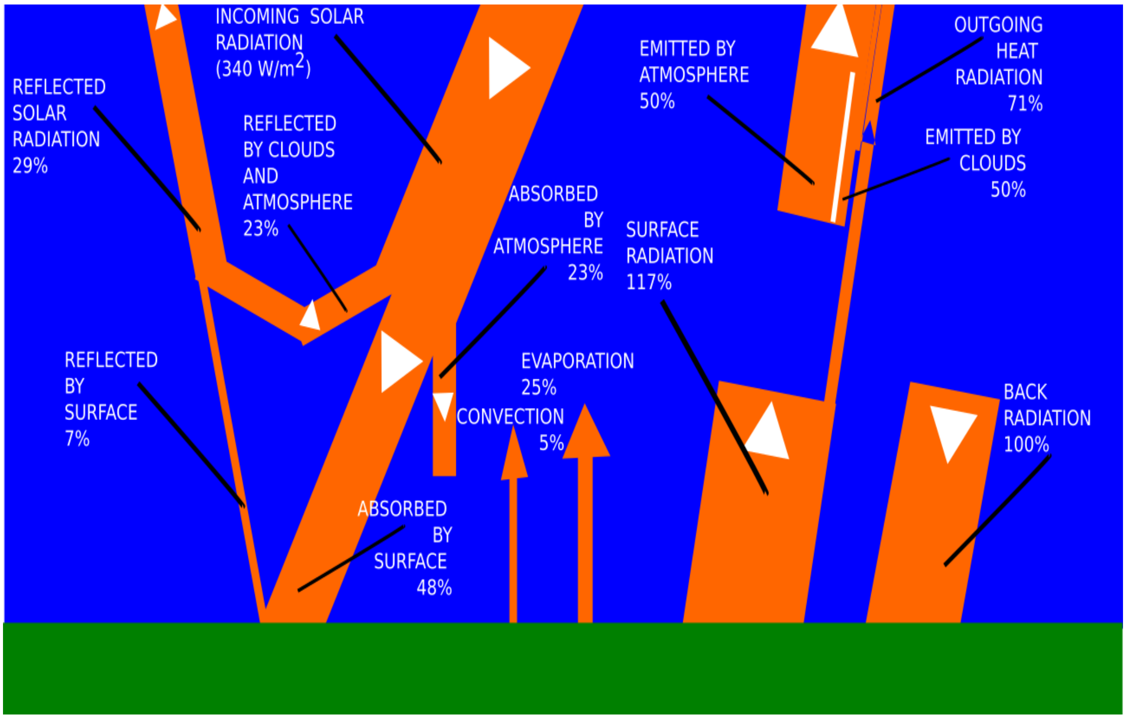

Figure 5. Schema of Earth's energy exchanges

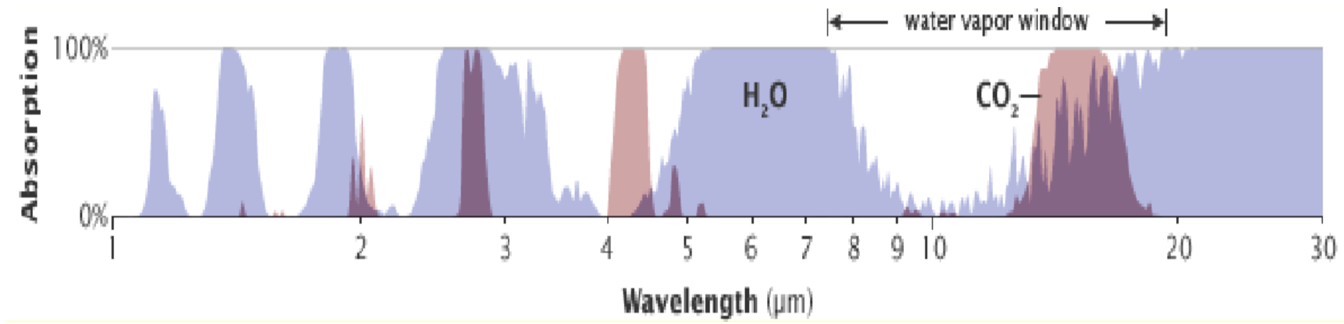

Figure 6. Patterns of energy absorption through atmospheric gasses

Greenhouse gases partially absorb the radiated thermal infrared energy, increasing their temperature and radiating higher thermal infrared energy in all directions. The upward radiated heat encounters new greenhouse gasses that absorb heat and increase the energy they radiate. An amount of energy is radiated toward the ground. It ultimately reaches Earth's surface, consequently increasing its temperature compared to the one reached by direct solar heating (Figure 5).

This heating mechanism is the natural greenhouse effect. It allows the Earth to reach an average temperature of around 288.3 K, which is the ideal condition for human life. Without a natural greenhouse effect, the surface temperature would be around 258 K. The natural greenhouse effect does not cause a relevant increase in surface temperature because it acts in a condition of unstable equilibrium. The energy radiation from Earth's surface always increases faster than the temperature, and the outgoing energy increases with the fourth power of temperature. The Earth's radiation increases to reach 117% of net solar radiation. The energy radiated to the atmosphere is stabilized at around 17% of the solar radiation.

2.6 Climate forcings and global warming

Any change that affects the amount of energy entering and leaving the Earth's radiative equilibrium can force climatic responses by raising or falling temperatures [28].

The elements that alter the planet's radiative equilibrium are called "climate forcings." These include changes in the Sun's brightness, Milankovitch cycles (small variations in the shape of Earth's orbit and its axis of rotation that occur over thousands of years), and large volcanic eruptions that inject light-reflecting particles into the Stratosphere. In addition, anthropic forcing is caused by aerosols (particle pollution) that absorb and reflect incoming sunlight; deforestation that changes how soil reflects and absorbs sunlight and reduces photosynthesis; and rising concentration of atmospheric CO_2 that traps infrared radiation and decreases heat radiated to Space.

The anthropic forcings generate negative effects:

- Increase in atmospheric CO_2 and water vapour absorbs an increased amount of infrared radiation in the atmosphere;

- Reduce global radiative emissions by reducing snow and ice in the mountains and poles.

Water vapour absorbs radiation with frequencies far from the peak of average terrestrial radiation. CO_2 reduces this window, forcing the energy budget out of balance. The most important window by water vapour is centred around 10 μm and extends between 8 and 14 μm. CO_2 reduces this fundamental window and absorbs thermal infrared energy with wavelengths longer than 12 μm. The window that allows thermal radiation outgoing from Earth's atmosphere is reduced to 8 to 12 μm, reducing the radiation that could escape because of CO_2 [29]. Reducing the emissive window and increasing CO_2 means Earth absorbs about 70% of incoming solar energy. However, a lower amount can leave and increase the stored energy.

3. METHODS

3.1 Anthropic effects on the climate

Before the industrial era, incoming and outgoing radiations were in equilibrium, keeping the terrestrial temperature relatively stable [30]. Natural temperature variations could be evaluated over a thousand years. Therefore, the temperature increase trend accelerated from a baseline year (1750 AC) because human activity altered this balance [31, 32]. This is related to the increase of greenhouse gases in the atmosphere, as the gases trap heat and prevent it from being reflected into Space.

On the other hand, other related factors were later considered. The most relevant seem to be the following ones:

- *Deforestation* is an important problem because it increases the ground's absorption of solar radiation, leading to increased absorption of solar radiation in darker areas. In addition, it limits photosynthesis and reduces the absorption of carbon dioxide in the atmosphere.
- *Aerosols* are particles released into the atmosphere from multiple sources, such as combustion exhausts and natural causes, including volcanoes. Depending on their nature, they can have multiple effects on radiative forcing. Bright aerosols (e.g., sulfates) cool the atmosphere and reflect sunlight. Dark ones (e.g., black carbon from diesel exhausts) absorb heat and directly contribute to warming.
- Changes in the *intensity of solar radiation* can directly increase heating phenomena.

3.2 Effects of increasing radiative forcing effects

Radiative forcing explains the disequilibrium of the terrestrial atmosphere according to the first law of thermodynamics. It describes how radiative energy enters the Earth's atmosphere and how infrared radiation is emitted into Space. Solar radiation is the planet's energy source. It is partially absorbed by lands and oceans [33]. About 30% of solar radiation reflects Space, while the rest is absorbed by the atmosphere and the planet's surface and is reflected in Space.

Radiative forcing measures the energy imbalance between incoming short-wave radiation from the Sun and the long-wave one reflected. The imbalance between the incoming and emitted radiation produces effects on the Earth's climate, being captured and increasing the temperature of the atmosphere and troposphere. Indirect data [34] cannot exactly measure the amount of the Earth's energy imbalance. They derive from satellite and ocean-based observations. NASA and ESA agree that this imbalance is around 0.8 W/m^2 and increases with the growth of CO_2 in the atmosphere. The imbalance can be verified by observing sea warming, sea level rise, and the amount of water vapour in the atmosphere [35].

If a forcing (e.g., an increase in greenhouse gases) bumps the energy budget out of balance, the average surface temperature does not change instantaneously. Reaching the full impact of the change in a forcing may take years or even decades. This delay between when an imbalance occurs and when its impact on temperature is fully achieved depends mostly on the immense heat capacity of the oceans, which ensures a thermal inertia that slows the surface warming or cooling. However, it cannot stop the weather change.

Changes in Earth's temperature are a response to the energy imbalance caused by greenhouse gases released so far. The average surface temperature has increased between 0.6 and 0.9℃ at different latitudes in the past century. In addition, experimental data on atmospheric composition allow for the prediction of a rise in surface temperature of at least 0.6℃ because of the actual energy imbalance.

If the surface temperature rises, radiated heat will rapidly increase. If the concentration of greenhouse gases stabilizes, Earth's climate will again stabilize at a higher temperature.

The continuous increase in greenhouse gas concentrations generates a growth of the absorbed solar energy, which exceeds the amount of thermal infrared energy that irradiates Space. Therefore, the energy imbalance increases continuously, and the surface temperatures rise.

3.3 Uncertainty in radiative forcing analysis

The radiative forcing method correlates climate change and its causes. Therefore, they present uncertainties regarding short-time phenomena [36, 37]. They do not allow for the precise definition of a correlation between a change in atmospheric carbon dioxide (CO_2) and other GHGs. In addition, the climate system is so complex that radiative forcing methods are precluded from establishing direct correlations between changes in the intensity of solar radiation and Earth's climate. The same limit emerges for correlating aerosols and deforestation changes to global atmosphere temperature. Radiative forcing methods miss and according to the second law of thermodynamics precise correlations between forcing and atmospheric energy and related phenomena such as wind speeds, rain intensity, etc. (as shown in Figure 7) [38].

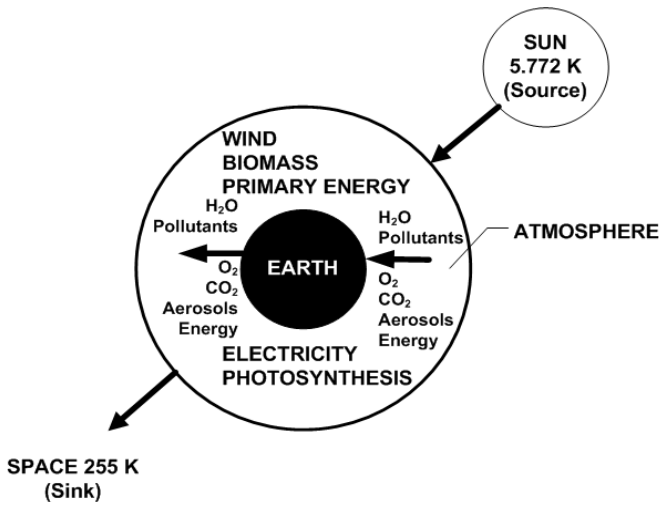

Figure 7. Thermodynamic model of Earth's atmosphere as an open domain with heat and mass exchanges with Earth

Some researchers have introduced some corrections to assess better responses to changes in forcing [39, 40] as observed from effective measures. However, further and deeper research is necessary to assess the global climate sensitivity to the forcing factors that influence the climate globally and locally. The above uncertainties have orders of magnitude that could be better to evidence that radiative forcing models and related conclusions could be false or misleading. However, there is evidence that more accurate methods or integration could better explain the physics of climate change or improve the results [41, 42].

Different models agree on global heating trends but differ in terms of forecasts for temperature increase. Scafetta [43] estimates a lower temperature growth rate through a semi-empirical model based on natural oscillations and not considering radiative forcing. This work estimates a lower limit to temperature, neglecting the anthropic contribution.

3.4 A thermodynamic approach

Bejan [44, 45] states that most general systems are unsteady and that it is possible to perform instantaneous thermodynamic assessments in the form of mass, energy, and Entropy inventories. Accordingly, Earth can be described by thermodynamic heat and mass transfer balances (Figure 7). They assume that Earth and Earth's atmosphere, like any other living body, are far from equilibrium systems. Hence, defining the thermodynamic balances regarding heat and work transfer rates can be useful. In the case of Earth, mass flow rates are neglected because the mass transfer between the atmosphere and the surrounding Space is null. According to Bejan, the model of a physical system is fully defined through the laws of thermodynamics [46, 47].

The Earth system is a closed system (Figure 1) formed by three fundamental subsystems: lithosphere, ocean, and atmosphere. These subsystems receive solar thermal radiation and disperse it into Space. In addition, they are open subsystems that exchange heat (Figure 2) with Space.

In the atmosphere, Eq. (4) expresses the equilibrium of the system according to the first law of thermodynamics.

$$\dot{E} = \frac{dE}{dt} = \sum_{i=1}^{n} \dot{Q}_i - \dot{W} + \sum_{in} \dot{m}h - \sum_{out} \dot{m}h \quad (4)$$

$$\frac{d \ \ln \ P}{d(1/T)} = \frac{\Delta Dh_o}{ZR}, \quad (5)$$

where, $\dot{S}_{gen}$ is the entropy generation rate, and h is the sum of specific enthalpy, kinetic energy, and potential energy at the boundary. Eqs. (4) and (5) consider Earth's atmosphere as an open system with heat exchanges with the surrounding Space and heat and mass exchanges with the biosphere, troposphere and oceans. Eq. (5) is the total entropy generation rate, $\dot{S}_{gen}$, which satisfies the second law inequality $\dot{S}_{gen} \geq 0$, which is the origin of irreversibility. Earth is a closed system. Eqs. (4) and (5) can neglect the terms expressed in terms of mass flow rate.

The first law of thermodynamics is energy conservation and applies to systems in equilibrium with the surrounding environment. Therefore, the principle of conservation of energy describes an evolving system through a succession of stationary images of the considered system. The second law of thermodynamics applies to evolving systems, describing entropy changes over time. This model applies to unsteady systems and describes their evolution.

The entropy generation rate changes with the evolution of one or more quantities along the system boundary. In particular, selecting environmental heat transfer as the floating variable as $\dot{S}_{gen}$ varies eliminates the environmental heat transfer term between Eqs. (1) and (2) [48-50]. The result allows for expressing the irreversibility of the system:

$$T_0 \dot{S}_{gen} = \dot{W} + \dot{E} + \sum_{i=1}^{n} \dot{Q}_i \left(1 - \frac{T_0}{T_1}\right) - \sum_{in} \left(\dot{m}h - T_0 s\right) + \sum_{out} \left(\dot{m}h - T_0 s\right) \quad (6)$$

3.5 Gibbs free energy

Gibbs [51] free energy is "t*he greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition*".

It becomes:

$$G = H + T\Delta S = U + pV - TS \quad (7)$$

G is evaluated at T, p of the system in equilibrium with the surrounding environment. It is a static magnitude that applies to an unsteady system and describes a particular state of equilibrium.

Fasman [52] and Dimian et al. [53] prove that Gibbs energy change is the maximum work produced before and after a transformation or a transformation step. It is time- independent and does not deliver information about the path and evolution over time of the transformation.

3.6 Exergy analysis

The concept of exergy emerges from Carnot's demonstration of the impossibility of perpetual motion [54] and Gibbs' [51] availability function, representing the freely available work. Later, Rant exhaustively defined the concept of exergy [55]. Sciubba and Wall [56] and Kotas [57] have defined exergy as *"the maximum work obtainable when a given system is brought from the environmental state (p0, T0, z) to the standard dead state (p0, T0, z0)."*

The exergy of a system is the maximum shaft work that the system must perform to reach the dead state (environmental conditions). It is the maximum work a thermodynamic system produces going in equilibrium with its environment. These definitions encompass three fundamental implications:

1. Exergy is useful energy that can be converted into work;
2. Exergy, such as entropy, describes energy and environment-related processes during their evolution;
3. Exergy measures the deviation of the system from equilibrium with its environment by a certain process.

Exergy measures the maximum useful work obtained from an energy source as it is brought into equilibrium with the environment. It accounts for the quality and quantity of energy within a system. By considering Eqs. (1) and (2) and the definition of boundary work, it results:

$$\delta Wb = p_0 dV \quad (8)$$

It allows deriving the differential work that can be extracted from the system:

$$\delta W = -\,dU + p_0 dV + T_0 dS + \sum_i (hi,0 - T_o\, ds_{i,0})\, dN_i + -T_0 dS_{gen} \quad (9)$$

The maximum work that can be extracted by performing adiabatic reversible transformations (no generation of entropy) becomes:

$$W_{max} = (U + p_0V + T_0S) + \sum i(h_{i,0} - T_o s_{i,0})\, Ni \tag{10}$$

The exergy of a system can be formulated by Eq. (6) and, neglecting chemical, gravitational and kinetic transformations become:

$$B = H + T_0\Delta S = U + P_0V - {}_{T0S} \tag{11}$$

where, B is the exergy, U is the system's internal energy, $P0V$ represents the pressure-volume work, $T0S$ is the temperature-entropy product, and the subscript 0 refers to the environmental conditions. The relation between exergy and entropy describes dynamic systems far from equilibrium. These systems present a constant interplay between the increase in entropy due to irreversible processes and a decrease in exergy as the only useful part of energy because it can be transformed into work, and only a part of useful exergy produces mechanical work being partially dissipated in the form of waste heat.

Eq. (11) shows the correlation between exergy and entropy, which helps in understanding the efficiency and sustainability of a system as it undergoes non-equilibrium processes.

As Wall et al. [58] state, *"Exergy is the fuel for dissipative systems, i.e. systems sustained by converting energy and materials, e.g., a living cell, an organism, an ecosystem, the Earth's surface with its material cycles, or a society"*.

The exergy concept applies to energy and material conversions in society. This approach describes the use of physical resources and environmental impacts. An exergy-based model of the biosphere and atmosphere allows coupling natural and anthropic phenomena and determining their weight on climate change.

In addition, most physical phenomena allow correlating energy and available exergy (Table 1).

Table 1. The exergy factors of some common energy forms

Energy Form	Exergy Factor
Mechanical energy	1.0
Electrical energy	1.0
Chemical energy	1.0*
Nuclear energy	0.95
Sunlight	0.93
Hot steam (600°C)	0.6
District heat (90°C)	0.2 - 0.3**
Heat at room temperature (20°C)	0 - 0.2**
Thermal radiation from Earth	0

*May exceed 1, depending on the definition of system boundaries and final states.

**Depends on the environmental temperature.

4. EARTH ATMOSPHERE EXERGY BALANCE

Exergy analysis allows for estimating the maximum work (Carnot Work) from physical processes or substances concerning a reference state (dead state). The reference state is arbitrary but must necessarily make sense of the considered phenomena. In the case of terrestrial energy conversion processes, the concept of exergy is most effective if related to the environmental conditions on the surface of the Earth. In the case of the phenomena that involve the Solar system, the Earth, and its climate, the ideal reference environment is the surrounding Space.

The various forms of exergy refer to multiple phenomena, such as heat and mass transfer, thermal exchanges, kinetic energy, potential energy, and changes in the concentration of species relative to a reference state.

4.1 The reference state

The exergy analysis requires evaluating a resource's potential to produce work with respect to the dead state or reference environment, which has zero work potential. Soils, oceans, and the atmosphere are considered reference environments for Earth-related phenomena. They must be large enough to remain unmodified by the required interactions over the necessary time scale for the heat and mass exchanges related to the analyzed transformations.

The surrounding Space is the environment that must be assumed to describe the global phenomena in Earth's atmosphere, ocean, and crust.

Any stationary state can be defined by its intensive properties as position functions. To perform an effective environmental analysis, the environmental reference state (a stationary state) requires assuming the following reference values: mean temperature (Tref), pressure (Pref), and the chemical potential μi for all relevant species i (atomic, molecular, or nuclear) in the Earth environment.

The exergy analysis of the environment must consider the properties of the atmosphere, biosphere and both natural and human-induced processes. Exergy analysis of Earth's environment and atmosphere and their changes require a macroscopic vision of the natural environment. In particular, the model of the Earth system in Fig. 5 and 8 can be analyzed in more detail. It can be observed that the Earth's surface is formed by land and seas. Therefore, Earth can be considered made by two domains: hydrosphere, the reference environment for oceanic water, and lithosphere, which aggregates the reference environment.

4.2 Earth system exergy and internal energy

The Earth's climate is a solar-powered system. Over the year, the Earth—land surfaces, oceans, and atmosphere—absorbs an average solar power of about 240 W/m^2. The sunlight absorbed drives photosynthesis, fuels evaporation, melts snow and ice, and warms the Earth.

The Sun does not heat the Earth evenly. Being a sphere, the Sun heats equatorial regions more than polar ones. Solar heating imbalances in the atmosphere and oceans produce non-stop internal work through the evaporation of surface water, convection, rainfall, winds, and ocean circulation. The coupled atmosphere and ocean circulation is Earth's heat engine. The Earth's largest resource flow is solar radiation. The Sun is a finite resource. The solar radiation produced is renewable because of Earth's rapid replenishment rate. Solar radiation travels through Space, a medium for transmitting radiation to the Earth and a sink for radiative dissipation.

The climate's heat engine redistributes the incoming short-wave radiation from the equator toward the poles and reflects lower-frequency heat radiation from Earth's surface and lower atmosphere to Space. Earth's temperature does not infinitely rise because of the heat radiated to Space by lands, ocean surfaces, and the atmosphere during nighttime. Otherwise, Earth and the atmosphere endlessly heat up. The balance of the fluxes is Earth's energy budget.

The flow of internal resources includes wind and water cycles in the atmosphere, tides, waves, ocean currents, and rivers on the land surface. The natural flows occur in an Earth-related reservoir, divided into a resource reservoir environmental reservoir. These flows occur in terrestrial an and environments and are generated by gradients between reservoirs. For example, winds are generated because of the difference in pressure, kinetic energy and temperature between atmospheric volumes (reservoirs). They are named renewable resources because of the relatively short time scales that allow their regeneration. The flows produce a work and can be easily represented in terms of exergy. The efficiency of the Earth's Carnot engine is:

$$\eta = \frac{T_{in} - T_{out}}{T_{in}} \tag{12}$$

where, the input and output temperatures can be calculated from the entropy definition.

$$T_{in} = \frac{Q_{in}}{S_{in}} \tag{13}$$

$$T_{out} = \frac{Q_{out}}{S_{out}} \tag{14}$$

Only a fraction of Qin produces useful work on the surroundings, increasing entropy or dissipating exergy. Internal exergy disruption is associated with heat and mass transfer inside the Earth's system. Exergy disrupts frictional dissipation of kinetic energy and internal heat exchanges within the system by radiation, conduction, diffusion, irreversible chemical reactions and phase changes (Figure 8).

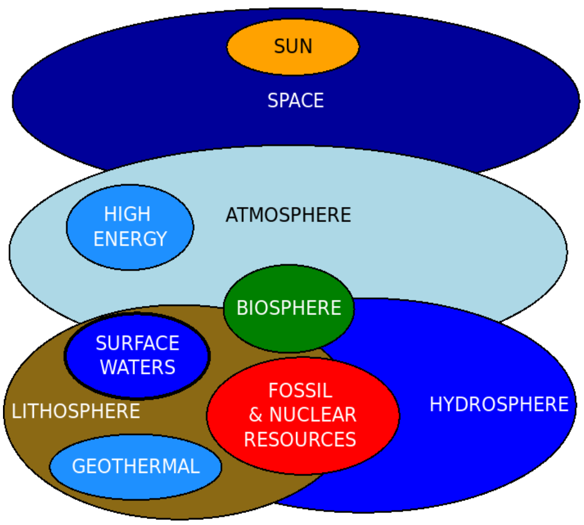

Figure 8. Thermodynamic model of Earth's natural environment, reservoirs and resources

Environmental reservoirs are out of equilibrium and can drive a change. Therefore, exergy transfers between the reservoirs produce work and exergy dissipation, allowing life on Earth and in its three environmental reservoirs [59].

The planet is a multi-reservoir system. The related exergies can be measured for the Earth's system equilibrium state if stationary or the Earth's reservoirs' equilibrium (stationary state) if it is driven. Earth is a driven multi-reservoir system. It can be modelled according to the mutual stationary state of the constitutive reservoirs from the exergy of the reservoirs, their subsystems, and interactions can be measured.

A stationary state is defined by its intensive properties as a function of position. The reference state can be determined by assuming the reference values to perform an effective environmental analysis: mean temperature (T_{ref}), pressure (P_{ref}), and the chemical potential μi for all relevant species i (atomic, molecular or nuclear) in the Earth environment [60].

Writing an Eq. for reversible and irreversible processes close to equilibrium is possible Eq. (11).

$$dU = T \quad dS - P \quad dV + \sum_{i=1}^{n} \mu_i dN_i \tag{15}$$

dU is the change of internal energy, *dS* is the change of Entropy, DV is the volume change, and *dNi* is the change in the number of particles of the species *i*. It can be remarked that other work terms, such as those involving electric, magnetic, gravitational, and dissipative terms related to friction and fluid resistance, may be added.

4.3 Exergy and the Earth's environment

Exergy is a useful system for estimating environmental impacts. Exergy measures the departure of the system's state, including the environmental one. Even if it is not a state function, it is an attribute of the system and environment together [61, 62]. Once the environment is specified, a value can be assigned to exergy in terms of property values for the system only so that exergy is an extensive property of the system. However, working with it on a unit mass or molar basis is often convenient. The specific exergy on a mass basis, e, expressed as the sum of thermal, mechanical and chemical contributions is:

$$b = \underbrace{(u - u_0) + p_0(V - V_0) - To(s - s_0)}_{physicalexergy} + \\ + \underbrace{\frac{v^2}{2}}_{kineticexergy} + \underbrace{gz}_{potentialexergy} + \underbrace{b_{CH}}_{chemicalexergy} \tag{16}$$

It is now possible to better analyze the terms of Eq. (12) and to explain different exergy-related terms. When calculating physical exergy, we include the thermal, mechanical, kinetic, and gravitational energy.

a. Physical exergy

Physical exergy is a physical system's maximum (reversible) work while bringing it reversibly to the reference conditions. It includes exergy due to temperature and pressure, resulting in Eq. (17).

$$B_{ph} = B(\Delta T) + B(\Delta P) \tag{17}$$

which can be expressed in the more detailed formulation in Eq. (18).

$$B_{ph} = \Delta h - T_0 \Delta S = h - h_0 - T_0(S - S_0) \tag{18}$$

where, $h0$ and $s0$ are the standard enthalpy and entropy.

Since exergy is an extensive property, the exergy change in a flow or between two states of the same system derives from its input and output states.

$$B_{ph} = h1 - h_2 - T_0(S_1 - S_2) \tag{19}$$

b. Chemical exergy

Chemical exergy describes the evolution of the chemical energy of the molecules inside a considered system. Absolute chemical exergy results by subtracting the extractable energy from the system molecules into the free conversion of their constituent elements [63-67]. For an ideal mixture, chemical exergy is expressed by Eq. (20).

$$E_{ch,m} = \sum_i x_i E_{0,i} + RT_0 \sum_i x_i \gamma \ln x_i \tag{20}$$

where, $E_{0,i}$ is the molar exergy of each component, and xi is the molar component. The exergy is influenced by the concentration of the species and their reactivity being lower than the calculated exergy of the chemical bonds. Therefore, the relative abundance of species in a substance must be compared with their average concentration in the reference state. For these reasons, an activity coefficient, γ, can be introduced in a real mixture to calculate chemical exergy.

$$B_{ch}=G+(T-T_R)S \tag{21}$$

Eq. (17) determines the most general expression of chemical exergy. Chemical exergy can be related to Gibbs free energy and traditional biochemistry analysis.

$$B_{ch} = G + (T - T_R)S \tag{22}$$

c. Solar and cosmic radiation exergy

Exergy of radiating energy can be determined for solar energy and terrestrial heat radiation. Radiating energy is emitted in terms of electromagnetic radiation. The following formula can calculate the exergy of solar energy:

$$B_{solar} = Q - T_o(S_{gen} - S_{out}) \tag{23}$$

where, Q is the heat energy input from the Sun; T_0 is the reference temperature; Sgen is the entropy generated; Sout is the entropy of the output energy. The exergy of solar energy is the maximum useful work obtainable from solar energy.

The exergy of solar energy is the maximum useful work obtainable from solar energy.

$$\frac{B_{rad}}{E_{rad}} = 1 - \frac{4T_0}{3T} + \frac{1}{3}\left(\frac{T_0}{T}\right)^4 \tag{24}$$

The exergy of terrestrial heat radiation allows for understanding Earth's thermal energy that really dissipates.

d. Ocean thermal gradient

Oceans are fundamental because of their thermal inertia. The exergy caused by the oceanic thermal gradient derives from the difference in temperature between thermal reservoirs (surface and deep water). The physical exergy associated with the flow of water in different thermal conditions between two reservoirs of fluid at different temperatures is:

$$B_{ocean\ gradient} = mc_{p,avg}(T_w - T_c)(1 - \frac{T_W}{T_W}). \tag{25}$$

For a temperature difference of 20 K, the exergy content is approximately 7% of the thermal energy.

e. Winds and oceanic currents

The exergy of fluid currents relates to the kinetic energy of the fluid. Hence, the exergy losses relate to fluid friction and turbulence [68, 69]. The maximum work from moving fluids is extracted when the fluid velocity relative to the reference state is brought to zero. Therefore, a fluid flow's exergy equals the fluid's kinetic energy [70].

$$B_{fluid} = \rho v_0^3 \tag{26}$$

The wind has a variable nature and characteristics caused by the pressure difference between the air volumes that generate them. Therefore, they must be approached using statistical methods [71, 72] to describe the wind speed at a specific site and altitude.

The exergy flux depends on the power of the wind; thus, the average wind velocity could not completely describe the average exergy fluxes in a specific location. In addition, wind velocities increase with altitude up to the tropopause and lower Stratosphere, where the jet streams occur.

The same laws apply to oceanic currents, even if they decrease velocity as they move far from the Earth's surface [73].

f. Oceanic surface waves

As we have foreseen, the atmosphere and hydrosphere interact. The winds blow in preferential directions. Therefore, over large water surfaces, they generate little surface irregularities and waves with increased gravitational potential energy.

The waves deliver the kinetic energy the water surface receives over many kilometres and deposit it on the coastline. The related exergy is determined by the period and the amplitude [74]. For an approximately sinusoidal deep ocean wave, the length-specific exergy flux is:

$$B_{fluid} = \frac{1}{2}\rho \upsilon_0^3 \tag{27}$$

where, *Vwave* is the wave speed and *l* is the amplitude.

Ocean waves have a high degree of variability and superposition. Assuming the water level in a certain area is known over time, statistical parameters can provide an average available energy from superimposed surface waves of arbitrary amplitude and period.

g. Precipitations

The specific exergy of atmospheric precipitation has a physical component caused by a gravitational field and a chemical component due to the different composition between fresh water and seawater.

The physical exergy of a flowing body of water at the reference temperature and pressure is equivalent to its gravitational potential energy. The exergy associated with a steady-state flow of water is a straightforward relationship between the distance above the reference height and the flow rate. For a specific replenishing body of water, such as a dammed reservoir, the gravitational potential exergy is:

$$B_{precipitation} = \dot{m}gz \tag{28}$$

where, m is the mass flow rate, z is the vertical distance from the water level to the reference sea level height, and g is the acceleration of gravity.

The second component is the diffusive exergy due to the difference in chemical potential between freshwater and seawater. Since dissolved salts primarily cause the difference, this value can be computed directly as reversible osmosis. The exergy identified by the work done against the osmotic pressure is:

$$B_{diff} = RT\ \ln(1 - y_{solute}) \tag{29}$$

where, solute is the mole fraction of solute in the water [55]. Assuming an average seawater content of approximately 1.9 mol/kg ions dissolved at a salinity of 35 ppt, the diffusive exergy of freshwater is 4.9 kJ/kg.

h. Tidal energy

The interactions between the Earth, Sun, and Moon and their mutual position cause tides, which deliver tidal energy caused by the change in the gravitation potential. The related exergy is the gravitational potential of a designated water reservoir, or ocean area averaged over many tidal cycles. Exergy exists for both rising and falling tides. The specific tidal exergy of a designated area of ocean or enclosed reservoir is a function of the minimum and maximum levels and the period between the levels. Lunar and solar-induced rises in ocean levels have different periods. They are subject to orbit variations and the effect of ocean floor topology with consequent diffusion or concentration effects [75].

The alternate moving up and down of tides allows for estimating an average exergy flow by considering the local difference between the ocean levels.

$$B_{tidal} = \frac{1}{n}\sum_{n} \frac{\rho g \int_{zn}^{zn+1}}{data} \tag{30}$$

where, t is the period, a is the area of the reservoir at height z, and n is the index number for each maximum or minimum. This formula can be applied to an area of open ocean or a partially enclosed body of water such as a bay.

i. Geothermal energy

Exergy from geothermal resources relates to physical exergy, which originates from a fluid in the deep Earth, which receives a substantial amount of thermal energy. Most authors prefer to describe the potential of a geothermal site by considering the properties of a pumped or natural fluid when it reaches the surface [56, 57].

The first expresses the thermal exergy of a compressible natural or working fluid at the wellhead.

$$B_{geo} = h - h_0 - T_0(s - s_0) \tag{31}$$

Seawater inclusions usually produce geothermal energy, and the chemical exergy associated with the dissolution of ions is always negligible. The flux associated with these sources depends heavily on the thermal exchange rate between surrounding rocks and fluid. Reservoirs may cause fluid temperature or pressure drops if the energy or fluid removal rate is too high.

j. Carbon-based fuels

The exergy derived from fossil reservoirs and biomass is due to the chemical energy of carbon-based molecules. It can be estimated through the chemical reactions involved in the combustion process. The chemical exergy is based on the entropy and enthalpy of the reactants and the products. Usual combustibles include a wide variety of hydrocarbons. Therefore, the exergy calculation based on the species is difficult. Using Gibbs free energy relations and empirical data, we can assume that the entropy of a fuel can be obtained by summing the entropies of the constituent elements of the mixtures.

The natural reservoirs of hydrocarbons include oil shale, tar sand, and heavy oil or bitumen. Oil shale and tar sand are heavy oil and/or bitumen mixtures with various inorganic substances (e.g. sand and carbonates). Heavy oil, bitumen, and the organic portions of the mixtures are high molecular weight hydrocarbons derived from degradation, weathering, and bacterial conversion of pure oil. Usually, they do not include lightweight hydrocarbons but only asphalts high in sulfur and metal content. Eq. (18) estimates a chemical exergy of about 40 MJ/kg for representative elemental compositions of heavy oil and bitumen.

k. Coal

Coal is a large, interconnected graphite-based carbon structure with high metal concentrations and sulfur impurities. Since there is no simple way to compute thermodynamic properties for such structures from a molecular point of view, it is necessary to use experimental methods and Eq. (18). Usually, it results by considering the mass fraction of the two usual components of coal mixtures. They are Blacksville bituminous (29,81 MJ/kg) and Absaloka sub-bituminous (19.87 MJ/kg).

l. Natural gas

Natural gas is a mixture of low-mass hydrocarbons, helium, nitrogen, and carbon dioxide. According to Eq. (16), chemical exergy calculations can approach the composition and interaction between species of conventional natural gas by summing the chemical exergy of each component for the reaction with oxygen.

$$C_aH_b + (a + \frac{b}{4})\ \ O_2 = a.CO_2 + b.H_2O \tag{32}$$

Eq. (32) quantifies the stoichiometry of the relation for chemical exergy calculation associated with the specific properties relative to their composition. Inert species such as nitrogen and carbon dioxide only contribute to the diffusive exergy component. For a representative composition of natural gas and a relative humidity of 80%, this analysis yields a specific exergy of around 50.5 MJ/kg.

m. Methane clathrate

A technologically unexploited energy reservoir is natural gas stored in clathrate hydrates in the permafrost regions of continents or sediments on the ocean floor along coastal areas of any continent. Water crystalline structures encapsulate molecules of gas called clathrate hydrates at near-freezing temperatures and pressures above atmospheric ones. The most common natural clathrate hydrate traps one molecule of CH4 for every five molecules of water. Nearly pure methane clathrate hydrates dissociate when their temperature rises to about 275 K or the pressure falls under 3 MPa.

The exergy of natural clathrate hydrates is due to the chemical exergy of the guest CH_4 molecules reduced by the exergy necessary for dissociating the crystalline encapsulation. The dissociation energy can be determined directly from T and P at equilibrium for a given clathrate hydrate using a modified Clausius–Claypeyron Eq. (33).

$$\frac{d \ \ln \ P}{d(1/T)} = \frac{\Delta Dh_o}{ZR}, \tag{33}$$

where, Z is the compressibility factor, and ΔDh is the dissociation energy of the clathrate. Exergy for representative methane clathrate hydrate in Mid-America Trench (methane with 85% water mass) results in about 4.8 MJ/kg.

n. Biomass

Harvesting biomass for energy conversion is a biological and biochemical method that allows conversion into energy, a renewable resource generated by solar radiation. Biomass consists of long cellulose chains, which are difficult to estimate in terms of biochemical and thermodynamic properties. Therefore, the chemical exergy of harvested biomass fuel can be determined similarly to that of other carbon-based fuels of a complex composition.

Biomass consists mostly of cellulose, lignite, protein, and ash. The exergy content of biomass depends on the carbon content and increases proportionally to the carbon content of the specific material. Lignite (common in woody biomass) have a carbon content of around 60 and A specific exergy of about 25 MJ/kg. Cellulose has a carbon content of 40% to 45% and a specific exergy range of 16-18 MJ/kg. Therefore, ash, common in marine biomass, contributes little energy and decreases the overall biomass-specific exergy.

o. Nuclear transformations

The actual objective of the present paper will not require an analysis of the exergy from nuclear ores, even if it is the source of solar energy. In addition, on Earth, nuclear energy derives primarily from the strong nuclear force potential energy in the selected nuclides that this study presumes are available for fission or fusion. The exergy of nuclear transformations is a function of the mass defect between products and reactants of a proposed nuclear reaction. This analysis neglects the neutrino energy, which means that nuclear binding release is approximated to be entropy-free because of the extreme temperatures of the nuclear reaction.

5. RESULTS: NATURAL EXERGY RESOURCES

5.1 Solar radiation exchanges

As we have seen, solar radiation is primarily the exergy input to the terrestrial domain. Solar radiation drives most of Earth's activity, including physical phenomena and life-related biophysical processes.

Solar radiation has an average exergy density of approximately 1270 W/m^2 but varies in intensity based on latitude and local cloud cover. As solar radiation enters Earth's environment, it is absorbed or reflected. About 23% of solar radiation energy passes through the atmosphere, while the rest is absorbed or reflected into Space.

The absorption of solar radiation by Earth's surface is critical for energy conversion processes. It converts solar energy into thermal or chemical energy, driving essential Earth processes like photosynthesis.

Solar radiation entering Earth is around 162,000 TW. However, significant portions are reflected or scattered back into Space, highlighting the intricate balance of solar energy flow on Earth. The exchanges of exergy between the Sun, Earth, and Space contribute to our planet's overall energy and exergy balance.

5.2 Earth's thermal radiation exchanges

The Earth's surface emits low-temperature radiation back into Space, driving the Earth's thermodynamic engine. Beyond solar radiation, extra-solar radiation, including microwave background radiation, influences Earth's exergy balance. The net average exergy density due to Earth's emissions to radiation exchange at the outer edge of the Stratosphere plays a crucial role in Earth's overall exergy balance. Understanding the intricate balance of exergy flow from various sources is crucial in comprehending Earth's energy dynamics.

5.3 Wind

Wind is a powerful and renewable energy source generated by the uneven heating and cooling of the atmosphere. As the Sun heats the Earth's surface, the air above it expands and rises, creating low pressure areas. Cooler air from surroundings flows into low-pressure zones, generating winds.

The amount of wind available at a given location depends on several factors, including:

- Latitude - Wind speeds are generally higher at higher latitudes, where the temperature difference between poles and the equator is greater.
- Altitude - Wind speeds increase with altitude as the air is less dense and has less resistance to flow.
- Surface characteristics - Morphology affects wind speeds, creates turbulent areas that can reduce wind speeds.

The wind's kinetic energy is its energy of motion. The global wind potential is estimated to be around 870 TW, more than enough to meet the world's electricity needs.

5.4 Ocean thermal gradient

The oceans cover approximately 71% of Earth's surface. They play a pivotal role in regulating our planet's climate and sustaining life. Within these huge bodies of water, natural thermal gradients drive the global ocean circulation. This circulation is crucial for maintaining thermal energy balance and distributing heat around the globe.

Solar radiation warms seawater in tropical regions, while radiative losses cool the water in the polar regions. This differential heating creates thermal and density gradients. Warmer water is less dense than colder water, so it tends to rise, while colder water tends to sink.

These currents, driven by temperature and density, form the basis of global oceanic circulation. Colder, denser water sinks at the poles, creating deep currents that flow towards the equator. As these currents reach the tropics, they encounter warmer, less dense water, causing them to rise. This upwelling process brings nutrient-rich water to the surface, supporting marine ecosystems.

Exergy is associated with the thermal gradients. Cold, deep water has a higher exergy content than warm, surface water due to its lower temperature. As the deep water rises and warms, its exergy decreases. This decrease in exergy is converted into kinetic energy, driving the circulation patterns.

The global seawater circulation transports approximately 2000 TW of thermal energy from the tropics to the poles. Assuming an average temperature difference of 20 K between the surface and deep water corresponds to an exergy flow of about 100 TW. This vast amount of energy plays a significant role in regulating Earth's climate.

5.5 Tides

Tidal energy results from different gravitational fields by the Moon and Sun. The Earth rotates through the gravitational field gradients of the Moon and Sun. It is subject to evident motions on the surface of the Earth in response to changes in gravitational attraction. This effect causes oceanic water to change local surface level in response to these gravitational forces. Exergy associated with this motion dissipates as friction and decreases the rotational kinetic energy of the planet. About 3.7 TW tidal energy dissipates worldwide. Around 2.5 TW dissipation occurs in the shallow ocean and continental shelves, 1.0 TW in the deep ocean, and 0.2 TW as friction in the solid Earth surface. The moon is responsible for 70% of the total dissipation, and the Sun for the remaining 30%. The specific tidal exergy is equivalent to the gravitational potential energy due to the height difference between the tidal maximum and minimum over the tidal record. For a given range of time between inflexion points, tides have a specific exergy of 10 kJ for 1 m^2 of the reservoir and each m of height difference.

5.6 Ocean waves

The ocean is a vast and dynamic environment subject to various forces that shape its currents, waves, and other phenomena. One of the more significant drivers of ocean dynamics is the wind, which is a boundary layer that contacts boundary layer that contacts the oceanic surface and transfers momentum and energy. This interaction generates surface waves, which are crucial in oceanic processes.

As the wind blows over the ocean surface, it exerts a frictional force on the water. This force creates shear stress, which causes the water to move toward the wind. The resulting motion generates surface waves that propagate away from the wind source. These waves' height, wavelength, and speed depend on the wind speed, duration, and fetch. The momentum transferred from the wind to the waves drives ocean currents. These currents transport vast amounts of water and heat around the globe, influencing climate patterns and marine ecosystems.

The total exergy produced by wind-driven surface waves is estimated to be around 60 TW. However, this exergy is only partially utilized because a significant portion is lost through various processes.

As surface waves propagate towards the shore, they encounter obstacles such as landmasses, reefs, and currents. These obstacles cause the waves to break, releasing their energy. The breaking process generates turbulence and converts some wave exergy into heat. Additionally, internal friction arises because of water viscosity and the interaction between different water layers, reducing the wave exergy.

The combined effects of the dissipation reduce the exergy of surface gravity waves by approximately 3 TW. This exergy loss is significant, as it reduces the potential for wave energy for power generation or other purposes. Moreover, the average specific exergy of surface waves ranges from 10 to 100 kW/m (kilowatts per meter), with higher values during storms. This exergy further reduces as the waves break on the world's coasts. The resulting wave energy dissipation can significantly impact coastal erosion, sediment transport, and marine habitats.

5.7 Global water cycle

The global water cycle regulates the Earth's climate and ecosystems. Understanding the energy and exergy flows in the water cycle is essential for better understanding our planet. The exergy of precipitations relates to the gravitational exergy due to its potential energy relative to a reference level, typically sea level, and the chemical exergy due to the salinity difference between freshwater and seawater.

Assuming cloud characteristics, an average water vapour height of 1.7 km can be estimated. Solar radiation around 41 PW generates water evaporation from the oceans, forming clouds with an average gravitational energy of about 300 TW and chemical exergy of about 90 TW. An average of 18 Tg/s of water precipitates to the Earth's surface. Of this, 3.9 Tg/s falls on land or ice to an average surface height of 670 m, delivering a gravitational exergy flux of 25 TW and a chemical exergy of 19 TW.

Freshwater transpiration from plants reintroduces 2.0 Tg/s of water into the atmosphere, while the remaining 1.9 Tg/s does not pass through plants. About 0.4 Tg/s of this evaporates, and 1.5 Tg/s enters the oceans as a liquid.

Additionally, a gravitational exergy of 7.2 TW and chemical exergy of 5.4 TW reaches the oceans, delivering 1.1 Tg/s of atmospheric precipitations through the world's major rivers. Based on the precipitation-weighted average elevation, the gravitational exergy density of freshwater is estimated to be 6.57 kJ/kg. Considering an average ocean salinity of 35 ppt, the chemical exergy density of freshwater is calculated to be 4.9 kJ/kg.

Understanding the exergy flows in the water cycle affects water resource management. It highlights the importance of considering the quantity and water quality when evaluating its availability and potential uses. Regions with access to freshwater at higher elevations or salinity levels have a higher potential for exergy extraction. Conversely, regions with limited freshwater resources may need to implement measures to minimize exergy losses, such as reducing evaporation and promoting efficient water use.

5.8 Photosynthesis

The Earth's climate system is driven by the energy received from the Sun. The total solar radiation exergy incident on the land and oceans is about 86,000 TW. Around 20,000 TW are absorbed by plants and algae. This energy converts sunlight into chemical energy through photosynthesis, which uses sunlight to convert carbon dioxide and water into glucose and oxygen. Photosynthesis efficiency is around 1%, meaning that only about 1% of the solar radiation absorbed by plants is converted into chemical energy. However, the net productivity of photosynthesis is around 90 TW, which is a significant amount of exergy.

Plants on the land surface produce 65 TW of chemical energy through photosynthesis, and algae in the oceans produce around 25 TW. These flows of energy feed the biosphere energy reservoirs. The terrestrial reservoirs are assumed to have an average residence time of 10 years and can be estimated at 30 ZJ. Oceanic reservoirs are assumed to have a residence time of 1 month and are about 0.1 ZJ.

In addition to providing energy for the biosphere, photosynthesis converts atmospheric CO_2 into O_2. The most relevant flux of CO_2 is between the atmosphere and the biosphere. An increase in atmospheric CO_2 could increase the efficiency of photosynthesis, giving effective feedback in response to changes in atmospheric composition. However, reducing forest areas, such as Amazonia, lowers Earth's potential for limiting the CO_2 in the atmosphere.

5.9 Geothermal heat

Geothermal energy, harnessed from the Earth's internal heat, offers a renewable and sustainable energy source. It is created in deep lithosphere inclusions generated during Earth's formation through gravitational collapse and tidal interactions. Earth's internal radioactive decay produces the necessary heat within the Earth's interior.

Geothermal exergy is unevenly distributed on Earth and is influenced by geological formations and depth. An approximately 40 km deep temperature gradient between the crust and mantle drives the conduction of heat towards the Earth's surface, resulting in a geothermal energy flow into the crust.

The specific exergy of a geothermal site, representing the available energy per unit mass, is influenced by factors such as rock composition, fluid temperature, and pressure. For example, a brine at 436 K with a reference temperature of 286 K has a specific exergy of approximately 125 kJ/kg.

Geothermal fluids drive turbines that generate electricity, and geothermal heat is also used to heat buildings, industrial processes, and other applications. Using geothermal sites alters the reservoir's thermal or fluid properties, creating a new equilibrium. This process involves converting geothermal energy. The estimated amount of geothermal exergy destroyed or converted worldwide is about 25 GW for electrical generation and 3 GW for direct thermal use.

6. RESULTS: ANTHROPIC ACTIVITY

6.1 Biomass

Biomass is a renewable energy source derived from plants and animals. It can produce heat, electricity, and transportation fuels. Biomass has a specific dry matter exergy between 15 and 20 MJ/kg, which depends on its carbon and ash content. Woody biomass tends to have higher carbon content, while marine biomass often has high ash content.

The use of biomass for energy production has several advantages. Biomass is a renewable resource, meaning that it can be replaced as it is used. It is also a carbon-neutral fuel, meaning that when burned, it releases no additional CO_2 into the atmosphere. In addition, biomass allows the realization of various energy products, making it a versatile fuel source.

However, some challenges are associated with using biomass for energy production. One challenge is that biomass is a bulky fuel, making it difficult to transport and store. Another challenge is that biomass can produce air pollution when it is burned. However, these challenges require the adoption of proper technology and management practices.

6.2 Deforestation

Deforestation prevention and afforestation promotion are strategies to slow climate change and global warming. Indirectly, deforestation releases CO_2 into the atmosphere and exerts a warming effect on Earth's climate. It has important effects on reducing global capacity by removing CO_2 by photosynthesis. However, the biophysical effects of deforestation must be considered. They include changes in land surface albedo, evaporation and transpiration, and cloud cover, which also affect climate. In addition,

Large-scale deforestation presents important consequences for the global carbon cycle and climate model and the biochemical interactions between land, atmosphere, and ocean. It has contradictory effects on climate. On one side, it causes long-term warming because it reduces the global carbon cycle capability. Otherwise, it causes net cooling associated with albedo, evaporation, and transpiration.

Deforestation and afforestation have different impacts in different positions. Afforestation projects in the tropics would be beneficial in mitigating global-scale warming. They would be counterproductive if implemented at high latitudes and offer marginal benefits in temperate regions. The efficacy of mid and high-latitude afforestation projects for climate mitigation, forests remain environmentally valuable resources for many reasons unrelated to climate.

6.3 Fossil fuels

Fossil fuels, such as coal, petroleum, and natural gas, are the predominant energy sources in modern society. Fuels are formed from the remains of ancient organisms buried under sediment and subjected to heat and pressure over millions of years. The conversion of organic matter into fossil fuels represents the storage of chemical exergy, the energy available for useful work. Approximately 40 GW of biological matter is buried under sediment. Geological processes convert a small fraction of the organic matter into fossil fuels. The fluid portion of these fuels can migrate into geologic traps, where they may remain for millions of years without being exposed to the atmosphere and oxidized.

Estimated occurrences of coal, petroleum, and natural gas are 270, 110, and 50 ZJ, respectively. Coal and methane clathrates are found in solid form, while petroleum and natural gas exist as fluids. Methane clathrates are particularly abundant in permafrost and ocean sediments, with estimated occurrences of 4 ZJ and 400 ZJ, respectively.

The specific exergy of fossil fuels varies primarily with carbon content and the percentage of inert components. Coal's specific exergy ranges from 20 to 30 megajoules per kilogram (MJ/kg). Petroleum and natural gas have specific exergies of 42 MJ/kg and 50 MJ/kg, respectively. Methane clathrates' lower specific exergy of 4.8 MJ/kg depends on their water content. Fossil fuels have been used for centuries to meet society's energy demands. Currently, the human use of conventional petroleum is about 5.0 TW, while unconventional petroleum use is about 0.1 TW. Natural gas consumption stands at 3.2 TW. Commercial efforts currently need to be made to extract and convert methane clathrates [76-80].

6.4 Nuclear energy processes

Uranium and thorium are heavy elements formed in stellar events billions of years ago. They can produce nuclear fission and release immense energy when their atoms split. These elements have a significant presence on Earth, representing a vast potential energy source. This paragraph explores the abundance, distribution, and energy potential of uranium and thorium, as well as the role of light nuclides in fusion energy.

Uranium and thorium are found throughout Earth's crust, but their concentrations vary widely. Concentrated uranium deposits, estimated at 13 Tg, contain an exergy reservoir of 1 YJ with a specific exergy of 77 TJ/kg. Thorium resources, estimated at 4 Tg, hold an exergy of 300 ZJ with a specific exergy of 78 TJ/kg. In addition to ores, uranium exists in the ocean. With approximately 1.4 Yg seawater, the seawater uranium exergy reservoir exceeds 350 YJ.

Nuclear fission is when a heavy atomic nucleus splits into two or more lighter nuclei, releasing substantial energy. Uranium-235 (U-235) and thorium-232 (Th-232) are the primary fissile isotopes utilized in nuclear reactors.

Fusion energy combines two light atomic nuclei into a heavier one, releasing significant energy. Deuterium (D) and tritium (T), both isotopes of hydrogen, exhibit the lowest ignition temperature for fusion. Deuterium is abundant in the ocean, but tritium must be bred from lithium. Concentrated lithium occurrences of 14 Tg provide an exergy reservoir of 3.1 YJ for the deuterium-tritium cycle. Deuterium can also be fused with itself at higher temperatures. The resulting exergy oceanic resources are estimated to be around 10 million YJ.

7. CONSTRUCTAL ANALYSIS

As we have seen, the exergy analysis allows the Earth's exergy balance in natural conditions. It allows for the estimation of the effects of natural forcing. It shows that human contribution to climate change directly regards the increase of GHGs and the reduction of the capacity of photosynthesis conversion of CO_2 into O_2. It allows for the evaluation of the increased heat absorbed in the atmosphere and the ground. Being Earth an irreversible system, the work lost, Wirr, because of irreversibility, dissipation and friction effects, according to Bejan and Lorente [81], results:

$$W_{irr} = B_{in} - B_{out} - W \tag{34}$$

where, B refers to exergy and in and out refer to inflow and outflow, respectively.

An evolving system is considered. The exergy that enters the system remains constant, and the exergy exiting the system decreases; it is evident that the work increases. This consideration allows understanding of the increased work dissipated by the atmosphere and the instability of weather because of the increased amount of GHGs in the atmosphere.

This problem leads to considering the constructs defined by Bejan [82] as derived from the consciousness of the importance of configurations in nature, physics, and engineering. Flow configurations are universal phenomena in physics, biology, and thermodynamics. The definition of a constructal law is reported here: *"For a finite-size flow system to persist in time (to live), it must evolve to provide greater access to the currents that flow through it"*.

Constructal law is a self-standing law of physics distinct from the second law of thermodynamics. Even if, as we can see from IPCC data, it influences the natural evolution of thermodynamic phenomena. Natural flow systems evolve in time to develop the flow architecture that maximizes flow access under the physical constraints posed to the flow.

Earth's climate is made by fluxes and phenomena that allow the planet to be a living body that transforms and evolves. Earth does not exchange matter with the surrounding Space. It exchanges energy, receives solar radiation, and emits thermal infrared radiation into Space. Therefore, Earth is formed by different interconnected and interacting open sub-domains exchanging energy and mass. The lithosphere, hydrosphere, and atmosphere interact and form intersecting domains of the biosphere and anthroposphere.

Constructal law explains how multiple heat and mass fluxes develop on the Earth. The anthropic GHG emission that absorbs heat in the atmosphere and limits the long-wave radiation emitted by the planet opposes both the natural design of the climate system and negates the constructal law because it increases the resistance to the dissipated heat outgoing to Space. This alteration of planet equilibrium causes the Earth to absorb more heat. It increases the temperature in the oceans, the land surfaces, the atmosphere, the amount of water vapour in the atmosphere, and the work to be necessarily dissipated by Earth's environment with extreme events due to higher energy in the atmosphere and higher kinetic energy of the meteorologic phenomena.

Increasing temperatures are reducing the ice-covered areas at the poles, mountains, and permafrost near the poles. Therefore, Earth's heat absorption increases and the direct reflection of short-wave sunlight decreases. As constructal law demonstrates, violent climatic events and the increase in rain intensity accelerate changes in soil morphology. These events may accelerate the development of undesired geological phenomena such as landslides and mudslides and the frequency of floods and inundations.

The analysis of climate-related phenomena at a global scale according to constructal law has been briefly discussed. It requires a detailed analysis, even if it clearly shows that deviating the development of a physical system from the natural evolution described by constructal law may cause problems and create conditions that make life more difficult.

8. CONCLUSIONS

Francis [83] exhorts us to act against global warming and fundamental environmental issues that put the future of humanity and life on Earth at risk. It is caused by the atmospheric increase in greenhouse gases and the evolution of optical properties of lands and oceans near the poles. Understanding the mechanisms driving climate evolution is crucial for devising mitigation strategies. This paper has analyzed the scientific evidence for global warming, explored the forcing method describing climatic evolution, examined energy fluxes within the Earth's system and discusses the potential of exergy analysis to assess climate-related phenomena.

Experimental analysis provides evidence for global warming. The IPCC found that the global mean temperature has grown by about 1°C since the preindustrial age. The warming trend is generated by human activities, particularly fossil fuels, which release carbon dioxide and other greenhouse gases, such as methane and nitrous oxide, into the atmosphere. Data analysis shows a convergence between methods proposed by scientific research to describe climate evolution and its influencing factors. These methods include:

- Radiative Forcing measures changes in net energy flux at the top of the atmosphere due to changes in the concentration of greenhouse gases and other factors. It considers the combined effects of radiative forcing and adjustments in Earth's climate system (cloud cover and albedo).

- Earth System Models - These complex models incorporate Earth subsystems, including the atmosphere, oceans, land surface, and biosphere, to predict future climate scenarios.

The first law of thermodynamics states that energy cannot be created or destroyed in a closed system in equilibrium conditions, only transferred or transformed. Even if Earth is an unstable and far from equilibrium physical system, the first law of thermodynamics allows describing it in ideal equilibrium conditions and identifying the main energy fluxes:

- Incoming Solar Radiation – It is the primary source of energy for the Earth system;

- Outgoing Long-wave Radiation - The energy emitted by the Earth's surface and atmosphere;

- Sensible Heat Fluxes: heat transfer between Earth's surface and the atmosphere;

- Latent Heat Flux: energy released or absorbed by water changes of phase.

The first law explains Earth's heat engine, which describes internal heat and mass fluxes, including oceanic and atmospheric currents, winds, and waves.

The second law of thermodynamics describes the evolution of Earth as a dynamic system based on entropy and entropy generation. Entropy measures the quality of available energy. Entropy generation occurs whenever energy is transferred or transformed, and it is always positive in real-world processes. Exergy measures a system's useful work potential. It represents the maximum amount of work that can be extracted from a system under specified conditions.

Analyzing climate-related phenomena regarding entropy and entropy generation has provided valuable insights. Increased atmospheric entropy due to GHG emissions can change atmospheric circulation patterns and precipitation.

Exergy analysis is a powerful tool for assessing the quality and efficiency of energy utilization. The various energy forms and fluxes within the Earth system in terms of exergy, it has been possible to define the necessary instruments for:

- Comparing the exergy content of different resources, such as fossil fuels, solar energy, and geothermal energy;

- Identifying inefficiencies and areas for improvement in energy conversion and utilization systems;

- Assessing the potential for sustainable energy development and greenhouse gas mitigation.

In conclusion, a set of instruments for describing and approaching climate change has been provided. By leveraging these tools, this paper can contribute to informed decision-making and effective mitigation strategies to address global warming and its consequences.

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NOMENCLATURE

Acronyms

GHG	Greenhouse gas
IPCC	Intergovernmental panel on climate change
NASA	National aeronautics and space Administration
UN	United Nations
WWII	Second World War

Physical magnitudes

A	area, m^2
B	exergy, J
E	energy, J
H	enthalpy, J
P	power, W
Q	heat, J
S	entropy, J/K
T	temperature, K, °C
U	internal energy, J
V	volume, m^3
W	work, J
b	exergy, J
g	acceleration of gravity, 9.81 m/s^2
h	sum of specific enthalpy (J/kg)
m	mass, kg
p	pressure, Pa
u	specific internal energy, W/kg
v	velocity, m/s

Greek symbols

α	thermal diffusivity, $m^2 . s^{-1}$
β	Wien's displacement constant, 2.898×10^{-3} m·K
ε	emissivity factor
λ	wavelength, μm
σ	Stefan-Boltzmann constant, 5.670×10^{-8} $W{\cdot}m^{-2}{\cdot}K^{-4}$.

Subscripts

in	input
out	outlet
0	reference state