

Topics in Current Chemistry 371

Harun Tüysüz
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Solar Energy for Fuels

 Springer

Harun Tüysüz • Candace K. Chan
Editors

Solar Energy for Fuels

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ISSN 0340-1022

ISSN 1436-5049 (electronic)

Topics in Current Chemistry

ISBN 978-3-319-23098-6

ISBN 978-3-319-23099-3 (eBook)

DOI 10.1007/978-3-319-23099-3

Library of Congress Control Number: 2015954168

Springer Cham Heidelberg New York Dordrecht London

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Preface: Solar Energy for Fuels

Few scientific researchers would deny that, as a result of various factors such as funding cycles, overall political climate, and stagnation in progress, the intensity of activity in any particular research field is cyclical. This is particularly true for research areas related to renewable energy conversion and storage, with the return of interest in solar energy related fields in the last decade corresponding with increasing concerns about climate change and depleting fossil fuel energy sources.

Solar energy can be used to create an extremely energy-dense fuel, namely hydrogen gas, from water. The hydrogen can be used in hydrogen fuel cell vehicles or to create syngas with carbon monoxide to make synthetic liquid fuels in the Fischer–Tropsch process. Additionally, solar energy can be used to photoelectrochemically or electrolytically drive the reduction of carbon dioxide to carbon-based fuels such as methane, carbon monoxide, or alcohols.

The use of solar energy to create fuels is attractive, as it makes use of an abundant resource. In Chap. 1 by Kleidon et al., a detailed analysis regarding the potential of solar energy conversion using principles of thermodynamics and conversion limits is presented. The conversion of solar energy to make fuels occurs in nature via the process of photosynthesis. Substantial efforts have been made to better understand the natural photosynthetic mechanisms in order to discover how artificial photosynthetic systems can be engineered, especially for overcoming the kinetic bottlenecks in the water oxidation reaction. In Chap. 2, Pantazis et al. provide an overview of the key features of Photosystem II, the natural enzyme that catalyzes water oxidation. The adoption of these concepts to form biomimetic water oxidation catalysts is described in Chap. 3 by Kurz.

Several different approaches and device configurations are possible for realizing solar fuel production. Slurry photocatalysts are a low-cost extension of photoelectrochemical cells, whereby a semiconductor particle decorated with co-catalysts for the hydrogen and oxygen evolution reactions can be used to split water and co-generate the products simultaneously. Takanabe describes the fundamental processes involved during overall water splitting on slurry photocatalysts in Chap. 4.

Since the first demonstrations of solar fuel production in the 1970s, the global scientific community has become equipped with several advantages to better tackle the energy problem. For instance, the development of nanoscience as a field and its accompanying synthetic and characterization tools have enabled a fresh look at old materials, as well as completely novel approaches. Nanostructured materials have unique and different physical and chemical properties in comparison to their bulk counterparts. In Chap. 5, Osterloh describes the key parameters in nanomaterials that can be exploited to improve photocatalytic performance.

Aside from using nanostructuring strategies, researchers have also developed new ways to boost the overall performance of the photocatalysts. In Chap. 6, Marschall describes how advanced heterojunctions can be engineered in powdered materials to produce composite photocatalysts with better efficiency. Another strategy is to load the surface of a light-harvesting semiconductor with a co-catalyst that provides catalytic sites for the oxidation or reduction reactions and promotes separation of the photogenerated charges. In Chap. 7, Nocera et al. gives a detailed overview of the properties of water oxidation co-catalysts based on cobalt oxido thin films. Then, in Chap. 8, Tüysüz et al. describes how surface plasmons, an optical property found in nanostructured metals, can be used to improve the visible light harvesting efficiency and enhance the photocatalytic activity of semiconducting particles.

Finally, in operando and in situ techniques have also been applied to photocatalysis and photoelectrochemistry to gain a better understanding of catalytic processes and monitor materials under reaction conditions. Increasingly advanced setups have allowed for unprecedented experiments involving light excitation, electrical biasing, and introduction of water for conducting microscopy and spectroscopy on electrocatalyst and photocatalyst materials during solar-to-fuel reactions. An overview of several in situ characterization tools that have recently been developed is given in Chap. 9, as well as different strategies for implementing high throughput screening of solar fuel materials properties.

Harun Tüysüz
Candace K. Chan

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Physical Limits of Solar Energy Conversion in the Earth System

Axel Kleidon, Lee Miller, and Fabian Gans

Abstract Solar energy provides by far the greatest potential for energy generation among all forms of renewable energy. Yet, just as for any form of energy conversion, it is subject to physical limits. Here we review the physical limits that determine how much energy can potentially be generated out of sunlight using a combination of thermodynamics and observed climatic variables. We first explain how the first and second law of thermodynamics constrain energy conversions and thereby the generation of renewable energy, and how this applies to the conversions of solar radiation within the Earth system. These limits are applied to the conversion of direct and diffuse solar radiation – which relates to concentrated solar power (CSP) and photovoltaic (PV) technologies as well as biomass production or any other photochemical conversion – as well as solar radiative heating, which generates atmospheric motion and thus relates to wind power technologies. When these conversion limits are applied to observed data sets of solar radiation at the land surface, it is estimated that direct concentrated solar power has a potential on land of up to 11.6 PW (1 PW = 10^{15} W), whereas photovoltaic power has a potential of up to 16.3 PW. Both biomass and wind power operate at much lower efficiencies, so their potentials of about 0.3 and 0.1 PW are much lower. These estimates are considerably lower than the incoming flux of solar radiation of 175 PW. When compared to a 2012 primary energy demand of 17 TW, the most direct uses of solar radiation, e.g., by CSP or PV, have thus by far the greatest potential to yield renewable energy requiring the least space to satisfy the human energy demand. Further conversions into solar-based fuels would be reduced by further losses which would lower these potentials. The substantially greater potential of solar-based renewable energy compared to other forms of renewable energy simply reflects much fewer and lower unavoidable conversion losses when solar radiation is directly converted into renewable energy.

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Keywords Carnot limit · Global estimates · Photosynthesis · Solar energy · Theoretical potentials · Thermodynamic limits · Thermodynamics

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1 Introduction

Renewable energy provides a sustainable form of energy generation which is not associated with the emission of greenhouse gases. It thereby forms a critical component to avoid greenhouse-induced global climate change and to avoid the consequences of depleting fossil fuel resources. Among the different forms of renewable energy, solar energy is seen as the most abundant source of renewable energy [1]. Its potential is often described as being so huge [2] that it is not a limiting factor in meeting human energy demands within this century. The deployment of solar energy technology, mostly in form of photovoltaic electricity generation, is rapidly growing, so that solar energy already contributes a sizable percentage to electricity generation in some industrialized countries.

Yet, as with any other resource on the planet, the generation of renewable energy by the Earth system is limited, and so is the potential of using solar radiation as an energy resource. Quantitative estimates of the theoretical potential of solar energy are based on physical limitations rather than what is currently technologically possible. These estimates play an important role in allowing us to assess which form of renewable energy has the greatest potential to meet human energy demands. The difference between the theoretical potential and what is currently technologically possible also informs us about the extent to which technology can be developed further. Hence, theoretical potentials provide an important foundation for establishing the options for future sustainable energy developments.

Theoretical potentials of renewable energy are derived from the combination of thermodynamics, which provides a general, physical formulation of the limits associated with energy conversion, and Earth system science, which provides the context in which energy conversion takes place. Thermodynamics describes general rules for energy conversions, and yields well-established, fundamental conversion limits, such as the Carnot limit of a heat engine. This limit is set by the heat flux through the engine, but also by the entropy exchange, which limits how much of the

heat can be converted into physical work (which is also referred to as exergy). Analogous to the heat engine example, it is possible to calculate a thermodynamic conversion limit for a radiation energy converter [3–5] which can be used to quantify how much of the solar radiative flux can be converted into renewable energy. In addition to the magnitude of the solar radiative flux at the surface, a critical component that is needed is the entropy associated with the radiative flux. This property of radiation, however, is not commonly available and needs to be estimated from available data. Nevertheless, the combination of this theoretical conversion limit with the conditions at the Earth's surface allows us to quantify a theoretical potential for solar renewable energy which is solely based on the limits of physical conversion processes within the Earth's environment and which is independent of the available technology. This conversion limit is not constrained solely to physical conversions either, so that it also applies to any form of photo-chemical conversion, including photosynthesis. It thus sets an upper limit to the potential by which solar radiation can supply renewable energy for human energy use.

What has just been described sets the limit for the conversion of solar radiation into a general, non-radiative form of energy. In the case of photovoltaics, for instance, the resulting form of energy is in electric form. The further conversion of this energy into some chemical form to yield solar-based fuels would likely be associated with further conversion losses, thus lowering the potential to convert solar radiation into chemical fuels. Here, however, we focus on the limits imposed on the first step from solar radiation to energy in non-radiative form, and discuss the implications for conversions to solar-based fuels at the end of this chapter.

In this chapter, we describe the theoretical background of these conversion limits for solar radiation and combine these with climate data sets based on observed solar radiation fluxes at the Earth's surface to obtain estimates of solar renewable energy potential. We also describe the closely related thermodynamic conversion limit which applies to the radiative heating after solar radiation is being absorbed by the Earth's surface, which drives atmospheric convection. The subtle difference of the latter limit is that it does not convert solar radiation, but rather solar radiative heating, so that this thermodynamic limit represents the well-established Carnot limit of a heat engine. This limit constrains the generation of atmospheric motion and thus provides an estimate for the theoretical potential of wind energy. We also briefly describe the theoretical and observed limits associated with photosynthesis, which also act to convert solar radiation into another energy form which can be used as a renewable form of energy in the form of biofuels. We then estimate and compare these solar-based renewable energy potentials using observed solar radiative fluxes at the surface. This comparison shows that the direct use of solar radiation represents by far the most efficient way to generate renewable energy as it involves the fewest conversions of solar radiation to renewable energy. We close with a brief summary and conclusion, where we also outline the possible application of such thermodynamic considerations to further conversions into solar-based fuels.

2 Thermodynamic Background

Thermodynamics is a physical theory which describes rules for energy conversions at a very fundamental level. At the center are the first and second laws of thermodynamics. The first law essentially states the conservation of energy during the conversion of one form of energy into another. The second law requires that the entropy during an energy conversion process does not decrease. Although entropy seems to be an abstract thermodynamic property, it can loosely be seen as a measure for the dispersal of the energy at the microscopic scale of atoms and molecules [6]. The more a given amount of energy is dispersed within a system, the higher its entropy is going to be. This requirement stated by the second law is so profound in physics that it has been labeled the arrow of time [7].

When the first and second laws are combined, they provide a constraint on the magnitude of energy conversion. This is schematically illustrated in Fig. 1, in which a fraction of an incoming flux of energy, J_{in} , is converted into another form of energy at a rate G which represents some form of free energy which can be used to perform work. This conversion rate, G , represents the power of the engine, although we use G here as it also refers to the generation rate of free energy. For instance, a classical heat engine converts a fraction of the influx of heat (J_{in}) into mechanical work (G). For solar energy conversion, the influx is represented by the flux of solar radiation (J_{in}), and the conversion rate G is associated with the rate by which, for instance, electric energy is generated.

The first law of thermodynamics then states that energy is conserved during the conversion process. In a steady state of the conversion process in which the energy content inside the converter is unchanged, this translates into the requirement that

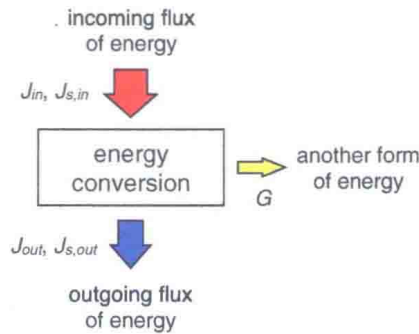


Fig. 1 Illustration of a generic energy converter which generates power at a rate G . The magnitude of energy conversion is constrained by the combination of the two laws of thermodynamics: the first law states energy conservation associated with the energy fluxes J_{in} , J_{out} , and G (i.e., $J_{in} = J_{out} + G$), and the second law requires that the entropy export, $J_{s,out}$, is greater or equal to the entropy import, $J_{s,in}$ (i.e., $J_{s,out} \geq J_{s,in}$). The ideal case of $J_{s,out} = J_{s,in}$ sets the upper limit on the conversion rate

the incoming flux of energy, J_{in} , is balanced by the generation rate and a waste flux of energy, J_{out} which leaves the converter:

$$0 = J_{\text{in}} - J_{\text{out}} - G. \quad (1)$$

The second law of thermodynamics adds a further constraint on the conversion process. It requires that the entropy does not decrease during the conversion process. In the steady-state setting considered here, the second law imposes a constraint on the entropy balance of the conversion process. This entropy balance consists of the import of entropy, $J_{s,\text{in}}$, associated with the incoming flux, J_{in} , with the entropy export, $J_{s,\text{out}}$, associated with the outgoing flux, J_{out} , and, potentially, of the entropy production, σ , within the system. We thus obtain for the entropy balance in steady state

$$0 = J_{s,\text{in}} - J_{s,\text{out}} + \sigma. \quad (2)$$

In the context of this entropy balance, the second law requires that $\sigma \geq 0$. In the ideal case, where $\sigma = 0$, there are no inefficiencies during the conversion process which would constitute irreversible losses, such as frictional or diffusive losses. This condition then sets the upper limit on an energy conversion process.

To illustrate how the combination of the two laws yields a conversion limit, we use the common example of a heat engine. For heat fluxes, the entropy fluxes are simply given by $J_{s,\text{in}} = J_{\text{in}}/T_{\text{in}}$ and $J_{s,\text{out}} = J_{\text{out}}/T_{\text{out}}$, where T_{in} and T_{out} are the temperatures at which the heat fluxes J_{in} and J_{out} are added or removed from the conversion process. When the expressions for the entropy fluxes are used in the entropy balance in the ideal case of $\sigma = 0$, this then yields the condition

$$\frac{J_{\text{in}}}{T_{\text{in}}} - \frac{J_{\text{out}}}{T_{\text{out}}} = 0. \quad (3)$$

When we now use the first law (1) to replace J_{out} in (3) and solve it for G , we obtain the upper limit of G that is permitted by the second law:

$$G = J_{\text{in}} \times \frac{T_{\text{in}} - T_{\text{out}}}{T_{\text{in}}} = J_{\text{in}} \times \eta_{\text{Carnot}}, \quad (4)$$

which is the well-known Carnot limit of a heat engine. In this equation, the expression $\eta_{\text{Carnot}} = (T_{\text{in}} - T_{\text{out}})/T_{\text{in}}$ is the so-called Carnot efficiency and informs us about how much of the heat flux J_{in} can be converted into free energy.

The conversion limit expressed by (4) only used the first and second law in its derivation for a generic energy conversion process in steady state, without any details on how this conversion is being performed. It thus represents a fundamental limit on energy conversion which is set by the laws of thermodynamics. However, the expression given by (4) is only applicable to the conversion of heat into work, because it specified the entropy fluxes as being thermal entropy fluxes. When

thermodynamics is applied to derive limits on the conversion process of solar radiation, we need to use expressions of radiative entropy fluxes, which are somewhat different than for heat.

3 Limits to Converting Solar Radiation

To obtain theoretical limits of the conversion of solar radiation, we need expressions of the entropy associated with radiative fluxes. These expressions go back to the original work by Max Planck [8], who introduced statistical mechanics to the description of radiation to derive radiation laws. Without going into the details of this formulation, one can show that the entropy of a radiative flux is of similar form to a heat flux, so that it is proportional to the magnitude of the radiative flux, and inversely related to the temperature at which the radiation was emitted. Because solar radiation is emitted at a much higher temperature of about $T_{\text{sun}} = 5,760$ K compared to when radiation is re-emitted by the Earth system of about $T_r = 255$ K, solar radiation has a much lower entropy than the terrestrial radiation emitted by Earth. This low entropy of solar radiation is reflected in the much shorter wavelength of solar radiation around 550 nm in the visible range, whereas the emitted radiation from Earth is centered around 11 μm in the infrared range. When one uses the particle view of radiation, then a given flux of solar radiation represents a flux of fewer and more energetic photons, whereas terrestrial radiation represents a flux of many more, but less energetic photons. This difference in entropy in the radiative exchange between Earth and space ultimately drives the dynamics of the Earth's climate system [9, 10]. However, in contrast to the entropy associated with heat fluxes, there is an additional contribution by radiation pressure to the entropy flux, and the spatial concentration over the solid angle also plays a role. This latter aspect in particular plays an important role in deriving theoretical limits, as it yields different limits for the potential of photovoltaic and direct concentrated solar power. For details on the formulation of radiative entropy within the Earth system, see, e.g., the recent review by Wu and Liu [11]. The following derivations of the thermodynamic limit of solar energy conversion follow the works by Petela [3], Press [4], and Landsberg and Tonge [5].

The incoming solar radiative flux at the Earth's surface can be expressed as

$$R_{s,\text{in}} = B\epsilon\sigma_b T_{\text{sun}}^4, \quad (5)$$

where B is a geometric factor, ϵ is a so-called dilution factor, $\sigma_b = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is the Stefan-Boltzmann constant, and $T_{\text{sun}} = 5,760$ K is the emission temperature of the Sun. The two factors B and ϵ describe the concentration of solar radiation over a small region of the sky. At the top of the atmosphere, where solar radiation has not been altered since it was emitted, the dilution factor is $\epsilon = 1$, that is, it is nearly undiluted blackbody radiation. The geometric factor is $B = \Omega_{\text{sun}}/\pi$, where $\Omega_{\text{sun}} = 6.8 \times 10^{-5} \text{ sr}$ (steradian, the SI unit for solid angles) is the solid angle

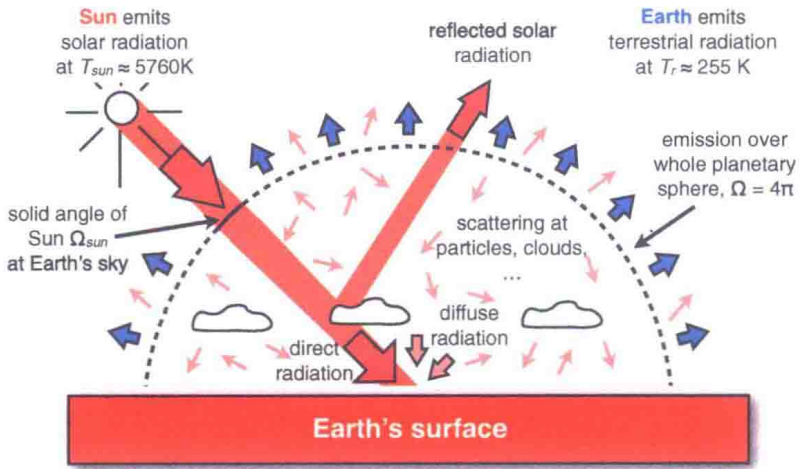


Fig. 2 Illustration of the solar radiative flux at the Earth's surface and the properties that affect its magnitude and entropy. The solar radiative flux at the surface consists of the direct component (*red arrow*) which is non-scattered solar radiation which still maintains its narrow solid angle, $\Omega_{\text{sun}} \approx 6.8 \times 10^{-5}$ sr, and a diffuse component (*pale red arrow*), which represents scattered solar radiation with approximately the same spectral composition, but reflecting a much broader solid angle of $\approx 2\pi$. Emitted radiation of the Earth (terrestrial radiation, *blue arrows*) is emitted over the whole area of the Earth and represents a solid angle of 4π

of the Sun (see Fig. 2). This solid angle expresses the size of the Sun at the orbital distance of the Earth, so that the solar radiative flux inside this solid angle is the same as the solar radiative flux when it was emitted from the solar surface. This solar radiative flux has a magnitude of $\sigma_b T_{\text{sun}}^4 = 62.4 \times 10^6 \text{ W m}^{-2}$ (i.e., the Sun is really bright), but its brightness is constrained into a very narrow section of the sky. When combined, these factors yield a mean incoming flux of solar radiation at the top of the atmosphere of about $R_{s,\text{in}} = 1,370 \text{ W m}^{-2}$, a value known as the “solar constant”.

When solar radiation is scattered in the atmosphere, the magnitude of the flux does not change, but the relative values of B and ϵ change. In the extreme case, solar radiation is scattered over the whole hemisphere, which corresponds to a solid angle of $\Omega = 2\pi$. In this case the value of B would substantially increase and the dilution factor would become much less. The spectral composition of this diluted radiation would still be relatively unaffected (although some scattering processes alter the wavelength). This scattered radiation is then referred to as “diluted” blackbody radiation. In the following, scattered, diluted solar radiation is referred to as diffuse solar radiation, whereas the non-scattered solar radiation is referred to as direct radiation.

The entropy of the solar radiative flux, J_s , is then described as

$$J_s = \frac{4}{3}BX(\varepsilon)\sigma_b T_{\text{sun}}^3, \quad (6)$$

where the function $X(\varepsilon)$ expresses the effect of dilution on the entropy flux. This function can be derived analytically, and a numerical approximation of this function is given by [5] as

$$X(\varepsilon) = \varepsilon \times (0.9652 - 0.2777 \ln \varepsilon + 0.0348 \varepsilon). \quad (7)$$

Note that the expression of the radiative entropy flux is similar to the entropy of a heat flux, except for the factor $4/3$, which originates from the contribution of radiation pressure (e.g., [11]), and for the effect of dilution, $BX(\varepsilon)$.

With these expressions of the solar radiative and entropy flux, one can derive the thermodynamic limit for solar radiative energy conversions. This derivation is analogous to the derivation of the Carnot limit in the previous section. The first law is represented in steady state by

$$R_{\text{in}} = R_{\text{out}} + J + G, \quad (8)$$

where R_{in} is the incoming flux of solar radiation, R_{out} is the emission of longwave radiation, J is a heat exchange flux with the surroundings, and G is the potential to generate free energy from the conversion process. The entropy balance of the conversion process is given by the import of entropy by R_{in} , the export of entropy by radiative emission, R_{out} , and the entropy exchange produced by J :

$$J_{s,\text{in}} = J_{s,\text{out}} + \frac{J}{T}, \quad (9)$$

where T is the environmental temperature. To obtain the upper limit, it is again assumed that there is no irreversible entropy production associated with the conversion process. This then yields a limit on the generation rate, G , given by

$$G = R_{\text{in}} - R_{\text{out}} - T(J_{s,\text{in}} - J_{s,\text{out}}). \quad (10)$$

A specific expression for the generation limit is obtained when the expressions for the radiative energy and entropy fluxes from the above are used. With (5) and (6) we obtain

$$\begin{aligned} G &= R_{\text{in}} \left(1 + \frac{1}{3} \left(\frac{T}{T_{\text{sun}}} \right)^4 - \frac{4X(\varepsilon)}{3\varepsilon} \frac{T}{T_{\text{sun}}} \right) \approx R_{\text{in}} \left(1 + \frac{4X(\varepsilon)}{3\varepsilon} \frac{T}{T_{\text{sun}}} \right) \\ &= R_{\text{in}} \times \eta_{\text{rad}}. \end{aligned} \quad (11)$$

The second term in the first expression on the right hand side can be neglected for conditions on Earth because $T \ll T_{\text{sun}}$. The last expression in (11) again

formulates the generation rate in terms of the influx of solar radiation, R_{in} , and a conversion efficiency, η_{rad} :

$$\eta_{\text{rad}} = 1 - \frac{4}{3} \frac{X(\epsilon)}{\epsilon} \frac{T}{T_{\text{sun}}}. \quad (12)$$

This expression describes the theoretical maximum efficiency of converting solar radiation into other forms of energy.

To obtain estimates for the maximum efficiency from (12), we not only need information on the surface temperature, T , but also on the nature of the solar radiation in terms of how much it has been diluted so that we can determine the value of ϵ and $X(\epsilon)$. For this we consider two cases. The first efficiency we derive is for the conversion of direct, i.e., non-scattered solar radiation at the surface. Direct radiation is used, for instance, by solar technologies in which solar radiation is focused by mirrors onto a small area to reach a high temperature (“direct concentrated solar”, DCS). Direct radiation is characterized by a value of epsilon of $\epsilon = 1$ and $X(1) = 1$. With a mean surface temperature of about $T = 288$ K, this yields a maximum efficiency of $\eta_{\text{direct}} = 93\%$. Note how the value of the efficiency differs from the Carnot limit because of the effect of the radiation pressure. The efficiency is almost 1, indicating that it can almost be completely converted into another form of energy. This high efficiency is ultimately produced by the high radiative temperature difference between the Sun and the radiative temperature of the Earth. The second efficiency we derive concerns the use of diffuse solar radiation. An example of this conversion type is photovoltaics or photochemistry, as these do not make specific use of the concentrated nature of direct radiation. We consider diffuse radiation that is completely scattered, i.e., diluted to a solid angle of $\Omega_{\text{diffuse}} = 2\pi$, but for which the radiative flux is unchanged, so that the product $B\epsilon$ is the same for direct and diffuse radiation. This yields the condition $B_{\text{dir}}\epsilon_{\text{dir}} = \Omega_{\text{sun}}/\pi = B_{\text{diffuse}}\epsilon_{\text{diffuse}}$, from which the value of $\epsilon_{\text{diffuse}}$ can be inferred from the respective solid angle of completely scattered solar radiation, $\Omega_{\text{diffuse}} = 2\pi$. This yields an efficiency of $\eta_{\text{diffuse}} = 73\%$, which is notably less than η_{direct} . This reduced efficiency is because the scattering of solar radiation is an irreversible process which produces entropy, so the diffuse solar radiation has a higher entropy.

When these thermodynamic limits of solar energy conversion are compared with solar radiative fluxes at the Earth’s surface, one can infer solar energy potentials associated with the use of direct and diffuse radiation. These estimates are obtained by multiplying the efficiencies with the respective radiative flux, as in (11).