

# Modelling the Exergy of Solar Radiation: A Review

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**Abstract:** Exergy is a thermodynamic property that represents the quantification of the maximum useful work that can be extracted from a system interacting with the environment. Regarding solar radiation, radiative exergy has been a matter of study over the last 60 years where the main models applied describe the radiation as undiluted and diluted. The exergy of solar radiation is useful in the preliminary assessment of the performance of solar technologies, since the efficiency of the system depends directly on this value. The present paper describes a review of the main models reported in the literature considering these two approaches, analysing the main differences between the models and the main assumptions applied. A comparative analysis is carried out for the models of diluted and undiluted radiation, where the behaviour of every expression is discussed in detail. For the undiluted expressions, the behaviour of every model within a temperature range is analysed. For black-body radiation at a source temperature of 6000 K, the model proposed by Jeter determines an exergy factor of 0.96, while Spanner, Petela, Press and Badescu calculate a value of 0.93. Parrott's model obtains a value of 0.99, which is above the value for Carnot efficiency. The diluted exergy expressions were evaluated according to wavelength and temperature range, where the trend in each comparison was that the exergy calculated from Karlsson, Candau and Petela was always the lowest. This result is attributed to the fact that these expressions consider the spectral entropy of the medium the radiation passes through. Finally, some new approaches are analysed which consider empirical correlations based on meteorological variables to model the exergy of solar radiation.

**Keywords:** solar radiation; exergy; diluted solar radiation; exergy analysis



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## 1. Introduction

In thermodynamics, exergy is a property that describes the maximum useful work possible during a process that brings a system into equilibrium with the environment. Thus, exergy combines the state of the system and its environment. The irreversibilities observed in actual thermodynamic processes induce entropy generation that causes exergy destruction. Exergy analysis is a methodology that takes into account these irreversibilities through each component of the system [1]. Such analysis has been used to determine the limits of the available useful work of thermodynamic processes. In the field of renewable energy, exergy analysis has been used to evaluate the performance of novel designs of photovoltaic-thermal systems [2,3], thermoeconomic assessment of a solar polygeneration plant [4], thermodynamic performance of light olefin production systems from biomass [5], among many other applications.

The exergy of solar radiation has been a matter of study since the 1960s, aiming to determine the maximum useful work that can be extracted from solar radiation. The total energy emitted by the Sun is about  $3.8 \times 10^{20}$  MW [6], of which only a fraction reaches our planet. The power emitted by the Sun received on a surface normal to the direction of

its propagation outside of the Earth's atmosphere (at a distance equivalent to the mean distance between the Earth and the Sun), is called the solar constant, which has been estimated at a value of  $1367 \text{ W/m}^2$  [7]. The radiation that enters the atmosphere undergoes different phenomena, such as refraction, absorption, and scattering, due to the effect of different particles in the atmosphere [8]. These phenomena are known as atmospheric attenuation, as the particles suspended in the atmosphere affect the transmittance of the solar radiation at different wavelengths, causing the energy of photons to decrease as they pass through the layers of the atmosphere. Consequently, the incident radiation on Earth's surface has a lower magnitude than the solar constant, requiring long-term measurements and/or satellite estimation to assess its time-dependent magnitude and variability, as well as the potential yield of solar technologies [9–11]. However, it is also important to consider the upper limit of the useful work that can be extracted from solar energy to facilitate the design of solar technologies [12,13].

Analysis of the exergy of solar radiation can show the potential that different locations have for the development of solar technologies. An exergy analysis of a system can show how well the system will work in a given location, where the exergy of solar radiation plays an important role, as it defines the upper limit of the efficiency at which the system will perform. An analysis using the second law of thermodynamics allows the evaluation and optimisation of energy conversion processes. Thus, the expression for the exergy of solar radiation is crucial for an accurate analysis and to determine the radiation exergy reliably to properly identify the sources of irreversibility in solar conversion systems. In this regard, expressions for the exergy of solar radiation have been used in different research areas, such as the evaluation of how to improve the reflectivity of flat-plate collectors [14] or the evaluation of the exergy budget of the Earth, with their implications for global sustainability [15–17]. Moreover, the exergy of solar radiation has been evaluated to estimate the potential of energy conversion in different regions, such as Italy [18], Turkey [19], Uruguay [20], and Europe [21]. Finally, radiative exergy expressions have also been used to evaluate the performance of photovoltaic-thermal systems in different climates [22,23].

The exergy of solar radiation can be evaluated by considering the radiation as undiluted and diluted. Radiation is considered as undiluted when there is no attenuation of any kind as it passes through the atmosphere. An expression for quantifying the exergy of undiluted solar radiation was initially proposed in the 1960s by Petela [24], who considered the radiation confined in a thermodynamic cylinder-piston model. Through this model, he concluded that the expression defining the exergy of undiluted solar radiation is a function of the Sun's temperature and the Earth's temperature of the environment. This first analysis initiated wide discussion that stimulated several alternative models for quantifying the solar exergy. Dilute solar radiation, on the other hand, takes into account the effects of atmospheric attenuation and scattering. Several expressions for dilute solar radiation have been proposed that consider the evaluation of the entropy generated by the interaction between photons and particles in the atmosphere. The first expression developed for dilute solar radiation was reported in 1979 by Landsberg and Tonge [25]. This expression, like many proposed later, is mainly a function of the wavelength. In recent years, the determination of radiative exergy has been explored through empirical analysis. The goal of these empirical analyses is to correlate exergy with another meteorological variable that is easy to measure. Since 2016, researchers began developing ways to correlate radiative exergy with other variables, such as the clearness index or the average day length [26–29].

The present review aims to analyse the differences in the mathematical models used to describe the exergy of solar radiation developed since the 1960s. Hence, the present review is organised according to how models commonly consider the exergy of solar radiation including those which focus on exergy of undiluted radiation, exergy of diluted radiation, and empirical models for specific locations. In addition, a comparative analysis is carried out considering models that have similarities in their conception and assumptions, allowing evaluation of the differences in the results delivered by each model. This comparison pro-

cedure was applied to dilute and undiluted radiative exergy models. Finally, a discussion section analyses the methodologies for the dilute and undiluted exergy models. The exergy analyses performed to date used the expression of undiluted exergy models to evaluate the exergy of solar radiation. Through this review, it is proposed that a better approach should be the evaluation of the exergy of solar radiation considering the undiluted exergy expression.

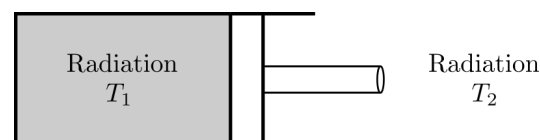
## 2. Undiluted Solar Radiation Exergy

Models that evaluate the exergy of undiluted solar radiation start by considering a system with a non-participating medium and a Carnot engine located between the radiation source and a heat sink. These models differ in the way they define the work being done by the Carnot engine, as well as regarding some minor changes within the elements considered in the thermal engine model. By performing analyses based on the first law of thermodynamics, several studies have formulated different correlations that aim to estimate the maximum work that can be extracted from undiluted radiation. These studies are described in this section where their main assumptions, the idealised thermal system, and the proposed equation are described in detail. All these models are summarised in Table 1.

**Table 1.** Undiluted solar exergy models where  $\psi$  is the exergy factor.

Author	Expression
Petela [24]	$\psi_P = 1 - \frac{4}{3} \frac{T_2}{T_1} + \frac{1}{3} \left( \frac{T_2}{T_1} \right)^4$
Spanner [30]	$\psi_s = 1 - \frac{4}{3} \left( \frac{T_2}{T_1} \right)$
Press [31]	$\psi_{Pr} = 1 - \frac{4}{3} \frac{T_2}{T_1} + \frac{1}{3} \left( \frac{T_2}{T_1} \right)^4$
Parrott [32]	$\psi_{Pa} = 1 - \frac{4}{3} \frac{T_2}{T_1} (1 - \cos \delta)^{\frac{1}{4}} + \frac{1}{3} \left( \frac{T_2}{T_1} \right)^4$
Jeter [33]	$\psi_{Je} = 1 - \frac{T_2}{T_1}$
Badescu [34,35]	$\psi_{Ba} = 1 - \frac{4}{3} \frac{T_2}{T_1} + \frac{1}{3} \frac{T_2}{T_H} \left( \frac{T_2}{T_1} \right)^4$

Petela [24] was the first author to develop a mathematical model for the exergy of thermal radiation in 1964. He considered a cylinder-piston system, as depicted in Figure 1. The system considers that the radiation density is encapsulated inside the cylinder, where the inner walls of the cylinder are frictionless mirrors.



**Figure 1.** Encapsulated radiation in a frictionless cylinder-piston.

Due to the radiative pressure difference, the piston in Figure 1 moves to the right if  $T_1 > T_2$ . Hence, an adiabatic and reversible expansion occurs until equilibrium is reached. The work delivered by the piston during the expansion process is [24],

$$W_{1-2} = \int_1^2 P dV - P_2(V_2 - V_1) \quad (1)$$

where  $P$  is the pressure, which is defined as  $P = \frac{a}{3} T^4$ . The useful work (exergy)  $W_{1-2}$  is determined by combining Equation (1) and considering that the expansion follows the relation  $P = (\text{constant}) V^{-4/3}$ ,

$$W_{1-2} = U_1 \left[ 1 - \frac{4}{3} \frac{T_2}{T_1} + \frac{1}{3} \left( \frac{T_2}{T_1} \right)^4 \right] \quad (2)$$

where  $U_1$  is the initial internal energy of the system. Considering the efficiency of a heat engine ( $\eta$ ) as  $\eta = \frac{W_{1-2}}{U_1}$ , the exergy factor ( $\psi_P$ ) is defined by Petela [24] as,

$$\psi_P = 1 - \frac{4}{3} \frac{T_2}{T_1} + \frac{1}{3} \left( \frac{T_2}{T_1} \right)^4 \quad (3)$$

where  $T_1$  and  $T_2$  are considered as the temperature of the Sun's outer layer and the ambient temperature, respectively. The model proposed by Petela has been a subject of debate since the day of its publication, mainly because of the consideration of radiation as thermal or radiant energy. In addition to this, the cylinder-piston system is an idealised model that considers the environment as producing isotropic black-body radiation at constant pressure, which is far from the actual behaviour of the terrestrial environment.

In the same year, Spanner [30] proposed a different model for the exergy factor of undiluted radiation. The expression was based in a different approach than Petela's, yet considering the same system as depicted in Figure 1. The main difference between Petela's and Spanner's models concerns the definition of the work produced during the expansion of the system. While Petela's model describes the work as useful work, Spanner's considers absolute work,

$$W_{1-2} = W_u + W_e \quad (4)$$

where  $W_u$  is the useful work and  $W_e$  is the work developed against the environment. Since  $W_e$  is unavailable, the exergy factor  $\psi_s$  of the system is considered as follows,

$$\psi_s = \frac{W_{1-2}}{U_1} = 1 - \frac{4}{3} \left( \frac{T_2}{T_1} \right) \quad (5)$$

As noted, the expression proposed by Spanner is similar to the one developed by Petela; however, it has one term less. Nevertheless, it is important to note that an inconsistency is observed in Spanner's formulation, since the expression becomes negative for  $T_1 > 3/4 T_2$ . This restriction means that the temperatures  $T_1$  and  $T_2$  cannot constitute a small temperature ratio.

Some years later Press [31] analysed the maximum useful work that can be extracted from beam radiation, aiming to determine the difference with respect to the maximum useful work of undiluted radiation. The author considered an idealised cylinder-piston system, equivalent to Petela's. Analogously, through an adiabatic expansion, work is produced until reaching an equilibrium with the environment. The maximum useful work that the system can deliver is governed by the following equation,

$$G(T_e) = E - ST_e + \frac{1}{3} a T_e^4 \quad (6)$$

where  $E$  is the radiative energy,  $S$  the radiative entropy,  $T_e$  the ambient temperature,  $a$  the radiation constant and  $G(T_e)$  the total Gibbs free energy in the system. The radiative energy and entropy are computed by considering the volume density of photons as the sum of different diluted black body contributions,

$$E = a T^4 \left( \frac{\Omega}{4\pi} \right) \varepsilon \quad (7)$$

$$S = \frac{4}{3} a T^3 \left( \frac{\Omega}{4\pi} \right) \varepsilon (0.9652 - 0.2777 \ln \varepsilon - \varepsilon \cdot (0.0348 + f(\varepsilon))) \quad (8)$$

where  $\varepsilon$  is the dilution factor,  $\Omega$  the solid angle and  $f(\varepsilon)$  is a piece-wise function where:  $f(\varepsilon < 0.01) = 0$ ,  $f(1) = 0$ ,  $f(0.1) = 0.0114$  and  $f(0.01) = 0.012$ . The beam radiation

occupies a fractional solid angle that represents the size of the Sun's disk in the sky for an observer on Earth's surface ( $\Omega/4\pi = 5.4 \times 10^{-6} \equiv \delta$ ). The maximum useful work is calculated considering the expression of Equations (6)–(8), as follows,

$$G(T_e) = \delta a T_1^4 \left[ 1 - \frac{4}{3} \frac{T_2}{T_1} + \frac{1}{3} \left( \frac{T_2}{T_1} \right)^4 \right] \quad (9)$$

where  $T_1$  is the temperature of the source (Sun) and  $T_2$  the ambient temperature. Press considered the term in brackets of Equation (9) as the maximum useful work from beam radiation  $\psi_{Pr}$ , which is the expression that resulted from Petela's work ( $\psi_P = \psi_{Pr}$ ). The function  $f(\epsilon)$  that Press described is not explicitly defined, but rather expressed as a constant for different intervals of the dilution factor.

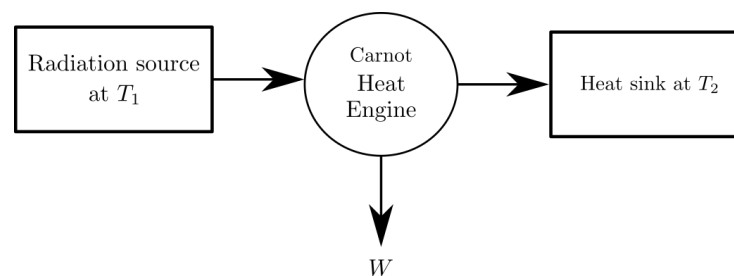
In 1978, Parrott [32] proposed a new expression for the exergy of undiluted solar radiation taking into account the directional component of the radiation. Parrott considered a volume  $V$  containing radiation the direction of propagation of which is limited to a cone of half angle  $\delta$ , representing the cone subtended by the solar disk. By performing a thermodynamic analysis as in a piston-cylinder, Parrott determined that the maximum useful work done by the black-body radiation considering the direction of the radiation is

$$\psi_{Pa} = 1 - \frac{4}{3} \frac{T_2}{T_1} (1 - \cos \delta)^{\frac{1}{4}} + \frac{1}{3} \left( \frac{T_2}{T_1} \right)^4 \quad (10)$$

As depicted in Equation (10), the model proposed by Parrott has one additional term more than Petela's. In fact, both models give the same numerical values only when the solid angle is equivalent to  $\delta = \pi/2$ . Parrott considered the radiation as isotropic and uniformly distributed in the subtended cone of the Sun. Thus, this model does not consider any scattering or absorption of the black-body radiation as it passes through the atmosphere, which is not correct.

Jeter [33,36], in 1981, considered a Carnot heat engine, as depicted in Figure 2, that receives energy from a radiative source at a temperature  $T_1$ . Then, this radiation is converted into work by a Carnot heat engine, where part of the heat is released to a heat sink at ambient temperature  $T_2$ . Hence, the efficiency of the system proposed by Jeter  $\psi_{Je}$  is the well-known Carnot efficiency,

$$\psi_{Je} = 1 - \frac{T_2}{T_1} \quad (11)$$



**Figure 2.** Carnot heat engine receiving radiation and converting it into work [33].

In the idealised system proposed by Jeter, it is considered that thermal radiation has an equivalent definition as heat, which means his approach implies that the exergy of undiluted radiation is the Carnot efficiency. However, the radiative energy of the black-body radiation is different from the thermal energy. It is because of the above that the model of Jeter considers the Sun as a thermal source and not a radiative source.

The models mentioned above have been a subject of debate since the date of their publication. As an example, Gribik and Osterle [37] in 1984 compared the models proposed by Petela, Spanner, Parrott and Jeter. Gribik and Osterle argued that Parrott's model is not correct, because the assumption of considering the radiation passing through the cone as

isotropic black-body radiation is not correct, since the black-body radiation has an energy and spectral entropy that depends on its frequency. The model developed by Jeter was also considered incorrect since it considers the radiation as a flow, which is associated with a gas, but does not correspond to the behaviour of a photon gas. Finally, the model of Petela was directly compared with Spanner's, with the conclusion that the model of Spanner is the "correct" one because it considers that the radiation is destroyed when the temperature  $T_1$  drops to reach thermal equilibrium with  $T_2$ .

Bejan [38] in 1987 attempted to unify the theories proposed by Petela, Spanner and Jeter. After analysing each theory separately, the author concluded that all theories were correct in themselves and are related, since they all consider black-body radiation as isotropic, which comes from a high-temperature radiative source. The differences in each model arise from the ways they describe the work produced by thermal radiation and the conception of an appropriate model for the idealised system.

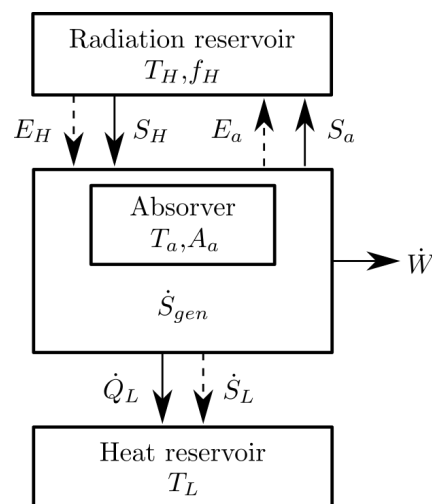
In 2002, Wright et al. [39] revisited Petela's model, analyzing its assumptions in depth, and concluded that the model represents the exergy of black-body radiation and the upper limit for converting solar radiation into useful work. The authors showed that the reversible transformation of black-body radiation into useful work is theoretically possible. Consequently, it is ensured that the exergy of the black-body radiation is equivalent to the exergy of the radiation enclosed in the idealised cylinder-piston system (Figure 1). Furthermore, the authors showed that the classical definition of the environment is sufficient to account for the thermal radiation, demonstrating that the environment defined by Petela serves to encapsulate and isolate the thermal radiation inside the cylinder.

In 2003, Petela [40] carried out a revision of his own model, analyzing the contributions from Spanner and Jeter. In his analysis, the author concluded, like Bejan, that all the models are correct and describe one type of work. However, the work delivered by each of these models is different. Spanner's model considers absolute work, whereas Jeter's, the net work of a heat engine, while the model of Petela [24] allows determination of the useful work from undiluted radiation exergy. Petela [40] concluded that the exergy of radiation (behaving as matter) exists at a certain instant, independently of what occurs at the next instant. Furthermore, Petela proposed a modification of the classical idealisation of a black-body radiation contained in a cylinder piston, to consider a system of two radiating surfaces where emission and absorption occur.

In 2008, Badescu [41] analyzed the exergy of solar radiation considering a different approach, considering quantum theory to derive an expression for the exergy of black-body radiation. The author based his analysis on the classical Wien theory and Planck quantum theory. An analysis was carried out considering the Planck occupation number and the Bose statistical entropy. In this way, the author concluded that the exergy expression for solar radiation is equivalent to Petela's expression. In addition to that, by considering Wien's occupancy number and Boltzmann's entropy, he finally arrived at Jeter's expression. This difference comes from the consideration of the energy state occupation number, since, according to Wien's theory, the radiation is composed of boltzon particles, while Planck's theory assumes it is composed of bosons. This new approach to radiation exergy proved to be compatible with thermodynamic analyses developed to date.

Subsequently, in 2014, Badescu [34,35] proposed a general formulation that included the different models of undiluted radiation exergy postulated up to that date. To this end, he proposed an idealisation of a reversible engine that generates useful work from incident radiation (Figure 3). The analysis considered, as a case study, the work  $\dot{W}$  produced from heat transferred from a high-temperature black-body radiation reservoir  $T_H$ , and releasing heat to a low-temperature heat sink  $T_L$ . In this system, the absorber is a Lambertian surface  $A_a$  at temperature  $T_a$  receiving radiation from all of the hemisphere. The energy and entropy emitted by the radiation reservoir are defined as  $E_H$  and  $S_H$ , respectively. Furthermore, the energy and entropy re-emitted by the absorber are defined as  $E_a$  and  $S_a$ , respectively.  $\dot{S}_{gen}$  is the entropy generated in the heat engine and  $\dot{Q}_L$  and  $\dot{S}_L$  are the heat and entropy transferred to the heat reservoir.





**Figure 3.** Idealised system proposed by Badescu for extracting useful work from a radiation reservoir [34,35].

The geometric factor of the radiation reservoir is a function of the solid angle ( $\Omega = 2\pi(1 - \cos\delta)$ ) and is expressed as,

$$f = \frac{\Omega}{\pi} \left( 1 - \frac{\Omega}{4\pi} \right) \cos\theta_z \quad (12)$$

where  $\delta$  is half the angle of the subtended cone of the sphere as seen from the observer, and  $\theta_z$  is the zenith angle. The geometric factor of the absorber is  $f_a = 1$ , which means that the absorber is receiving radiation over the whole hemisphere. The energy and entropy are defined as  $E = f\sigma T^4$  and  $S = \frac{4}{3}f\sigma T^3$ , respectively. The first and second law balances of the system are, respectively,

$$A_a E_H - A_a E_a - \dot{Q}_L = \dot{W} \quad (13)$$

$$A_a S_H - A_a S_a - \dot{S}_L + \dot{S}_{gen} = 0 \quad (14)$$

Hence, the efficiency of the work extractor ( $\eta_{Ba}$ ) in Figure 3 is represented as

$$\eta_{Ba} = \frac{\dot{W}}{\dot{Q}_H} = 1 - \frac{A_a E_a + \dot{Q}_L}{A_a E_H} \quad (15)$$

where  $\dot{Q}_H$  is the heat received by the absorber. The work  $\dot{W}$  is positive only if  $\dot{E}_H \geq \dot{E}_a$  and  $\dot{Q}_L \geq 0$ . Since the maximum work is obtained in a reversible process, it is assumed that  $\dot{S}_{gen} = 0$ . Therefore, the maximum efficiency of the system  $\psi_{Ba}$  is defined as

$$\psi_{Ba} = 1 - \frac{4}{3} \frac{T_2}{T_1} + \frac{1}{3f_H} \left( \frac{T_2}{T_1} \right)^4 \quad (16)$$

where  $f_H$  is the geometric factor of the heat reservoir.

Equation (16) describes the maximum work that can be extracted from a radiation reservoir when interacting with a heat sink. The equation ranges between a maximum value of 1 when  $\frac{T_2}{T_1} \rightarrow 0$  and a minimum of  $1 - f_H^{\frac{1}{3}}$  for  $\frac{T_2}{T_1} = f_H^{\frac{1}{3}}$ . The scenario for  $f_H < \left(\frac{T_2}{T_1}\right)^3$  is not possible because the work delivered by the system becomes negative, implying that the system consumes work instead of delivering it.

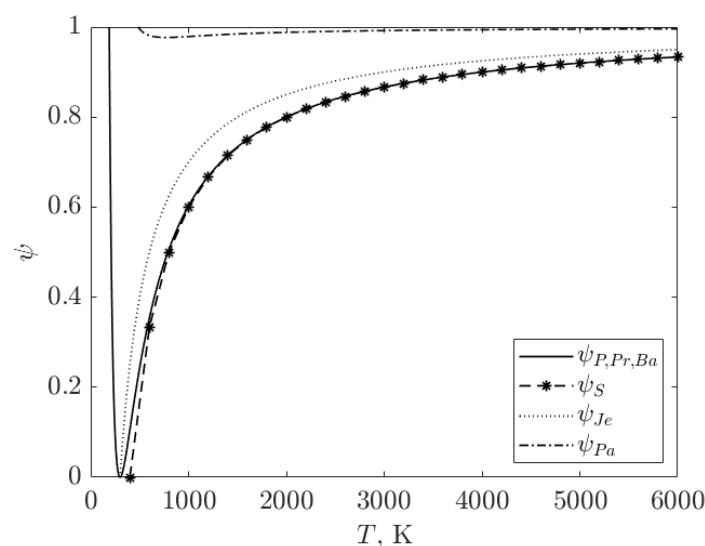
One year later Badescu [42] reported a revision of the model, comparing its results against the models proposed by Petela and Jeter. In this work, it is shown that Equation (16) might be transformed into Equation (3), when the geometric factor of the heat reservoir is equal to 1. Furthermore, if  $f_H = \left(\frac{T_2}{T_1}\right)^3$ , the expression developed by Badescu is equivalent

to the model proposed by Jeter. Hence, the equation proposed by Badescu provides a general formulation for the exergy factor of undiluted black-body radiation, based on an arbitrary geometrical factor and the temperatures of the radiation reservoir and the heat sink. Moreover, the formulations by Petela and Jeter represent a particular case for the general formulation reported by Badescu.

As described above, there are different approaches to describe the exergy of undiluted solar radiation, though all of them consider that there is no entropy generation by the medium as it passes through. These models are idealisations of thermodynamic systems where the black-body radiation is typically considered as enclosed in a cylinder-piston system with perfectly reflecting walls. Of the different models previously described, the one that has achieved a consensus over the years, that gives the exergy factor of the undiluted solar radiation, is the model proposed by Petela [24,40]. This model has been ratified by other work, such as that of Bejan [38], Wright et al. [39] and Badescu [42].

#### *Assessment of the Expressions for Undiluted Radiation*

To conduct an evaluation of the differences between the undiluted solar radiation exergy models, an assessment was applied to the exergy factor among the models of Petela  $\psi_P$ , Press  $\psi_{Pr}$ , Badescu  $\psi_{Ba}$ , Spanner  $\psi_S$ , Jeter  $\psi_{Je}$  and Parrott  $\psi_{Pa}$  estimated in a temperature range. Figure 4 shows the radiative exergy factors considering a constant ambient temperature  $T_2 = 300$  K and a half-angle of the subtended cone as  $\delta = 0.005$  rad. The models of  $\psi_P$  and  $\psi_{Pr}$  are the same, and the expression  $\psi_{Ba}$  is equal to  $\psi_P$  when a geometrical factor of the heat reservoir of  $f_H = 1$  is considered. The radiative temperature  $T_1$ , which theoretically represents the black-body temperature, is analysed in the range from 0 K to 6000 K. It is observed that the exergy factor proposed by  $\psi_S$  is negative when the radiative temperature is lower than 300 K. This situation also occurs with the model proposed by  $\psi_{Je}$ , which takes negative values at temperatures below 400 K. The models proposed by  $\psi_{P,Pr,Ba}$  and  $\psi_{Pa}$  diverge in the ranges lower than 300 K and 500 K, respectively. For temperatures higher than 300 K, the models proposed by  $\psi_{P,Pr,Ba}$ ,  $\psi_S$  and  $\psi_{Je}$  present similar behaviour, allowing observation of a strong increase in the exergy factor up to 2000 K. For higher temperatures, asymptotic behaviour is observed for all models.



**Figure 4.** Comparison of the radiation exergy for Petela, Press, Badescu, Spanner, Jeter and Parrott assuming  $T_2 = 300$  K,  $f_H = 1$  and  $\delta = 0.005$  rad.

It should be noted that the model proposed by  $\psi_{Je}$  always delivers higher values than the models of  $\psi_{P,Pr,Ba}$ . In turn, the latter give higher numerical values than  $\psi_S$ : ( $\psi_{Je} > \psi_{P,Pr,Ba} > \psi_S$ ). The behaviour of the model proposed by  $\psi_{Pa}$  is quite different from the others, since it delivers an exergy factor of 0.98 at 1000 K, while  $\psi_S$ ,  $\psi_{P,Pr,Ba}$  and  $\psi_{Je}$  give



values of 0.60, 0.60 and 0.70, respectively. As the radiative temperature increases, the model of  $\psi_{Pa}$  increases very slowly, with its curve on the graph presenting a very shallow slope. At the theoretical black-body temperature of 6000 K, the models of  $\psi_S$  and  $\psi_{P,Pr,Ba}$  equalise with a radiative exergy factor of 0.93.  $\psi_{Je}$  for this same temperature gives a value of 0.95, while  $\psi_{Pa}$  produces a value of 0.99. Since the exergy of the radiation is obtained by means of a thermodynamic idealisation of a thermal engine, the ideal efficiency that this engine can develop, according to the second law of thermodynamics, is the Carnot efficiency ( $\psi_{Je}$ ), so the model of  $\psi_{Pa}$  must be considered as inconsistent because it gives an exergy factor higher than Carnot's.

### 3. Diluted Solar Radiation Exergy

The idealised thermodynamic models described in the previous section were developed assuming that the medium is non-participating and the energy emitted by the Sun reaches the Earth's surface, disregarding any loss. However, the Earth's atmosphere constitutes a participating medium, where several phenomena affect the intensity of solar radiation. Indeed, solar radiation, as an electromagnetic wave composed of photons, suffers the phenomena of scattering, reflection, and absorption due to the different components in the atmosphere. Solar radiation presents an electromagnetic spectrum that entails different magnitudes of radiative power from the ultra violet to infrared wavelengths. Thus, different kinds of studies have been developed to estimate the exergy of solar radiation, as can be seen in Table 2, including attenuation effects, which can be divided into two main groups: those studies that consider a thermodynamic analysis between a radiation source and a sink, and those that consider an electromagnetic approach based on Planck equations. Hence, the following sections describe studies of diluted solar radiation exergy, divided into the aforementioned categories, analysing the main assumptions and methodology for each study. At the end of this section, a comparison is provided between models that are similar in their conceptions and assumptions with the aim of clearly highlighting the differences that arise from the different approaches, considering a wavelength and temperature range similar to the range of solar radiation.

**Table 2.** Diluted solar exergy models where  $\psi$  is the exergy factor and  $B$  the exergy flux.

Author	Expression	Radiation Type
Landsberg and Tonge [25,43]	$\psi_{L\&T} \leq 1 - \frac{4}{3} T \frac{\beta_{p1} T_{p1}^{*3} + \beta_{p2} T_{p2}^{*3}}{\beta_{p1} T_{p1}^{*4} + \beta_{p2} T_{p2}^{*4}}$	Black-body
Wright et al. [44,45]	$B_{Wr} = E - T_0 \left( \frac{4}{3} \left( \frac{\sigma}{\pi} \right)^{\frac{1}{4}} E^{\frac{3}{4}} \right) + \frac{\sigma}{3\pi} T_0^4$	Non-black-body
Candau [46]	$B_{Ca,\lambda} = E_{\lambda} - E_{0,\lambda} - T_0 (S_{\lambda} - S_{0,\lambda})$	Monochromatic non-black-body
Chen and Mo [47]	$B_{Ch,\lambda} = E_{\lambda} \left( 1 - \frac{T_0}{T_{\lambda}} \right)$	Monochromatic black-body
Zamfirescu and Dincer [48]	$\psi_{Z\&D} = 1 - \frac{T_0}{T_s} \frac{I_{sc}}{I_{T0}}$	Black-body
Zhou et al. [49]	$\psi_Z = 1 - \frac{k}{k-n} \frac{T_0}{T_{\lambda}} + \frac{n}{k-n} \left( \frac{T_0}{T_{\lambda}} \right)^k$	Monochromatic black-body
Badescu [50]	$\psi_{Ba,1} \equiv \alpha_a \left( 1 - \frac{a}{x} \right) \left( 1 - \frac{x^4}{f^4} \right)$	Black-body
Chu and Liu [51]	$\psi_{g,\lambda}^{TS} = \frac{B_{b,\lambda}^{TS} + B_{d,\lambda}^{TS}}{E_{b,\lambda}^{TS} + E_{d,\lambda}^{TS}}$	Monochromatic non-black-body
Petela [52]	$B_{b,\Omega,\lambda} = (E_{b,0,\lambda})_T - (E_{b,0,\lambda})_{T_0} - T_0 ([S_{b,0,\lambda}(E_{b,0,\lambda})]_T - [S_{b,0,\lambda}(E_{b,0,\lambda})]_{T_0})$	Black-body
Pons [53]	$B_{Pons,g} = B_{dr} + B_{df}$	Monochromatic non-black-body

Table 2. Cont.

Author	Expression	Radiation Type
Makhanlall [54]	$\begin{aligned} \psi_{\lambda}(r, s) &= \kappa_{g,\lambda} \left[ 1 - \frac{T_0}{T_{\lambda}(r,s)} \right] \\ &\quad (I_{\lambda}(r,s) - I_{bg,\lambda}[T_g(r)]) - \\ &\quad \kappa_{p,\lambda} \left[ 1 - \frac{T_0}{T_{\lambda}(r,s)} \right] (I_{\lambda}(r,s) - \\ &\quad I_{bp,\lambda}[T_p(r)]) - \sigma_{p,\lambda} \left[ 1 - \frac{T_0}{T_{\lambda}(r,s)} \right] \\ &\quad \left[ I_{\lambda}(r, s) - \frac{1}{4\pi} \int_{4\pi} I_{\lambda}(r, s') \Phi(s, s') d\Omega' \right] \end{aligned}$	Monochromatic non-black-body

### 3.1. Thermodynamic Approach

Landsberg and Tonge [25,43], in 1979, evaluated the maximum energy content that solar radiation can have by considering its spectral components and the atmosphere as a participating medium. For this purpose, the authors developed an expression that represents the energy attenuation in terms of entropy fluxes. The authors considered the energy ( $E_{\epsilon,T}$ ) and entropy ( $S_{\epsilon,T}$ ) of attenuated black-body spectral radiation as

$$E_{\epsilon,T} = \frac{B\epsilon\sigma T^4}{\pi} \quad (17)$$

$$S_{\epsilon,T} = \frac{4}{3} \frac{B\epsilon X(\epsilon)\sigma T^3}{\pi} \quad (18)$$

where  $\epsilon$  is the emissivity of the source of diluted black-body radiation, called the “dilution factor”,  $T$  is the temperature of the radiation source, called “undiluted”, and  $\sigma$  is the Stefan–Boltzmann constant.  $B$  is an expression in the form of  $B = \int \cos \theta_z d\Omega$ , where  $\theta_z$  is the zenith angle and  $\Omega$  is the solid angle.  $X(\epsilon)$  is a function obtained by considering the spectral entropy for a diluted black-body radiation in the complete wavelength range,

$$X(\epsilon) = \frac{45}{4\epsilon\pi^4} \int_0^\infty y^2 \cdot [(x+1) \cdot \ln(x+1) - x \cdot \ln(x)] dy \quad (19)$$

where  $x$  is the Bose factor and  $y$  is an expression defined as  $y = \frac{hv}{kT}$ .  $h$  is Planck’s constant,  $v$  the frequency and  $k$  is the Boltzmann’s constant. Landsberg and Tonge were the first to find a numerical solution to the function  $X(\epsilon)$ , which is only valid for emissivities lower than 0.1, and is expressed by the following expression,

$$X(\epsilon) = 0.9652 + 0.2777 \ln(\epsilon^{-1}) + 0.0511\epsilon \quad (20)$$

The major contribution by Landsberg and Tonge was indeed that numerical solution because it allows calculation of the black-body radiative entropy for a specific range of dilution factors. Thus, such a solution does not depend on the direction of the photons, nor on the wavelength. However, the validity range of the numerical solution is narrow, considering that the dilution factor ranges from 0 to 1.

In addition, Landsberg and Tonge proposed an expression for the exergy of the diluted solar radiation considering an idealised two-pump system where the solar radiation is viewed as a flow that is transported by two “pumps”: one for the direct and one for the diffuse component. These pumps take the black-body radiation to a receiver, where the radiation from the ambient is removed by a sink. The idealisation described before entails that the receiver only absorbs the radiation from the first and second pump. The first pump (direct radiation) is considered as undiluted and comprises a solid angle of  $\Omega$  subtended from the Sun to the Earth, a factor  $t$  is linked to the atmospheric attenuation and  $\alpha$  is the absorptivity of the receiver. The pump corresponding to the diffuse radiation involves a full solid angle of  $4\pi$ , where a dilution factor is considered due to scattering defined as

$\Omega/4\pi$ . Using this idealisation, the maximum conversion efficiency of the Landsberg and Tonge's system ( $\psi_{L\&T}$ ) is defined as

$$\psi_{L\&T} \leq 1 - T \frac{S_{p1} + S_{p2}}{E_{p1} + E_{p2}} \quad (21)$$

where  $S_{p1}$ ,  $E_{p1}$ ,  $S_{p2}$  and  $E_{p2}$  are the entropy and energy of the first and second pumps, respectively. The expression (21) in terms of the temperature can be rewritten as follows,

$$\psi_{L\&T} \leq 1 - \frac{4}{3} T \frac{\beta_{p1} T_{p1}^{*3} + \beta_{p2} T_{p2}^{*3}}{\beta_{p1} T_{p1}^{*4} + \beta_{p2} T_{p2}^{*4}} \quad (22)$$

where  $\beta = B\sigma\epsilon X(\epsilon)^4/\pi$  and  $T^*$  is the effective temperature of the diluted black-body radiation defined as  $\frac{1}{T^*} \equiv \frac{X(\epsilon)}{T}$ . The work developed by Landsberg and Tonge was the first to denote black-body radiation as diluted and undiluted, where the undiluted radiation corresponds to the direct, and diluted the diffuse, component. Landsberg and Tonge [25] assumed as constant both the dilution factor and the absorptivity of the receiver, disregarding the spectral distribution of the radiation.

Wright et al. [44,45], in 2002, discussed the validity of the assumption established by Petela, where the conversion of non-black-body radiation is considered as reversible. The authors showed that if the processes that the radiation undergoes present internal irreversibilities in a non-equilibrium system, the models give results that are theoretically not possible to achieve. They attributed this effect to the fact that the Gouy–Stodola theorem [55] cannot be considered due to the nature of the entropy of non-black-body radiation in a non-equilibrium system. Furthermore, it was suggested that reversible non-black-body radiation conversion is not theoretically possible because the interaction of non-black-body radiation with matter is an inherently irreversible process with entropy generation in a non-equilibrium system. Thus, Wright et al. proposed an expression for the non-black-body radiative exergy, based on a cylinder-piston system considering non-black-body radiation inside the cylinder. The proposed expression is as follows,

$$B_{Wr} = E - T_0 \left( \frac{4}{3} \left( \frac{\sigma}{\pi} \right)^{\frac{1}{4}} E^{\frac{3}{4}} \right) + \frac{\sigma}{3\pi} T_0^4 \quad (23)$$

where  $B_{Wr}$  is the non-black-body radiation exergy in  $W/(m^2 sr^2)$ ,  $E$  is the spectral energy and  $T_0$  is the ambient temperature. Due to the fact that radiation at the Earth's surface has a different spectral distribution than black body radiation, it is necessary to estimate the exergy value considering the actual spectrum and the irreversibilities generated by the atmosphere. The system described by Wright et al. aims to explain the behaviour of non-black-body radiation by means of a thermodynamic balance based on the second law of thermodynamics, just like the undiluted models. However, the system described assumes that the thermal radiation is isotropic and uniform, which is not its actual behaviour as its properties vary strongly with wavelength.

In 2003, Candau [46] proposed an expression for the exergy of monochromatic non-black-body radiation based on the idealisation of a Carnot engine operating between two radiation reservoirs with temperatures  $T_\lambda$  and  $T_0$ . The total work  $W$  that can be extracted from the reversible engine per unit etendue  $\theta$  is

$$W = \int_{T_0}^{T_\lambda} \left( 1 - \frac{T_0}{\theta} \right) \frac{dE_\lambda}{d\theta} d\theta \quad (24)$$

where  $E_\lambda$  is the spectral radiative intensity. The exergy of the monochromatic non-black-body radiation is produced when the maximum work is extracted from the Carnot engine. Therefore, the work (and exergy) of a reversible engine is assessed through Equation (24),

$$B_{Ca,\lambda} = E_\lambda - E_{0,\lambda} - T_0(S_\lambda - S_{0,\lambda}) \quad (25)$$

which is one of the results reported by Karlsson in 1982 with an electromagnetic approach. Candau also explained the scenario of a reversible system of monochromatic radiation coming into contact with a grey surface. Some of the incident radiation is reflected while some is refracted as it passes through the surface. If a real physical process is considered, the entropy of the reflected and refracted radiation should be included and it is found that the sum of them is larger than the entropy of the incident radiation. This implies that there was entropy generation in a process that was previously considered reversible.

Chen and Mo [47] developed a methodology for assessing the exergy of the photosynthesis, aiming to determine the effective temperature of solar radiation. The expression for the exergy content of monochromatic black-body radiation ( $B_{ch,\lambda}$ ) is defined considering a system comprising a Carnot engine operating between two radiation reservoirs at temperatures  $T_\lambda$  and  $T_0$ , as follows,

$$B_{Ch,\lambda} = E_\lambda \left( 1 - \frac{T_0}{T_\lambda} \right) \quad (26)$$

where  $E_\lambda$  is the radiation spectral energy,  $T_0$  the ambient temperature and  $T_\lambda$  the monochromatic temperature of the radiation source. The authors defined the monochromatic temperature as Wien's displacement law,  $\lambda T_\lambda = c_3$ . After solving the exergy integral of the monochromatic black-body radiation  $B_{ch} = \int_0^\infty B_{ch,\lambda} d\lambda$ , they found that the constant  $c_3$  has a value equal to  $c_3 = 5.33016 \times 10^{-3}$  mK. The definition of the thermodynamic system comprising a Carnot engine, led to an exergy expression equivalent to the Carnot efficiency, as previously defined by Jeter. Chen and Mo introduced the assumption that thermal radiation behaves as heat, which induced the model to perform as a thermal model and not as a radiative model.

Zamfirescu and Dincer [48] analysed the temperature associated with the solar radiation reaching a collector coupled to a thermal engine located on Earth's surface, considering that different attenuation and dissipation effects occur that cannot be modelled. Therefore, the authors considered the atmosphere as a heat and work sink, and modelled a thermal engine converting the incident radiation into useful work. The model considers the radiation reaching the outer layer of the Earth's atmosphere equivalent to the solar constant ( $I_{sc}$ ), and emitted at the same temperature as the Sun's outer layer ( $T_s$ ). The dissipation effect in the atmosphere was modelled as an irreversible thermodynamic cycle that acts as a "thermodynamic break", dissipating all the work produced. Hence, this thermodynamic break has an efficiency ( $\eta_{dis}$ ), operating between the Sun's and the collector temperature ( $T_c$ ), as follows,

$$\eta_{dis} = \frac{W_{dis}}{I_{sc}} = \frac{I_{sc} - I_{T0}}{I_{sc}} \quad (27)$$

The reversible work generated by the thermal engine ( $\eta_{rev}$ ) is,

$$\dot{W}_{rev} = \left( 1 - \frac{T_0}{T_c} \right) I_{T0} \quad (28)$$

where  $I_{T0}$  is the incident radiation normal to the collector. The maximum work is reached when the collector temperature is at its maximum, which means that  $T_c^{max} = \frac{I_{T0}}{I_{sc}} T_s$ . Replacing the previous expression in (28), it comes to the exergy of solar radiation ( $\psi_{Z\&D}$ ) proposed by Zamfirescu and Dincer,

$$\psi_{Z\&D} = 1 - \frac{T_0}{T_s} \frac{I_{sc}}{I_{T0}} \quad (29)$$

The analysis performed by Zamfirescu and Dincer follows the same criteria as the idealised undiluted radiation models. In this case, by bringing an earlier process of loss of useful work into the system, it introduces into the equation of Zamfirescu and Dincer

the clearness index  $\left(\frac{I_{sc}}{I_{T0}}\right)$  which represents the ratio of radiative energy between the extraterrestrial radiation and the normal total radiation.

In 2017, Zhou et al. [49] discussed the validity of expression for the exergy of black-body and monochromatic radiation. The authors presented a review regarding the models for undiluted radiation, concluding that a valid model for calculating the exergy of black-body radiation is the expression of Petela. Then, Zhou et al. developed an expression for monochromatic radiation using an infinite-stage Carnot engine for a reversible non-dissipative process. The useful work obtained from this system is expressed as,

$$W_u = \int_{v_0}^v h \left(1 - \frac{T_0}{T_v}\right) dv \quad (30)$$

where  $v$  is the frequency,  $h$  the Planck's constant,  $T_0$  the ambient temperature and  $T_v$  the equivalent temperature of the photon is represented in terms of frequency as

$$T_v^k = \frac{f T^m}{c^n} v^n \quad (31)$$

where  $T$  is the radiative temperature,  $c$  the speed of light in vacuum and  $k, f, m$  and  $n$  are constants. Thus, the proposed expression for the exergy of monochromatic black-body radiation is

$$\psi_Z = 1 - \frac{k}{k-n} \frac{T_0}{T_\lambda} + \frac{n}{k-n} \left(\frac{T_0}{T_\lambda}\right)^k \quad (32)$$

The equation of Petela [24] is a particular case of Equation (32), when the useful work is integrated over the full wavelength spectra. The infinite-stage Carnot engine used to derive the exergy expression does not include a specific term that could include atmospheric attenuation. Therefore, the expression of Zhou et al. is only valid for a non-participating medium. Badescu [50], in 2018, developed a model to estimate the conversion efficiency from diluted black-body radiative energy into work. Badescu defined a system called the “radiation energy converter” which operates between a high-temperature radiation reservoir ( $T_H$ ) and a low-temperature reservoir ( $T_L$ ). The radiation energy converter involves a radiation absorber and a work extractor (WE). The radiation energy conversion efficiency of the system is

$$\eta \equiv \frac{\dot{W}}{A_a \phi_H} = \left(1 - \frac{T_L}{T_a}\right) \left(\frac{\phi_{H,abs} - \phi_a}{\phi_H} - \frac{\dot{Q}_{loss}}{A_a \phi_H}\right) - \frac{T_L \dot{S}_{g,WE}}{A_a \phi_H} \quad (33)$$

where  $T_a$  is the temperature of the absorber,  $A_a$  the surface area of the absorber,  $\phi_{H,abs}$  the diluted black-body radiation absorbed,  $\phi_a$  the diluted black-body radiation emitted,  $\phi_H$  the diluted black-body received,  $\dot{Q}_{loss}$  the heat losses to the heat reservoir and  $\dot{S}_{g,WE}$  the entropy generation within the work extractor. For maximum conversion efficiency, heat losses and entropy generated must be zero ( $\dot{Q}_{loss} = 0$  and  $\dot{S}_{g,WE} = 0$ ). Thus, the expression in Equation (33) becomes,

$$\psi_{Ba,1} \equiv \alpha_a \left(1 - \frac{a}{x}\right) \left(1 - \frac{x^4}{i^4}\right) \quad (34)$$

where  $\alpha_a$  is the absorptance of the absorber and  $a, x$  and  $i$  are notations for  $a = T_L/T_H$  and  $x = T_a/T_H$ . The term  $i$  is called the “interaction factor”, and is expressed as follows,

$$i = \left(\frac{f_H \varepsilon_H}{f_a \varepsilon_a} \alpha_a\right)^{\frac{1}{4}} \quad (35)$$

$f_H$  is the view factor of the radiation reservoir from the absorber,  $\varepsilon_H$  the dilution factor from the radiation reservoir,  $f_a$  and  $\varepsilon_a$  are the geometric factor and the dilution factor of the

absorber, respectively. Badescu reported that for determining  $\psi_{Ba,1}$ , the optimal value  $x_{opt}$  should be found from the expression

$$x_{opt}^5 - \frac{3a}{4}x_{opt}^4 - \frac{i^4}{4}a = 0 \quad (36)$$

Badescu also analysed a secondary upper bound for the efficiency, independent of  $x_{opt}$ . This secondary efficiency is higher than the previous one ( $\psi_{Ba,1} \leq \psi_{Ba,2}$ ) and is expressed as

$$\psi_{Ba,2} \equiv \alpha_a \left[ 1 - \frac{4}{3} \left( \frac{a}{i} \right) + \frac{1}{3} \left( \frac{a}{i} \right)^4 \right] \quad (37)$$

The expression in Equation (37) can be solved analytically. For the case of undiluted black-body radiation,  $i = 1$  and the expression (37) is reduced to the expression proposed by Petela [24]. The system proposed by Badescu allows consideration of the atmospheric attenuation process as the absorption and emission process in a radiation absorber. However, the spectral component of the radiation is not considered. Moreover, as exemplified by Petela, the energy emitted by the absorber is a sum of the reflection in all directions and the emission by the body itself. In this case, Badescu considered radiation emitted by the absorber to be equivalent to its reflection, ignoring the absorber's emission due to its own temperature.

### 3.2. Electromagnetic Approach

The first analysis considering radiation as an electromagnetic wave was developed in 1982 by Karlsson [56], who proposed a spectral expression for the exergy of diluted solar radiation. It considered a system in which quasi-monochromatic radiation with a differential spectrum of frequencies ( $dv$ ) travels through a cone ( $d\Omega$ ), reaching perpendicularly to a differential surface ( $dY$ ). The total spectral energy and entropy of the radiation in this system are,

$$E = \left( \frac{2kv^2}{c^2} \right) [(1+n)\ln(1+n) - n\ln(n)] \quad (38)$$

$$S = \frac{2nhv^3}{c^2} \quad (39)$$

where  $v$  is the frequency,  $c$  the speed of light and  $n$  the mean occupation number of the quantum state. The black-body radiation temperature defined by Karlsson is,

$$T = \frac{hv}{k \cdot \ln \left[ \frac{2hv^3}{c^2 E} + 1 \right]} \quad (40)$$

where the surface  $Y$  has a temperature  $T_0$  and the spectral energy and entropy of  $E_0$  and  $S_0$ , respectively. It was applied to a thermodynamic balance based on the second law to derive an expression for the exergy flux of radiation:  $B_{K,\lambda} = E_\lambda - E_{0,\lambda} - T_0(S_\lambda - S_{0,\lambda})$ . Finally, considering Equations (38)–(40), and the definition of exergy efficiency ( $\psi = \frac{B}{E}$ ), the exergy factor of spectral radiation hold,

$$\psi_K = 1 - \frac{T_0}{T} + \frac{e^{\frac{hv}{kT}} - 1}{\frac{hv}{kT_0}} \ln \left( \frac{1 - e^{-\frac{hv}{kT}}}{1 - e^{-\frac{hv}{kT_0}}} \right) \quad (41)$$

The model developed by Karlsson delivers zero when  $T = T_0$  and is always positive for  $T \neq T_0$ . Hence, Petela's model represents a particular case of the Karlsson model by defining an average of the black-body radiation exergy  $\left( \frac{\text{Spectral exergy density}}{\text{Spectral energy density}} \right)$ . Equation (41) proposed by Karlsson establishes the exergy factor of monochromatic radiation, considering monochromatic radiation hitting a differential black body surface. This differential element produces a heat flux instead of useful work, as for the undiluted radiation models.



Chu and Liu [51], in 2009, carried out an analysis of the exergy of solar radiation applying the equation proposed by Candau (Equation (25)). The authors analysed the exergy of solar radiation considering terrestrial and extraterrestrial spectrums, considering the equations developed by Candau for the direct and diffuse components. Considering a horizontal surface where the incident radiation is extraterrestrial, the spectral exergy of the extraterrestrial solar radiation ( $B_{\lambda}^{ETS}$ ) is expressed as follows,

$$B_{\lambda}^{ETS} = \Omega \cos \theta_z [E_{\lambda}^{ETS} - E_{0,\lambda} - T_0(S_{\lambda}^{ETS}(E_{\lambda}^{ETS}) - S_{0,\lambda}(E_{0,\lambda}(T_0)))] \quad (42)$$

where  $\Omega$  is the solid angle of the Sun's disc,  $\theta_z$  the zenith angle,  $E_{\lambda}^{ETS}$  and  $S_{\lambda}^{ETS}$  are the extraterrestrial spectral intensity and the entropy of the black-body radiation, respectively. Whereas  $E_{0,\lambda}$  and  $S_{0,\lambda}$  are the spectral intensity and entropy of black-body radiation at temperature  $T_0$ , respectively. The exergy factor of extraterrestrial solar radiation is defined as

$$\psi_{\lambda}^{ETS} = \frac{B_{\lambda}^{ETS}}{E_{\lambda}^{ETS}} \quad (43)$$

The terrestrial solar radiation is divided into direct  $E_{b,\lambda}$  and diffuse  $E_{d,\lambda}$  spectral irradiance. Both components encompass different exergy content. The overall spectral irradiance  $E_{g,\lambda}$  incident on a horizontal surface is expressed as  $E_{g,\lambda} = E_{b,\lambda} + E_{d,\lambda}$ . The direct spectral radiation  $I_{b,\lambda}$  can be determined by geometrical considerations and considering the diffuse spectral radiation  $I_{d,\lambda}$ , assuming an isotropic hemisphere. Hence,

$$I_{b,\lambda} = \frac{E_{b,\lambda}}{\Omega \cos \theta_z} \quad (44)$$

$$I_{d,\lambda} = \frac{E_{d,\lambda}}{\pi} \quad (45)$$

Finally, the exergies of direct ( $B_{b,\lambda}^{TS}$ ) and diffuse ( $B_{d,\lambda}^{TS}$ ) terrestrial spectral radiation on a horizontal surface are,

$$B_{b,\lambda}^{TS} = \Omega \cos \theta_z [I_{b,\lambda} - I_{0,\lambda} - T_0(S_{\lambda}(I_{b,\lambda}) - S_{0,\lambda}(I_{0,\lambda}(T_0)))] \quad (46)$$

$$B_{d,\lambda}^{TS} = \pi [I_{d,\lambda} - I_{0,\lambda} - T_0(S_{\lambda}(I_{d,\lambda}) - S_{0,\lambda}(I_{0,\lambda}(T_0)))] \quad (47)$$

The exergy factors for the direct, diffuse, and global components of solar terrestrial radiation are shown below,

$$\psi_{b,\lambda}^{TS} = \frac{B_{b,\lambda}^{TS}}{E_{b,\lambda}} \quad (48)$$

$$\psi_{d,\lambda}^{TS} = \frac{B_{d,\lambda}^{TS}}{E_{d,\lambda}} \quad (49)$$

$$\psi_{g,\lambda}^{TS} = \frac{B_{b,\lambda}^{TS} + B_{d,\lambda}^{TS}}{E_{b,\lambda} + E_{d,\lambda}} \quad (50)$$

Using the simple model of the atmospheric radiative transfer of sunshine (SMARTS) software [57], the authors calculated the exergy of terrestrial and extraterrestrial solar radiation in the range of [0.28, 4.0], which is the range where the greatest amount of radiative energy is concentrated. Chu and Liu found that the exergy content of extraterrestrial radiation is always higher than that of terrestrial radiation for each wavelength. These results were expected due to the attenuation process occurring through the atmosphere.

In 2010, Agudelo and Cortés [58] revisited the fundamental concepts of the analysis of the second law of thermodynamics for thermal radiation. The article focused on describing the advances in the modelling of radiation's entropy and exergy, along with the processes of radiative transfer between surfaces. With respect to the exergy of thermal radiation,

the authors described the models developed for black-body and non-black-body radiation, analysing in depth the exergy of grey-body radiation. In the same year, Petela [52] introduced a new theory for thermal radiation between surfaces. The author considered a situation where a surface reflects most of the solar radiation it receives (snow, for instance). The radiosity of such a surface consists of the radiation reflected from the Sun, the radiation reflected from other surfaces, and its own emission. Therefore, the measurement of the radiosity should be close to the spectral emission from the Sun. Thus, any surface can emit black-body radiation, meaning that any surface emits black-body entropy and exergy. Due to this consideration, Petela defined a new concept called the “energetic emissivity” ( $\varepsilon_E$ ) of a surface, which is equivalent to the conventional emissivity ( $\varepsilon \equiv \varepsilon_E$ ). Therefore, it is defined as follows,

$$\varepsilon_E = \left( \frac{\int_{\lambda} \varepsilon_{E,\lambda} i_{b,0,\lambda} d\lambda}{\int_{\lambda} E_{b,0,\lambda} d\lambda} \right)_T \equiv \varepsilon \quad (51)$$

where  $\varepsilon_{E,\lambda}$  is the spectral energetic emissivity and  $E_{b,0,\lambda}$  is the monochromatic normal directional intensity. Similarly, the monochromatic entropy emissivity ( $\varepsilon_{S,\lambda}$ ) is defined as

$$\varepsilon_{S,\lambda} = \frac{S_{0,\lambda}}{S_{b,0,\lambda}} \quad (52)$$

where  $S_{0,\lambda}$  is the entropy of normal monochromatic directional intensity for a grey surface and  $S_{b,0,\lambda}$  is the entropy of normal monochromatic directional intensity for linearly polarised black-body radiation. The radiation exergy ( $B_{b,\Omega,\lambda}$ ) is based in Equation (25), which here is defined as the spectral exergy for a black radiation within a solid angle  $d\Omega$  and within a wavelength range  $d\lambda$ ,

$$B_{b,\Omega,\lambda} = (E_{b,0,\lambda})_T - (E_{b,0,\lambda})_{T_0} - T_0([S_{b,0,\lambda}(E_{b,0,\lambda})]_T - [S_{b,0,\lambda}(E_{b,0,\lambda})]_{T_0}) \quad (53)$$

where  $E_{b,0,\lambda}$  is the directional intensity of black-body monochromatic emission,  $T$  is the temperature of the surface and  $T_0$  the temperature of the environment. Equation (53) is an equivalent expression to that proposed by Candau and Karlsson in Equation (25). Petela defined the monochromatic exergy factor of black-body radiation ( $\psi_{P,\lambda}$ ) as follows,

$$\psi_{P,\lambda} = \frac{B_{b,\Omega,\lambda}}{E_{b,0,\lambda}} \quad (54)$$

Similarly, Petela defined the monochromatic exergy of grey surface emission ( $B_{\Omega,\lambda}$ ),

$$B_{\Omega,\lambda} = (\varepsilon E_{b,0,\lambda})_T - (E_{b,0,\lambda})_{T_0} - T_0([S_{b,0,\lambda}(\varepsilon E_{b,0,\lambda})]_T - [S_{b,0,\lambda}(E_{b,0,\lambda})]_{T_0}) \quad (55)$$

Equation (55) is the same as (54) but with the inclusion of the energetic emissivity ( $\varepsilon$ ) in the energy and entropy balances. Finally, Petela introduced a new concept called “exergetic emissivity”, which relates to the large difference in spectral exergetic content of grey surfaces compared to black surfaces. Thus, the monochromatic exergetic emissivity ( $\varepsilon_B$ ) is,

$$\varepsilon_{B,\lambda} = \frac{B_{\Omega,\lambda}}{B_{b,\Omega,\lambda}} \quad (56)$$

The equations proposed by Petela are only valid for an emitting surface because the emitted radiation of photon gas is always black. In his work, the author proposed three new concepts for the theory of thermal radiation: energetic emissivity, entropy emissivity and exergetic emissivity. In the case of the same temperature and wavelengths, the monochromatic entropy emissivity would be larger than the monochromatic energetic emissivity ( $\varepsilon_{S,\lambda} > \varepsilon_{E,\lambda}$ ). When the temperature is  $T > T_0$ , the exergetic emissivity is less than or equivalent to the energetic emissivity ( $\varepsilon_B \leq \varepsilon$ ). Finally, for  $T < T_0$  then  $\varepsilon_B \geq \varepsilon$ . This work contributed significantly to the understanding of surface radiation. However, the proposed concepts have no immediate practical application.

Pons [53] attempted to simplify the model proposed by Karlsson in which he included the instantaneous value of direct and diffuse solar radiation. The base expression for the exergy is  $\dot{B} = \dot{E} - T_0 \cdot \dot{S}$ , where  $\dot{B}$  is the exergy flux per unit time,  $\dot{E}$  the radiative density per unit time,  $T_0$  the temperature of the surrounding medium and  $\dot{S}$  the entropy density per unit time. The entropy of the direct and diffuse radiation is considered by the definition from Landsberg and Tonge (Equation (18)), which in this case is used as  $S = X(\epsilon)4E/3T$ , where  $X(\epsilon)$  corresponds to the expression (19),  $E$  is the radiative flux density and  $T$  is the temperature of the radiative flux. Pons found a numerical solution for  $X(\epsilon)$  that is only valid for a range of  $\epsilon$  for each component of the radiation. The range of the dilution factor ( $\epsilon$ ) of the direct and diffuse components is between 0.03 and 0.8 and between  $10^{-6}$  and  $10^{-5}$ , respectively. Therefore, the numerical solution considering the range is

$$X_{dr}(\epsilon_{dr}) = 0.973 - 0.275 \ln \epsilon_{dr} + 0.0273 \epsilon_{dr} \quad (57)$$

$$X_{df}(\epsilon_{df}) = 0.9659 - 0.2776 \ln \epsilon_{df} \quad (58)$$

The entropy flux for both components is as follows,

$$S_{dr} = X_{dr}(\epsilon_{dr}) \frac{4}{3} \frac{E_{dr}}{T_s} \quad (59)$$

$$S_{df} = X_{df}(\epsilon_{df}) \frac{4}{3} \frac{E_{df}}{T_s} \quad (60)$$

Finally, the exergy flux for each component is

$$B_{dr} = E_{dr} - T_0 S_{dr} \quad (61)$$

$$B_{df} = E_{df} - T_0 S_{df} \quad (62)$$

where the exergy flux of the global radiation is  $B_{Pons,g} = B_{dr} + B_{df}$ . The study developed by Pons was later evaluated using meteorological data from two stations and one satellite-derived database from different locations in France. The results show that the global radiation exergy is higher than the beam radiation at all three locations. An important contribution from Pons was the determination of an empirical solution for the function  $X(\epsilon)$  in terms of direct and diffuse radiation over a wide spectral range.

Makhanlall [54], in 2013, developed a second law analysis for thermal radiation in a two-phase particulate medium. The medium was considered as a grey particulate gas where a temperature difference is assumed between the gas phase and the discrete second phase of particles. Based on the expressions of Karlsson and Candau (Equation (25)), the two-phase spectral radiative exergy ( $\psi_\lambda(r, s)$ ) is,

$$\begin{aligned} \psi_\lambda(r, s) = & \kappa_{g,\lambda} \left[ 1 - \frac{T_0}{T_{\lambda(r,s)}} \right] (I_{\lambda(r,s)} - I_{bg,\lambda}[T_g(r)]) \\ & - \kappa_{p,\lambda} \left[ 1 - \frac{T_0}{T_{\lambda(r,s)}} \right] (I_{\lambda(r,s)} - I_{bp,\lambda}[T_p(r)]) \\ & - \sigma_{p,\lambda} \left[ 1 - \frac{T_0}{T_{\lambda(r,s)}} \right] \left[ I_{\lambda(r,s)} - \frac{1}{4\pi} \int_{4\pi} I_{\lambda}(r, s') \Phi(s, s') d\Omega' \right] \end{aligned} \quad (63)$$

where  $\kappa_{g,\lambda}$  is the spectral absorption coefficient of the gas,  $\kappa_{p,\lambda}$  the equivalent spectral absorption coefficient due to the presence of particles  $\sigma_{p,\lambda}$  the equivalent spectral scattering coefficient,  $T_0$  the ambient temperature,  $T_{\lambda(r,s)}$  the spectral radiative temperature for a position vector  $R$  and a unit direction vector  $s$ ,  $I_{\lambda(r,s)}$  the spectral radiative intensity,  $I_{bg,\lambda}$  the spectral black-body intensity of gas,  $I_{bp,\lambda}$  the equivalent spectral black-body intensity,  $T_g(r)$  the gas temperature,  $T_p(r)$  the particle temperature,  $\Phi$  is the scattering phase function and  $\Omega$  the solid angle. The first term from Equation (63) represents the increase in radiative exergy

due to the absorption and emission of the gas. The second and third terms represent the contribution of absorption, emission, and dispersion of the particulate phase, respectively. The expression developed by Makhanlall is highly useful in high temperature energy conversion systems, such as coal pulverisation processes.

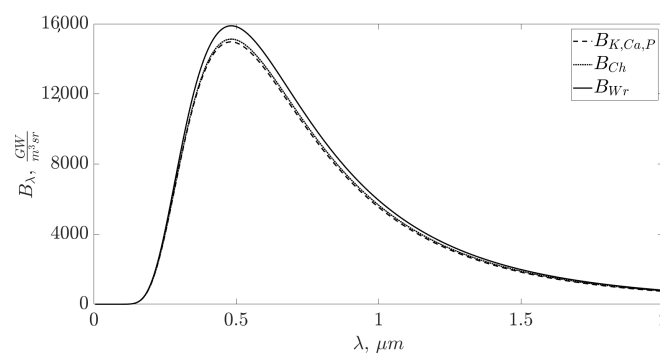
### 3.3. Comparison of the Diluted Expressions

Figure 5 shows a comparison of the exergy models for diluted radiation, considering those models similar in their conception and assumptions: Karlsson  $B_K$ , Candau  $B_{Ca}$ , Petela  $B_P$ , Chen and Mo  $B_{Ch}$  and Wright et al.  $B_{Wr}$ . The models of Landsberg and Tonge, Zamfirescu and Dincer, Zhou et al. and Badescu are different because the conception of the thermodynamic system is idealised with other components that are not present in the models above (e.g. the pumps in [25] or the thermodynamic break in [48]), which require inclusion of additional variables in those models. Furthermore, the models developed by Chu and Liu and Pons are derived from the models originally developed by Karlsson and Candau; however, they consider the particular context of solar radiation components. Finally, the expression developed by Makhanlall, which is based on the Karlsson and Candau equations, is recommended for a participating medium. To carry out this comparison, the energy  $E_{b,0,\lambda}$  and entropy  $S_{b,0,\lambda}$  of the monochromatic normal intensity for linearly polarised black radiation are defined following Planck's theory as

$$E_{b,0,\lambda} = \frac{c_0^2 h}{\lambda^5} \frac{1}{e^{\frac{c_0 h}{k \lambda T}} - 1} \quad (64)$$

$$S_{b,0,\lambda} = \frac{c_0 k}{\lambda^4} [(1 + Y) \ln(1 + Y) - Y \ln Y] \quad (65)$$

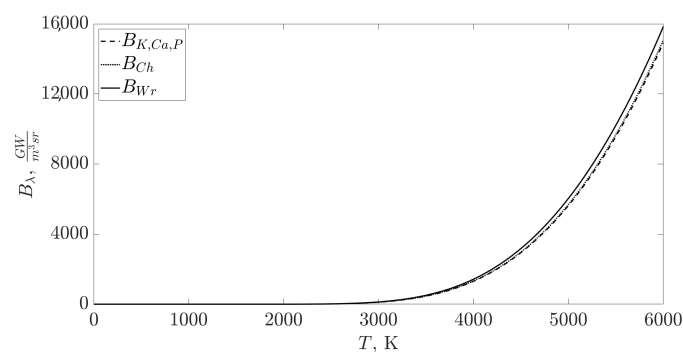
where  $c_0$  is the speed of light in vacuum,  $h$  is the Planck's constant,  $\lambda$  is the wavelength,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature and  $Y$  is equivalent to  $Y \equiv \frac{\lambda^5 E_{b,0,\lambda}}{c_0^2 h}$ . By these definitions of energy and entropy, the units for each are, respectively,  $\frac{W}{m^3 sr}$  and  $\frac{W}{m^3 K sr}$ .



**Figure 5.** Comparison of the radiation exergy for Karlsson, Candau, Petela, Chen & Mo and Wright et al. considering  $T = 6000$  K and  $T_0 = 300$  K.

As observed in Figure 5, the exergy models were evaluated for two black surfaces with constant temperatures at  $T = 6000$  K and  $T_0 = 300$  K, allowing assessment of the spectral energy (Equation (64)) and spectral entropy (Equation (65)) of solar radiation for a wavelength range from 0 to 2  $\mu m$  with an  $\varepsilon_\lambda = 1$ . For small wavelengths, all expressions give similar values. However, they show important differences for wavelengths higher than 0.3  $\mu m$ . The largest difference occurs for the respective maximum values of each curve. The maximum exergy obtained with the expression proposed by  $B_{K,Ca,P}$  is 14,960  $GW/m^3 sr$ .  $B_{Ch}$  delivers a maximum value of 15,120  $GW/m^3 sr$ , while  $B_{Wr}$  delivers 15,880  $GW/m^3 sr$ . All three expressions give similar values when approaching a wavelength of 1.6  $\mu m$ . It is observed that the  $B_{K,Ca,P}$  exhibits lower values than the other two expressions.

These results are contrasted with an additional evaluation where the temperature of the radiative source is varied within a range of 0 K to 6000 K, with a constant wavelength of  $\lambda = 0.5 \mu\text{m}$ . Observing the results in Figure 6, it can be seen that for temperatures below 2800 K the exergy delivered by all the expressions is quite low. However, from 2800 K onward, the exergy delivered starts to rise exponentially and differences between the values delivered by each model are evident. The  $B_{Wr}$  expression is the one that always reports higher values than the others for the whole temperature range, and the  $B_{K,Ca,P}$  expression is the one that gives the lowest exergy. Based on these results, it is observed that the definition of the spectral entropy in  $B_{K,Ca,P}$  is a constraint that the other two expressions do not consider, implying that  $B_{Ch}$  and  $B_{Wr}$  always deliver higher values within the same range of wavelength and temperature.



**Figure 6.** Comparison of the radiation exergy for Karlsson, Candau, Petela, Chen & Mo and Wright et al. considering a constant wavelength of  $\lambda = 0.5 \mu\text{m}$  and  $T_0 = 300 \text{ K}$ .

#### 4. Empirical Models

During the last decade, several studies have focused on estimating solar radiation exergy by means of empirical expressions that can link radiative exergy to other meteorological variables that are easier to measure. This type of method is useful in places where solar radiation measurements are not available, mainly due to the high cost of installation and maintenance in remote areas. The empirical models are developed by fitting the meteorological data of the place to be studied, which makes their estimates valid for the place where they were developed. These methods are generally performed by regression analysis, as shown in Table 3.

**Table 3.** Empirical models of the exergy of solar radiation.

Author	Variables	Analysis
Arslanoglu [26]	$\bar{n}, \bar{N}$	Regression
Mohammed and Mengüç [27]	$\bar{n}, \bar{N}, \bar{T}_0, \bar{v}$	Regression
Taki et al. [59]	$T_{ave}, T_{min}, T_{max}, RH, P, TST, WS$	Gaussian process regression
Jamil and Bellos [28]	$\bar{n}, \bar{N}, \bar{K}_T$	Regression
Khorasanizadeh and Sepehrnia [29]	$\bar{n}, \bar{N}$	Regression

Arslanoglu [26] developed the first empirical model for the exergy of solar radiation in Turkey. This model aims to estimate the clearness index by considering the monthly average daily sunshine duration  $\bar{n}$  and the monthly average day length  $\bar{N}$ . The model is based on Angstrom's model [60], considering the following modifications introduced by Page [61],

$$\frac{\bar{H}}{\bar{H}_0} = a + b \left( \frac{\bar{n}}{\bar{N}} \right) \quad (66)$$

where  $\bar{H}$  is the monthly daily global radiation on a horizontal surface,  $\bar{H}_0$  is the daily extraterrestrial radiation on a horizontal surface, and  $a$  and  $b$  are empirical constants

dependent on the location analysed. The exergy of the solar radiation ( $\psi$ ) was considered as undiluted using the model of Petela (Equation (3)) in the form of  $H_{ex} = \psi \cdot H$ . The solar radiation exergy factor is then computed by a regression analysis as follows,

$$\frac{H_{ex}}{H_0} = \psi \cdot \frac{H}{H_0} = f(a', b', c', d', \bar{n}, \bar{N}) \quad (67)$$

where  $a', b', c', d'$  are empirical constants. Arslanoglu developed three regression models in the form of linear, quadratic, and cubic equations. These models are,

$$\frac{H_{ex}}{H_0} = a' + b' \left( \frac{\bar{n}}{\bar{N}} \right) \quad (68)$$

$$\frac{H_{ex}}{H_0} = a' + b' \left( \frac{\bar{n}}{\bar{N}} \right) + c' \left( \frac{\bar{n}}{\bar{N}} \right)^2 \quad (69)$$

$$\frac{H_{ex}}{H_0} = a' + b' \left( \frac{\bar{n}}{\bar{N}} \right) + c' \left( \frac{\bar{n}}{\bar{N}} \right)^2 + d' \left( \frac{\bar{n}}{\bar{N}} \right)^3 \quad (70)$$

Arslanoglu used meteorological data from seven stations at different locations in Turkey to validate the models, which were evaluated using seven statistical indicators: coefficient of determination ( $R^2$ ), mean percentage error ( $MPE$ ), mean absolute percentage error ( $MAPE$ ), mean biased error ( $MBE$ ), mean absolute biased error ( $MABE$ ), root mean square error ( $RMSE$ ) and the T-statistic ( $t - stats$ ). Considering the results of the statistical analysis, the author concluded that all models are useful for estimating the exergy factor of solar radiation, since all achieved low errors for their respective indicators. However, Arslanoglu did not define which of the three models best fitted the data, since the lowest indicators were different for each location.

Some years later Mohammed and Mengüç [27] presented their own expression for the undiluted radiation exergy and also an empirical analysis of the radiative exergy. The expressions include the ambient temperature ( $T_0$ ) and wind speed ( $v$ ), aiming to consider the effects of weather conditions. The expression for the exergy of undiluted radiation was developed considering a radiative transfer system between a radiative source and an absorber sink in a constant volume system. An analysis of the second law of thermodynamics led to the following expression,

$$\psi_M = 1 - \frac{4}{3} \frac{T_0 T^3 - T_0^4}{T^4 - T_0^4} \quad (71)$$

where  $T$  is the temperature of the radiation source. The empirical expression of the solar radiation exergy is developed by means of a regression analysis considering the following expression

$$\frac{H_{ex}}{H_0} = f(A, B, C, D, \bar{n}, \bar{N}, \bar{T}_0, \bar{v}) \quad (72)$$

where  $A, B, C$  and  $D$  are empirical constants. Mohammed and Mengüç developed two expressions including average ambient temperature  $\bar{T}_0$  and average wind speed  $\bar{v}$  as follows,

$$\frac{H_{ex}}{H_0} = A + B \frac{\bar{n}}{\bar{N}} + C \bar{T}_0 \quad (73)$$

$$\frac{H_{ex}}{H_0} = A + B \frac{\bar{n}}{\bar{N}} + C \bar{T}_0 + D \bar{v} \quad (74)$$

These two expressions were compared with the ones reported in [26] considering the information from two locations in Iraq and two in Turkey, and using the same statistical indicators used in [26]. The results indicate that the models obtain lower errors than those in [26]. In particular, the model showing the best results corresponds to Equation (74),



since it contains more parameters taking into account more information about the climatic features of the location. This result suggests that considering a larger number of variables in the empirical model improves the results of the exergy factor. However, this increase may also mean that the models end up overfitting to the local data, losing the generality to describe locations different than those where they were developed.

Taki et al. [59] used a soft computing Gaussian process regression to model total solar radiation and solar radiation exergy. For the case of exergy, the author considered the Petela model to link this model with average  $T_{ave}$ , minimum  $T_{min}$  and maximum  $T_{max}$  temperature, average relative humidity  $RH$ , pressure  $P$ , total sunbathing time  $TST$  and average wind speed  $WS$  in the Hakkari province (Turkey). The evaluation of the best combination of variables was developed on the basis of two statistical indicators:  $MAPE$  and  $R^2$ . Through these metrics, it was found that the lowest errors were observed when using the meteorological variables mentioned above. In addition, a cross-validation process was carried out showing that the model achieved the lowest errors with a training and test data ratio of 70% and 30%, respectively. Similar to that work, several studies regarding the application of machine learning techniques for solar energy forecasting and prediction of solar radiation components have been undertaken ([62–64]). However, the work of Taki et al. is the first to use machine learning models to estimate the exergy of solar radiation.

In the same year, Jamil and Bellos [28] developed a regression analysis for computing the exergy of solar radiation using monthly averaged meteorological data from 23 stations in India. In their work, the authors considered the model of Petela to determine the global radiation exergy factor ( $\psi_g$ ) and a term called “global solar exergy factor ratio” ( $\psi_{go}$ ) which represents the ratio of the monthly global solar exergy to the monthly extraterrestrial solar radiation. The empirical correlations developed by Jamil and Bellos are based on the monthly average daily sunshine duration ( $\bar{n}$ ), the monthly average day length ( $\bar{N}$ ) and the monthly clearness index ( $\bar{K}_T$ ), as follows

$$\psi_g = f(a, b, c, d, e, \bar{K}_T) \quad (75)$$

$$\psi_g = f(a, b, c, d, e, \bar{n}, \bar{N}) \quad (76)$$

$$\psi_{go} = f(a, b, c, d, e, \bar{K}_T) \quad (77)$$

$$\psi_{go} = f(a, b, c, d, e, \bar{n}, \bar{N}) \quad (78)$$

For each of the four categories shown above, eight different models were developed: linear, quadratic, cubic, fourth degree polynomial, logarithmic, exponential, potential, and inverse functions. The validation was carried out using 10 statistical indicators:  $MBE$ ,  $RMSE$ ,  $MPE$ ,  $t$ -stats, mean absolute error ( $MAE$ ), uncertainty at 95% ( $U_{95}$ ), relative root mean square error ( $RRMSE$ ), maximum absolute relative error ( $erMAX$ ), mean absolute relative error ( $MARE$ ) and the correlation coefficient ( $R$ ). Since the statistical indicators present different trends of best fit to the data, Jamil and Bellos computed an indicator called the “global performance indicator” ( $GPI$ ), which combines the individual results of the statistical indicators to provide a single value. Hence, the authors reported the model that best fitted the data in each of the four categories. The work of Jamil and Bellos was the first to use the clearness index as one of the variables within the regression analysis. In addition, using an indicator that combines all statistical metrics makes it possible to select the appropriate model, which could not be accomplished by Arslanoglu. However, using the expression of Petela to determine the exergy of solar radiation, Jamil and Bellos introduced a bias in the model by not including the effect of atmospheric attenuation.

Khorasanizadeh and Sepehrnia [29] presented an empirical analysis of the solar radiation exergy in Iran. The data used are from eight stations located in the eight provincial capitals of the country. The radiative exergy expression used was the expression of Petela. The regression analysis is carried out on the basis of the monthly average daily sunshine duration ( $\bar{n}$ ) and the monthly average day length ( $\bar{N}$ ).

$$\frac{H_{ex}}{H_0} = f(a', b', c', d', \bar{n}, \bar{N}) \quad (79)$$

Through the expression in Equation (79), five models were developed for each season: linear, quadratic, cubic, exponential, and power law. The validation of the expressions was carried out on the basis of eight statistical indicators: *MBE*, *MABE*, *MPE*, *MAPE*, *RMSE*, *RRMSE*, *t-stats* and  $R^2$ . The authors selected the best model for each station by observing which model achieved the highest number of low statistical errors. The evaluation of the results of the statistical indicators shows different trends with the best fit of the data. However, no metric was used that could combine all indicators used, such as *GPI* or similar. In addition, the expression of Petela is again used to obtain the exergy of solar radiation, which does not account for the attenuation effects.

The empirical models developed to date have mostly been developed through the use of regression analysis, which is a method that aims to fit a polynomial equation to the data cloud to be evaluated. Machine learning is a set of techniques increasingly used in different areas of engineering, but for the assessment of solar radiation exergy it has been little studied. Therefore, it is of special interest to analyse the suitability of using such powerful tools for estimating solar exergy using different meteorological variables as input for the system.

## 5. Discussion

The development of expressions that can estimate the exergy of solar radiation serves to improve the thermodynamic analysis of energy conversion systems, such as photovoltaic panels or solar thermal collectors. Over the years, two main approaches have been developed, considering radiation as dilute or undiluted. This difference in approaches makes undiluted radiation a valid expression when a nonparticipating medium is present, so that they can be considered as valid expressions for estimating the exergy of extra-atmospheric radiation. The analysis from which these expressions are developed is by means of classical cylinder-piston thermodynamic analysis, which means that these expressions are generally only a function of the source temperature (Sun) and the low temperature reservoir (Earth). This analysis comes from considering radiation as a source of thermal energy, which means considering a photon gas that has the same thermodynamic properties as a substantial gas, with a volume and pressure that can push the piston through expansion and compression processes.

However, for practical purposes of energy conversion systems on the Earth's surface, estimations of the exergy of solar radiation must take into account the effects of a participating medium, such as the atmosphere. The exergy of dilute radiation considers the attenuation effects as entropy, which leads to the development of two approaches to evaluate this property: the thermal approach (based on the second law of thermodynamics), or the electromagnetic approach (based on an emitter and receiver surface). The thermodynamic approach presents significant differences between the expressions proposed for diluted and undiluted solar radiation. Indeed, the expressions for diluted solar radiation consider the first and second laws of thermodynamics, whereas for the expressions for undiluted solar radiation, only the first law is considered. In that context, the entropy of solar radiation is included as part of the methodological assessment for diluted radiation. Furthermore, these expressions were developed considering the radiation as monochromatic; thus, the expressions are functions of the wavelength of the radiation. The electromagnetic approach is mainly based on the definition of spectral energy and spectral entropy from Planck's equations, where the Gouy–Stodola theorem is considered to estimate the exergy of diluted radiation. It is important to note that both approaches use the Gouy–Stodola theorem to express the exergy of solar radiation. Wright et al. has been the only author that disregarded considering this theorem, due to the inherent irreversibilities that occur when radiation and matter interact. The main difficulty in the electromagnetic approach is associated with the evaluation of the spectral entropy (19), which is a function of the emissivity of the source.

The studies devoted to the exergy of dilute radiation also led to the possibility of calculating the exergy of direct and diffuse radiation separately. It is well known that the energy content of direct and diffuse radiation is different; therefore, the exergy content should also be assessed carefully. Solar thermal processes make primary use of direct radiation as an energy source, therefore determining the exergy associated with direct radiation is a step forward in improving the assessment of the system's efficiency.

Empirical expressions of solar radiation exergy have been developed that attempt to estimate this value using other easily measured meteorological variables. These models have been developed mostly by regression analysis, where the expression used to calculate the exergy of solar radiation is Petela's expression. Petela's expression is useful for evaluating the exergy of undiluted solar radiation. However, an empirical analysis should consider a diluted exergy expression, improving the analyses where the atmospheric attenuation is taken into consideration in the exergy balance.

Solar exergy assessment using machine learning algorithms can improve solar exergy estimation, since the algorithms are able to extract additional features from the meteorological data that could help developing a better representation of the variability than a simple regression approach. Deep neural network is a method that can help improve the extraction of characteristics from meteorological data. Such a method enables consideration of the data as a time series, where specific neural network methods, such as recurrent neural networks (RNN) and long short-term memory (LSTM) are examples of architectures able to deal with that type of data [65,66]. These methods have been used to estimate or predict the components of solar radiation, in similar applications to those where the assessment of the exergy of solar radiation has been considered. In addition, clustering methods can be used for the development of exergy maps, where a clustering algorithm identifies similar characteristics between each evaluated location and can help to classify each location [67,68]. However, like regression analysis, this method also relies on determining the exergy of solar radiation using one of the methods discussed above to compare with the results of the algorithm, so the dilute exergy expression should also be used to estimate this value.

## 6. Conclusions

Determining the useful work that can be extracted from solar radiation is an area of study that is still highly active. In this context, there are studies that proposed expressions to determine the undiluted radiative exergy, considering that there is no entropy generation by the medium it passes through. Of the different models described in this review, the one that has finally reached a consensus over the years, that gives the exergy factor of the undiluted solar radiation, is the model proposed by Petela, which has been ratified by other authors such as Bejan, Wright et al. and Badescu.

Regarding dilute radiation, the early studies focused on determining the exergy of spectral radiation, such as the model proposed by Karlsson, which was later ratified by Candau through a thermodynamic analysis of a Carnot engine-absorber. The way of defining the exergy of the spectral solar radiation has presented some small variations during the last decades, where the definition of the solar exergy proposed by Petela stands out, which introduces a theoretical term, denoted monochromatic exergy emissivity. The differences observed between the models are in the way that radiative entropy is defined, highlighting significant efforts in determining an exact solution for the function  $X(\epsilon)$ . The development of expressions to estimate the exergy of solar radiation is key to determining the efficiency of solar systems. The upper limit of the useful work that can be extracted from solar radiation is crucial for the yield assessment of solar technologies. Therefore, it is proposed that this analysis should include the diluted exergy models within the thermodynamic balance.

In recent years, empirical models have been proposed to determine the exergy of solar radiation. The aim of these models is to obtain the radiation exergy by means of some other meteorological variables, which are easy and inexpensive to measure. The method that most of the authors have applied when using empirical equations is regression analysis, that is,

a method that defines a polynomial equation to fit the data. Nevertheless, more advanced methods should be used to improve the feature extraction of the data, such as machine learning techniques. Machine learning techniques can improve the generalisation of the empirical models, allowing extension of the use of exergy assessment of solar radiation to sites where measurements of radiation components are not available and even developing particular regressions for direct and diffuse radiation components.

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