



Limiting efficiencies for photovoltaic energy conversion in multigap systems

Antonio Martí^{*}, Gerardo L. Araújo

Instituto de Energía Solar, Universidad Politécnica de Madrid, E.T.S.I. de Telecomunicación, Ciudad Universitaria, 28040 Madrid, Spain

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Abstract

Multigap systems are better matched to the sun's spectrum than single gap systems and are, therefore, more efficient as photovoltaic converters. This paper reviews the different *thermodynamic* approaches used in the past for computing the limiting efficiency for the conversion of solar energy into work. Within this thermodynamic context, the limit ranges from 85.4% to 95.0% depending on the assumptions made. Detailed balance theory provides a more accurate model of the photovoltaic converter. It leads to a limit of 86.8% for a system with an infinite number of cells, as already pointed out by other authors. In this work, however, we use the concepts of *angle* and *energy* restriction to emphasize that this limit is independent of the light concentration. Systems with a *finite* number of cells are also studied and their limiting efficiency is found to be higher than previously reported. Data for AM1.5 Direct spectrum, never computed before, are included.

Keywords: Photovoltaics; Multigap; Limiting efficiency; Thermodynamics; Solar cells

1. Introduction

A topic of interest in photovoltaics is the elucidation of the maximum efficiency of the photovoltaic conversion processes. A review of the literature shows that the different studies can be grouped in two main categories. In the first, authors studied the limiting efficiency of *single* gap solar cells. The present authors devoted a study to this subject [1]. In the second category, the limiting efficiency of multigap systems was used as a

^{*} Corresponding author. Email: amarti@etsit.upm.es

way to approach the absolute limit of photovoltaic energy conversion (PVEC) and this is the category to which this paper belongs.

Although the question of the limiting efficiency of PVEC is one that ought to have a unique answer, different figures appear in the literature as will be detailed later. Sometimes, authors made different assumptions and used different approaches leading them to different results. Most of the time, the new figure arose from the consideration of a new aspect previously overlooked which progressively completed our understanding of the photovoltaic processes.

Two complementary approaches have been used in the past to answer the question of the *limiting efficiency*. The first, based on thermodynamics, is independent of the nature of the converter and is briefly reviewed in this paper in the first section. The other, described in Section 2, is based on *detailed balance* arguments. It uses a more refined model that makes some assumptions about the nature of the converter: the solar cell. In Section 3, we make some remarks about the differences, concerning the limiting efficiency, between a system with an *infinite* number of cells and a system with a *finite* number of cells. The limiting efficiency for the *finite* system is higher than previously reported.

2. A brief thermodynamic review

Thermodynamics is the natural framework for the study of the upper bounds of the efficiency of those processes involving energy conversion: heat into mechanical work, light into heat, heat into chemical energy, etc., and in the case we are now dealing with, *light into electrical work*. By using *thermodynamics*, we claim there is a unique and definitive answer to the problem being analyzed. However, when reviewing the literature, some confusion appears because different figures for the limiting efficiency of PVEC are reported, all obtained by using *thermodynamic* concepts.

Analyses involving *thermodynamics* represent an attempt to obtain a result that is independent of the nature of the converter. To understand the different hypotheses and definitions that lead to different results, we find the general description given by Landsberg of an energy converter in [2] very useful. Indeed, most of the discussion and explanation that follows has arisen from Ref. [3].

Landsberg's description of a general converter is graphically sketched in Fig. 1. The converter, assumed to be at a temperature T_C , receives photons characterized by energy and entropy fluxes E_S and S_S respectively from an arbitrary source. In the general case, it also emits photons characterized by an energy and entropy fluxes, E_O and S_O , towards a sink. The *general* converter produces heat (Q') and work (W') and, if the process is not steady-state, has internal energy and entropy varying at a rate E_C and S_C , respectively. However, from now on, we will assume all processes are steady-state so that E_C and S_C are zero.

If these interchange processes occur irreversibly, we use S_g to represent the corresponding total rate of entropy increase. However, we shall assume for the moment that the interchange processes occur reversibly so that the additional entropy due to irreversibilities, S_g , will be taken as zero.

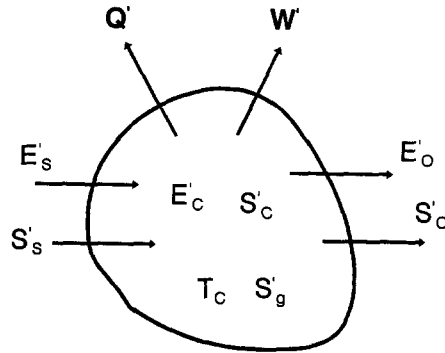


Fig. 1. Sketch of a general energy converter as described by Landsberg [2].

The computation of the limiting efficiencies is simplified by assuming the sun is a *black body* source of photons at a temperature T_s close to 6000K. Nothing essential will be lost in this preliminary discussion if, for simplicity, we also assume that the sun completely surrounds the converter. Hence, the energy and entropy fluxes the converter receives can be written as [2]:

$$\begin{aligned} E'_s &= \sigma T_s^4, \\ S'_s &= \frac{4}{3} \sigma T_s^3. \end{aligned} \quad (1)$$

The assumption that the sun completely surrounds the converter is equivalent to the solar cell being illuminated at the maximum possible light concentration with an ideal reflector placed at its rear side. This maximum concentration is given [4] by

$$X_{\max} = \frac{n^2}{\sin^2 \theta_s}, \quad (2)$$

where θ_s is the angle subtended by the solar disc at the Earth and n is the refraction index of the medium that surrounds the converter. As it will be shown later in the next sections, the maximum efficiency is independent of the concentration if we allow restriction of the *angle* with which photons are *emitted* from the converter. Therefore, the assumption that the sun completely surrounds the converter becomes unnecessary in the end. However, we shall retain this assumption to simplify the preliminary discussion.

One of the causes of divergence in the computations of the limiting efficiencies from basic thermodynamic approaches comes from the different working assumptions about the value of the energy and entropy fluxes entering the sink (E'_o and S'_o). For simplification, we will assume that the photon energy and entropy fluxes into the sink can be characterized as the ones that emerge from a black body at an effective temperature T_o . Therefore,

$$\begin{aligned} E'_o &= \sigma T_o^4, \\ S'_o &= \frac{4}{3} \sigma T_o^3, \end{aligned} \quad (3)$$

since the converter is assumed also to emit radiation in all directions.

Two balance equations corresponding to the energy and entropy conservation can now be written:

$$\begin{aligned} E'_S &= Q' + W' + E'_O, \\ T_C S'_S &= Q' + T_C S'_O, \end{aligned} \quad (4)$$

and, hence,

$$\begin{aligned} Q' &= T_C S'_S - T_C S'_O, \\ W' &= E'_S - T_C S'_S + T_C S'_O - E'_O. \end{aligned} \quad (5)$$

Two main definitions for *efficiency* now become available:

$$\eta_1 = \frac{W'}{E'_S - E'_O}, \quad (6a)$$

$$\eta_2 = \frac{W'}{E'_S}. \quad (6b)$$

The first one corresponds to the ratio between the power the converter produces as work and the power it consumes. Notice that the energy *it consumes* is the difference between the power received from the sun and the power emitted. The second definition is the definition of efficiency commonly used in photovoltaics: the ratio between the power extracted from the cell and the power received from the sun. This difference in definitions has been the source of some confusion [5].

With the first definition, Eq. 6a, the efficiency increases with T_O (see Fig. 2). The maximum efficiency is, therefore, achieved when $T_O = T_S$ (point A in Fig. 2) since, at higher temperatures, W' becomes negative which means that the surroundings are doing work on the system instead of the vice versa. At this point, the maximum efficiency

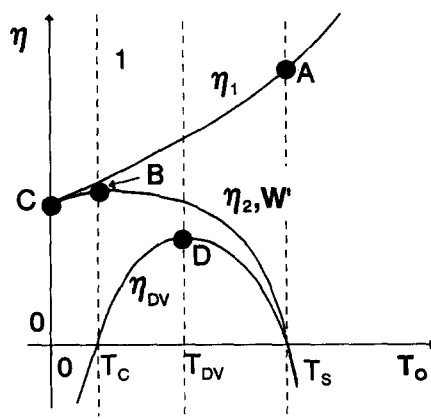


Fig. 2. Qualitative behaviour of the power W' , heat Q' and the efficiencies defined by Eq. (6) as a function of the emission temperature T_O . Curve labelled as η_{DV} corresponds also to definition 2 but, following [3], does not assume the photovoltaic process as reversible. See Table 1 for identification of the dot labels.

obtained is the same as the efficiency of a Carnot engine [6] operating between heat reservoirs at the sun's and Earth's temperature:

$$\eta_{1,\text{MAX}} = 1 - \frac{T_C}{T_S}. \quad (7)$$

Notice, however, that although the efficiency is maximum when $T_O = T_S$, then $W' = 0$ which is of no practical use. In this context, definition 2 in (6) is preferred. Substituting (5) and (1) into Eq. (6b), the following equation is obtained:

$$\eta_2 = 1 - \frac{4}{3} \frac{T_C}{T_S} + \left(\frac{4}{3} \frac{T_C}{T_O} - 1 \right) \left(\frac{T_O}{T_S} \right)^4. \quad (8)$$

Eq. (8) reaches its maximum for $T_O = T_C$ giving then:

$$\eta_{2,\text{MAX}} = 1 - \frac{4}{3} \frac{T_C}{T_S} + \frac{1}{3} \left(\frac{T_C}{T_S} \right)^4, \quad (9)$$

which corresponds to the Landsberg limiting efficiency [2], point B in Fig. 2. Notice that with definition 6b, maximizing the efficiency is equivalent to maximizing W' . Hence, when $T_O = T_C$, W' also is maximum. Henry [7] assumed that the maximum efficiency was for $T_O = 0$ since, intuitively, for this value no emission losses occur. He found then that:

$$\eta'_{2,\text{MAX}} = 1 - \frac{4}{3} \frac{T_C}{T_S}, \quad (10)$$

which corresponds to point C in Fig. 2.

However, when entropy flux conservation is taken into account as in Landsberg's approach described above, it is found that for $T_O = T_C$, although some emission losses exist, these losses are compensated because the Q' losses are lower than in the case in which $T_O = 0$. Table 1 includes the main results that have been described above. Notice, however, that in this discussion, still all the processes have been assumed reversible. The irreversible nature of photovoltaic energy conversion has been pointed out by several

Table 1

Summary of the main results about the limiting efficiency of the photovoltaic energy conversion considering thermodynamic approaches. Results refer to the sun assumed as a black body at $T_S = 6000\text{K}$ and Earth at $T_C = 300\text{K}$. Dots refer to Fig. 2

Author	Ref.	Def.	S'_g	T_O	Max. efficiency	Result
Carnot DOT A	[6]	η_1	0	T_S	$1 - \frac{T_C}{T_S}$	95.0%
Henry DOT C	[7]	η_2	0	0	$1 - \frac{4}{3} \frac{T_C}{T_S}$	93.3%
Landsberg DOT B	[2]	η_2	0	T_C	$1 - \frac{4}{3} \frac{T_C}{T_S} + \frac{1}{3} \left(\frac{T_C}{T_S} \right)^4$	93.3%
A. De Vos and Pauwels DOT D	[3]	η_2	(I-1) $S'_q = 2\sigma \left[\frac{T_C^4}{T_O^4} - \frac{4}{3} T_S^3 + \frac{1}{3} T_O^3 \right]$ (I-1) $\eta_{DV} = (1 - \frac{T_C}{T_O}) [1 - (\frac{T_C}{T_S})^4]$ (I-2)	$T_{DV} = 2540\text{K}$	(I-2)	85.4%

authors [3,8–11] and a detailed discussion is outside the scope of this paper. In any case, the computation of the entropy generation rate S'_g requires additional hypotheses, some of them based on assumptions from the detailed balance theory. They will lead us to the curve labelled as η_{DV} in Fig. 2 as will be discussed in the next section.

3. The detailed balance approach for a multigap system

Previous results were obtained assuming that the entropy generation rate, S'_g , was zero. Since no assumption was made about the nature of the converter, this hypothesis allowed us to compute an upper bound for the efficiency. We shall now present a different approach.

If some appropriate assumptions are made about the nature of the converter, the work rate W' can be computed directly. In our case, the converter will be a system of one or more *solar cells* and the framework of the detailed balance theory [12,13] will provide the necessary set of assumptions. This was reviewed in detail in other papers [1,14] at the time that the limiting efficiency of a system constituted by one cell was studied. For the convenience of the reader, we will briefly summarize here these assumptions and the conclusions they lead us to.

The basic structure of the solar cell considered is illustrated in Fig. 3b. It consists in a semiconductor slab sandwiched between some regions p^+ and n^+ arbitrarily thin. The following assumptions are made regarding the operation of the cell:

(a) Only radiative recombination processes take place. When describing the radiative generation–recombination mechanisms, photon absorption and spontaneous and stimu-

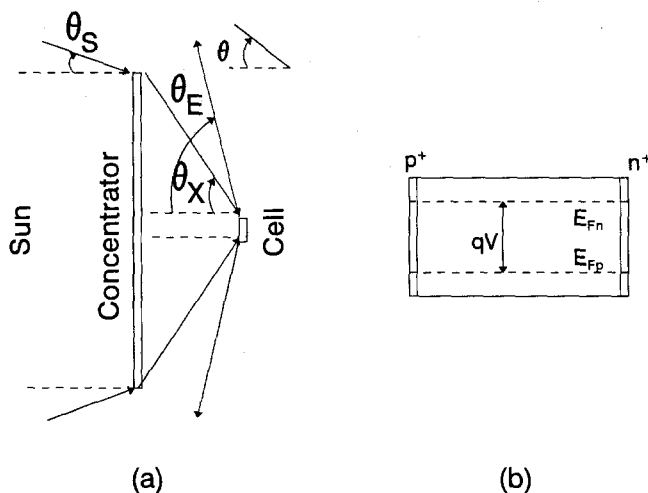


Fig. 3. (a) Elementary geometry for illuminating the cells in a concentration system. θ_s is the angle of the sun sphere when it is seen from Earth, θ_x is the maximum angle with which photons reach the cell after the concentrator, θ_e is the angle with which photons are emitted from the cell. (b) Basic solar cell structure used in the formulation of the detailed balance approach.

lated photon emission processes are considered. In addition, each photon is assumed to produce only *one* electron-hole pair when absorbed and vice versa: each electron-hole pair produces only *one* photon when recombined. Recently, attention has been given to the possibility that *one* photon generates *two* (or more) electron-hole pairs by means of optically induced impact ionization [15–17]. In this work, however, the *one to one* hypothesis will still be considered as the most likely absorption process. Furthermore, from the point of view of the limiting efficiency, it has been recognized [18] that the maximum efficiency of the hot carrier solar energy converter is essentially equivalent to that of an infinite stack of *one to one* solar cells.

(b) Carrier mobility is assumed to approach infinity so ohmic losses are neglected. Pseudo-Fermi level splitting becomes constant through the device and equal to the external voltage applied.

With these hypothesis, the current versus voltage characteristic of the solar cell was proved in [1] to be given by:

$$I = q(F_{\text{ABS}} - F_{\text{EM}}), \quad (11)$$

where F_{ABS} and F_{EM} are the number of photons absorbed and emitted per unit of time in the cell, respectively. These values can be computed from the following relationships:

$$F_{\text{ABS}} = q \int a b_s \cos \theta dE d\Omega dS$$

$$b_s = \begin{cases} \frac{2E^2}{h^3 c^2} \frac{1}{\exp \frac{E}{kT_s} - 1} & \theta < \theta_x \\ \frac{2E^2}{h^3 c^2} \frac{1}{\exp \frac{E}{kT_c} - 1} & \pi/2 > \theta > \theta_x \end{cases}, \quad (12)$$

where the equation for $\theta < \theta_x$ (see Fig. 3a for the definition of the angle θ) corresponds to photons coming from the sun characterized as a black body at a temperature T_s ; and the equation for $\theta > \theta_x$ corresponds to photons coming from the environment which is also taken to be at temperature T_c . Ω is the solid angle that θ sustains. The other term in Eq. (11) is given by

$$F_{\text{EM}} = \int e b(V) \cos \theta dE d\Omega dS$$

$$b(V) = \frac{2E^2}{h^3 c^2} \frac{1}{\exp \frac{E - qV}{kT_c} - 1}. \quad (13)$$

The terms a and e in (12) and (13) are the *absorptivity* and the *emissivity*, respectively, and in the most general case they have angular dependence. In principle, there is no a priori reason to assume $e = a$ under nonequilibrium conditions. However, in the framework of [1], it was proved that $e = a$ still holds in nonequilibrium conditions providing hypotheses “ $a - b$ ” are satisfied. It has to be emphasized that, when the

current voltage characteristic of the solar cell is written as in Eqs. (11) to (13), *photon recycling* effects have already been taken into account.

Given the solar spectrum, the usage of only one cell does not provide the maximum possible efficiency since, for example, no power is extracted from photons with energies lower than the bandgap energy. Two solar cells can better match the solar spectrum, and when the scheme is taken to the limit, an infinite number of cells provides the best approach [19–21].

Fig. 4 sketches a system that, based on spectral splitting, casts the sunlight between n cells. The splitter is assumed to be free of losses. Each cell is characterized by an energy gap $E_n > E_{n-1}$ and receives photons with energies in between E_n and E_{n+1} . In the limiting case of infinitely many cells, the gap of each cell is different from the former by an amount dE . The cells are supposed to have a perfect back reflector and therefore, no photons are emitted from the rear side of the cells. For a complete generalization, the system is supposed also to be capable of providing concentrated light to the cells. If X is the concentration, the invariance of radiance [4] establishes that photons have to impinge over the cells within a semiangle θ_X such that

$$\sin^2 \theta_X = X \sin^2 \theta_S, \quad (14)$$

assuming the cells are surrounded by air (of refractive index one). The symbol θ_S is the semiangle with which photons from the sun reach the Earth (See Fig. 3a).

The concepts of *angle* and *energy* restriction of the emitted photons [1–14] will be used here. They mean that, ideally, in order to achieve the maximum efficiency, we admit the possibility that the emissivity (absorptivity) of the cell can be tailored in the sense that the emission of photons with an angle greater than θ_X is restricted ($e = a = 0$ for $\theta > \theta_X$), as is the emission of photons with energies higher than $E + dE$. Considering each individual cell, there are no photons impinging with these angles and energies

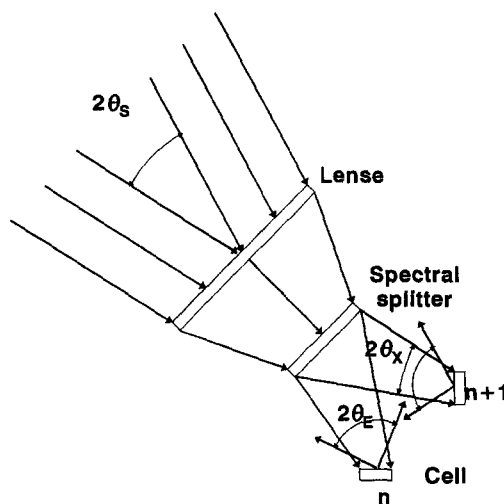


Fig. 4. General sketch of a multigap converter based on the splitting of the solar spectrum. When the limiting efficiency is discussed, θ_E is made equal to θ_X .

so there is no need to have an absorptivity (emissivity) equal to unity in these ranges and it can be set equal to zero. By doing this, the photogenerated current of the cell is not affected but, the emission of photons, and, therefore, the losses are reduced, and the efficiency increased. Elsewhere, the absorptivity (emissivity) will be assumed equal to unity. Readers interested in a discussion about when the assumption of unit absorptivity does not lead to maximum efficiency can refer to [1].

With these considerations, and taking the number of cells to infinity, if $V(E)$ is the operating voltage of the cell with gap E , the elemental power extracted from this cell per unit of area is

$$dw' = \sin^2\theta_x f(E, V) dE, \quad (15)$$

with

$$f(E, V) = q \frac{2\pi}{h^3 c^2} E^2 \left(\frac{1}{\exp\left(\frac{E}{kT_s}\right) - 1} - \frac{1}{\exp\left(\frac{E - qV}{kT_c}\right) - 1} \right) V dE, \quad (16)$$

where the integration in the solid angle has been carried out already. The total power is obtained by integrating (15) in energies:

$$w' = \sin^2\theta_x \int f(E, V) dE. \quad (17)$$

The efficiency, in the photovoltaic sense, is obtained by applying definition 6b. Therefore,

$$\eta_2 = \frac{\sin^2\theta_x \int f(E, V) dE}{X \sin^2\theta_s \sigma T_s^4} = \frac{\int f(E, V) dE}{\sigma T_s^4}, \quad (18)$$

where Eq. (14) has been used. This proves that the efficiency is independent of the concentration providing the angle of emission of photons is restricted to that of the incoming light as assumed above ($\theta_E = \theta_x$ in Fig. 3a).

Two different approaches have been used in the past to maximize (18). In the first one, described by De Vos and Pauwels [3], for illustrative and simplifying purposes, the operating voltage of each cell was linked to the photon energy in order to characterize the emission of photons from the system by means of an effective temperature T_O :

$$\frac{E - qV}{kT_c} = \frac{E}{kT_O}. \quad (19)$$

Then, Eq. (18) resulted in Eq. (I-2) in Table 1 and T_O was optimized to maximize the efficiency. The result was an optimum efficiency of 85.4% [3] which corresponds to an equivalent temperature $T_O = T_{DV} = 2540K$ (Point D in Fig. 2). For their computations they used maximum concentration. In this paper, however, it is emphasized that it is not necessary to assume that the cell operates at the maximum concentration to obtain the maximum efficiency providing that the angle of emission of photons is restricted

($\theta_E = \theta_X$). Therefore, the figure 85.4% is independent of the concentration. In any case, the simplification in Eq. (19) allowed De Vos and Pauwels to clearly illustrate how the photovoltaic conversion should be considered as an irreversible processes at the operating voltage that corresponds to the maximum efficiency. With some additional calculations involving entropy flux conservation, they computed the entropy generation S'_g due to the irreversibilities in the conversion processes (Eq. (I-1) in Table 1, Eq. (31) in Ref. [3]). These results have also been included in the summary of Table 1 for comparison with the other thermodynamic approaches discussed in Section 1. In later discussions [9–11], the nature of the irreversibilities was described more and they were associated to the coupling of the converter to the external world by means of the interchange of both energy and matter (*endoreversible* processes).

A slightly more complicated but otherwise more realistic approach to maximizing (18), also described in [3], consists in maximizing the operating voltage for each individual cell so that $V = V_m(E)$ with $V_m(E)$ satisfying

$$\frac{\partial}{\partial V} f(E, V_m(E)) = 0. \quad (20)$$

Computing (18) with $V = V_m(E)$, we also obtained the maximum efficiency as 86.8% with the novelty that this figure is independent of the concentration providing that $\theta_E = \theta_X$, as mentioned already.

For the discussion above, the splitting system sketched in Fig. 4 has been used as the starting point for simplicity. Some objections to the model can arise from the fact that an additional external element, the splitter, has been introduced in the system and that this splitter has been assumed to be free of losses. It can be proved (see next section) that a stacked system as the one sketched in Fig. 5, which will be discussed in the next two sections, leads to the same equations (15 to 18) when the number of cells increases to infinity and therefore, to the same value of the limiting efficiency without the necessity of an external element. However, this system has interesting features regarding the limiting efficiency when the number of cells considered is finite.

4. Limiting efficiency of a system with a finite number of cells

In a stacked system, N cells are ordered by decreasing gap as sketched in Fig. 5a. The first ($n = 1$) is the cell with the lowest bandgap. It is, therefore, placed at the bottom of the stack. Sunlight travels from left to right. A perfect back reflector is placed at the rear side of the last cell to prevent emission losses in that direction.

At cell $n + 1$, photons with energies lower than the gap of the cell, E_{n+1} , are allowed to pass through; then, the cell n absorbs those photons from the sun spectrum with energies $E_{n+1} > E > E_n$. We will analyze now two different cases differing in the way the radiative losses are handled.

In case ‘‘a’’, Fig. 5a, due to radiative recombination, cell n emits photons producing some energy losses for the cell. However, cell $n + 1$ and cell $n - 1$ benefit from these luminescence losses in cell n since cell $n - 1$ can collect all the photons that cell n

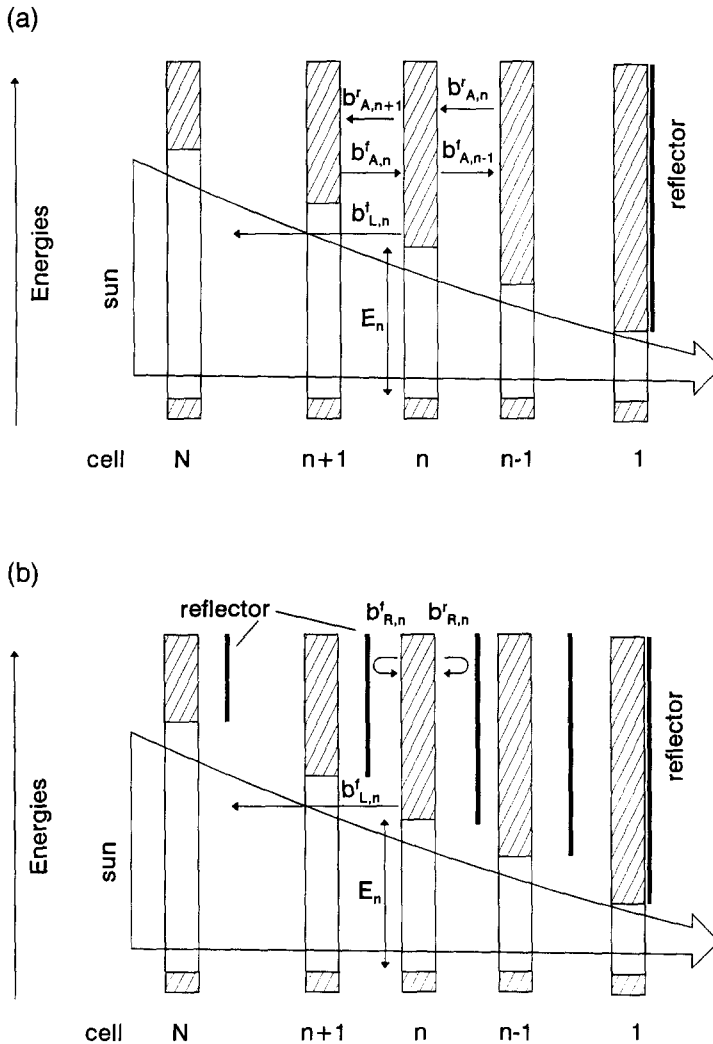


Fig. 5. Sketch of a stacked multigap system. In (a) no reflector is placed at the rear side of the cells and so, photons emitted from one cell can be absorbed by the others. In (b) a reflector is placed at the rear side. In this case, although the cells do not absorb photons from their neighbours, the radiative losses in each individual cell also decreases. In text it is discussed which approach give the maximum efficiency.

emits from the rear side and cell $n + 1$ can collect the portion of the photons emitted from the front side of cell n with energies higher than E_{n+1} . This effect is called *radiative coupling* between the cells. Then, only the portion of the emitted photons with energies $E_{n-1} < E < E_n$ are wasted.

In case “b”, a reflector is placed at the rear side of the cells (Fig. 5b). The emission losses of cell n will be reduced. However, cells $n - 1$ and $n + 1$ will not benefit from

the luminescent photons coming from cell n as in the previous case. The following question arises: has this configuration a higher limiting efficiency than the previous configuration? The answer is “yes” as it was anticipated in Ref. [22] for a system with two gaps. The discussion is generalized here to a higher number of gaps at the time that new results are presented.

To discuss these configurations simultaneously, we define the appropriate step function to describe the reflector at the rear side of cell n :

$$r_n = \begin{cases} 1(0) & E > E_n \\ 0 & E < E_n \end{cases} \quad (21)$$

The value “1” describes the situation for case b, in which reflectors are introduced, while “0” corresponds to case a. The absorptivity (emissivity) of cell n is given also by a step function.

$$a_n = \begin{cases} 1 & E > E_n \\ 0 & E < E_n \end{cases} \quad (22)$$

Considering the different sources for the photon radiance that cell n receives and its luminescent losses, the maximum power delivered by cell n is given by:

$$P_n = q\pi \sin^2\theta_X V_{m,n} \int_E (b_{S,n} + b_{A,n}^f(V_{m,n+1}) + b_{R,n}^f(V_{m,n}) + b_{A,n}^r(V_{m,n-1}) + b_{R,n}^r(V_{m,n}) - 2b_E(V_{m,n})) dE, \quad (23)$$

where $V_{m,x}$ is the optimum operation voltage in cell x to achieve the maximum

Table 2

Description of the different spectral photon radiance involved in a stacked system of cells

Notation	Value	Meaning
$b_{S,n}$	$(a_n - a_{n+1})b_S$	Coming from the sun and absorbed in cell n
$b_{R,n}^f(V_n)$	$r_{n+1}a_n b(V_n)$	Emitted from cell n , reflected in reflector $n+1$ and absorbed again in cell n
$b_{R,n}^r(V_n)$	$r_n a_n b(V_n)$	Emitted from cell n , reflected in reflector n and absorbed again in cell n
$b_{A,n}^f(V_{n+1})$	$a_n(1 - r_{n+1})a_{n+1} b(V_{n+1})$	Emitted from cell $n+1$ and absorbed again in cell n
$b_{A,n}^r(V_{n-1})$	$a_n(1 - r_n)a_{n-1} b(V_{n-1})$	Emitted from cell $n-1$ and absorbed again in cell n
$b(V_n)$	$\frac{2}{\hbar^3 c^2} \frac{E^2}{\exp((E - eV_n)/kT_c) - 1}$	Emitted from cell n , biased at V_n
$b_{L,n}^f(V_n)$	$(1 - a_{n+1})a_n b(V_n)$	Radiative losses in cell n not absorbed in any cell

(Note: Because cells with $n = N+1$ and $n = 0$ does not exist, it is necessary to make $a_{n+1} = 0$, $a_0 = 1$, $V_{N+1} = 0$ and $V_0 = 0$ to generalize the equations above)

efficiency. Notice that in Eq. (23), the concept of angle restriction has been applied. The meaning of the spectral photon radiances $b(V_{m,x})$ is summarized in Table 2.

After some manipulation, and taking into account that $a_n a_{n+1} = a_n$, $a_{n+1} r_{n+1} = r_{n+1}$ and $a_n r_{n+1} = r_{n+1}$ and the equations in Table 2, Eq. (23) can be rearranged as:

$$P_n = q\pi \sin^2 \theta_X V_n \int_E \left((a_n - a_{n+1}) b_s + [a_{n+1} b(V_{m,n+1}) - a_n b(V_{m,n})] - r_{n+1} [b(V_{m,n+1}) - b(V_{m,n})] + a_n (1 - r_n) [b(V_{m,n-1}) - b(V_{m,n})] \right) dE. \quad (24)$$

To achieve the maximum efficiency, the bandgap of the cells will still require optimization. Fig. 6 plots the optimum efficiency that results after the optimization of bandgaps and voltages. For comparison, we also plot the maximum efficiencies when terrestrial AM1.5 direct normal irradiance [23] is considered (instead of black body radiation at $T_s = 6000\text{K}$) as characterizing the illumination from the sun. Also, the values corresponding to $X = 1$ sun and values without restricting the angle of emission ($\theta_E = 90^\circ$) has been plotted. For reference, Table 3 summarizes the corresponding values. The following remarks can be pointed out:

(a) As it can be observed, both approaches (with and without reflectors) give the same result when the number of cells increase towards infinity. This result can be expected from Eq. (24) since, when number of cells tends to infinity, $V_{m,n+1} - V_{m,n} \rightarrow 0$. Eq. (24) can be written as:

$$dP(E) = q\pi \sin^2 \theta_X \left(b_s(E) - \frac{2E^2}{h^3 c^2} \frac{1}{\exp \frac{E - qV_m(E)}{kT}} \right) dE, \quad (25)$$

which is independent of whether reflectors are used or not. Notice that Eq. (25) is identical to Eq. (15) with P playing the role of w' and, therefore, the value for the limiting efficiency for an infinite number of gaps, 86.8% for the sun assumed as a black body at $T_s = 6000\text{K}$, is obtained as before. The figure corresponding to AM1.5 direct normal irradiance [23] has been computed here for the first time to our knowledge. It gives 85.0%. Linear interpolation of the data in Ref. [23] and trapezoidal integration have been used in the computations.

(b) However, when the number of cells is finite, the approach with reflectors gives a slightly higher efficiency than the approach without reflectors that in Ref. [20] was assumed to lead to the maximum efficiency. If we assume that the optimum voltages satisfies $V_{m,n+1} > V_{m,n}$, this result can be proved as follows:

If the system consists of N cells and has reflectors, the power delivered is given by:

$$P_{WR}(V'_m) = \sum_{n=1}^N P'_n(V'_m), \quad (26)$$

where V'_m represents the set of optimum voltages that maximizes the power and P'_n is

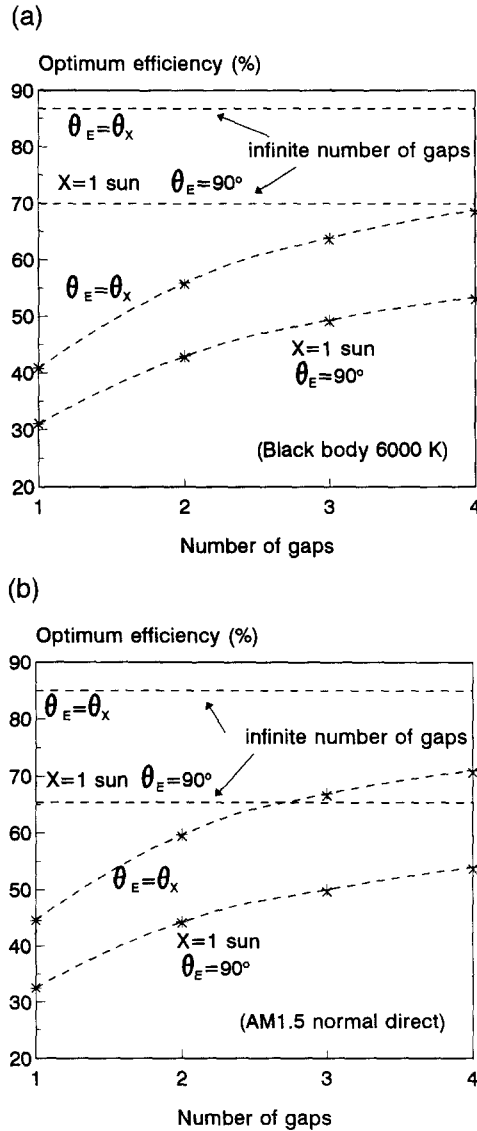


Fig. 6. Maximum efficiency as a function of the number of cells: (a) for the sun assumed as a black body at 6000K, (b) for AM1.5 direct normal irradiance [23]. In both cases, dots marked as “+” corresponds to the case with reflectors (illustrated in Fig. 5a) and dots marked as “X” to the case without reflectors (Fig. 5b). Both values are very close but the one corresponding to the case with reflectors is slightly higher.

given by Eq. (24) with the appropriate values for r (Eq. (21)). Conversely, if the system has no reflectors, the maximum deliverable power is given by:

$$P_{NR}(V_m) = \sum_{n=1}^N P_n(V_m), \quad (27)$$

Table 3

Optimum efficiency and bandgaps for multigap systems with different number of cells for the sun assumed as a black body at 6000K and for AM1.5 direct normal irradiance [23] (table below). The values of the efficiency are plotted in Fig. 6. "Reflectors" means whether back reflectors have been placed at the rear side of all the cells in the stack or not. Last cell in the stack always has a back reflector. The case labeled as "Maximum concentration" is equivalent also to the case of operation at one sun when the angle of the emitted photons from the cell is restricted to that of the incoming photons from the sun

N. cells	Description	Reflectors?	Optimum gaps (eV)				Eff (%)
			E1	E2	E3	E4	
(Black body at 6000K)							
1	1 sun, no angular restriction	Yes	1.31	–	–	–	31.0
	1 sun no angular restriction	No	1.31	–	–	–	31.0
	Maximum concentration	Yes	1.11	–	–	–	40.8
	Maximum concentration	No	1.11	–	–	–	40.8
2	1 sun, no angular restriction	Yes	0.98	1.87	–	–	42.9
	1 sun no angular restriction	No	0.98	1.88	–	–	42.7
	Maximum concentration	Yes	0.77	1.70	–	–	55.9
	Maximum concentration	No	0.78	1.71	–	–	55.6
3	1 sun, no angular restriction	Yes	0.82	1.44	2.26	–	49.3
	1 sun no angular restriction	No	0.83	1.45	2.26	–	49.1
	Maximum concentration	Yes	0.62	1.26	2.10	–	63.8
	Maximum concentration	No	0.63	1.27	2.11	–	63.5
4	1 sun, no angular restriction	Yes	0.72	1.21	1.77	2.55	53.3
	1 sun no angular restriction	No	0.73	1.23	1.78	2.56	53.0
	Maximum concentration	Yes	0.52	1.03	1.61	2.41	68.8
	Maximum concentration	No	0.53	1.05	1.68	2.41	68.4
∞	1 sun, no angular restriction	Yes	–	–	–	–	69.9
	1 sun no angular restriction	No	–	–	–	–	69.9
	Maximum concentration	Yes	–	–	–	–	86.8
	Maximum concentration	No	–	–	–	–	86.8
(AM1.5 direct normal irradiance)							
1	1 sun, no angular restriction	Yes	1.13	–	–	–	32.5
	1 sun no angular restriction	No	1.13	–	–	–	32.5
	Maximum concentration	Yes	0.94	–	–	–	44.6
	Maximum concentration	No	0.94	–	–	–	44.6
2	1 sun, no angular restriction	Yes	0.94	1.64	–	–	44.3
	1 sun no angular restriction	No	0.94	1.64	–	–	44.1
	Maximum concentration	Yes	0.71	1.41	–	–	59.7
	Maximum concentration	No	0.71	1.41	–	–	59.4
3	1 sun, no angular restriction	Yes	0.71	1.16	1.83	–	50.1
	1 sun no angular restriction	No	0.71	1.16	1.83	–	49.7
	Maximum concentration	Yes	0.69	1.16	1.84	–	67.0
	Maximum concentration	No	0.69	1.16	1.83	–	66.6
4	1 sun, no angular restriction	Yes	0.71	1.13	1.55	2.13	54.0
	1 sun no angular restriction	No	0.71	1.13	1.55	2.13	53.6
	Maximum concentration	Yes	0.53	1.13	1.55	2.13	71.0
	Maximum concentration	No	0.53	1.13	1.55	2.13	70.7
∞	1 sun, no angular restriction	Yes	–	–	–	–	65.4
	1 sun no angular restriction	No	–	–	–	–	65.4
	Maximum concentration	Yes	–	–	–	–	85.0
	Maximum concentration	No	–	–	–	–	85.0

V_m being the optimum set of voltages for the new arrangement and P_m given by Eq. (24) and with $r = 0$ in Eq. (21). Notice that, in general, $V'_m \neq V_m$ and, therefore,

$$P_{WR}(V'_m) \geq P_{WR}(V_m), \tag{28}$$

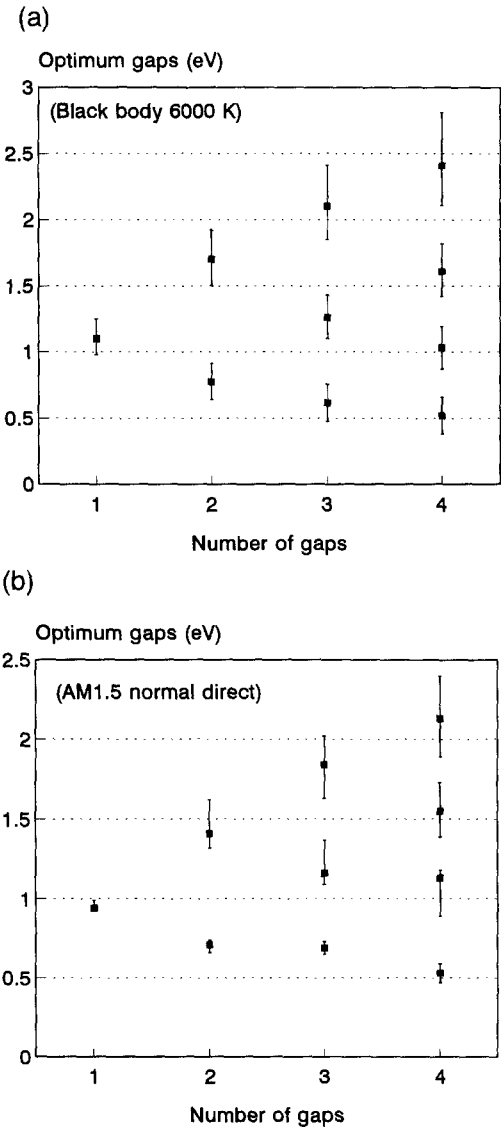


Fig. 7. (a) Optimum gaps as a function of the number of cells in the stack for the sun assumed as a black-body at $T_s = 6000\text{K}$. Reflectors at the rear side of each cell as described in Fig. 5b have been assumed. Maximum concentration (or, equivalently, total restriction of the photons emitted from the cell) has been considered. Bars indicate the tolerance in the value of the optimum gap to keep the maximum efficiency not less than 1% of its maximum value when the other values of the gaps remain constant and equal to their optimum value (square dots). (b) The same for AM1.5 direct normal irradiance.

since V_m are not the optimum voltages for the configuration with reflectors. A direct calculation shows that

$$P_{WR}(V_m) - P_{NR}(V_m) = e\pi \sin^2\theta_X \int_E \left\{ r_1 V_{m,1} (b_{E,1}(V_{m,1}) - b(0)) + \sum_{n=2}^N r_n (b_{E,n-1}(V_{m,n-1}) - b_{E,n}(V_{m,n})) (V_{m,n-1} - V_{m,n}) \right\} dE, \quad (29)$$

and, therefore, because $V_{m,n} > V_{m,n-1}$

$$P_{WR}(V_m) \geq P_{NR}(V_m), \quad (30)$$

which together with Eq. (28) leads to

$$P_{WR}(V'_m) \geq P_{NR}(V_m), \quad (31)$$

as we wanted to show.

(c) The sensitivity of the maximum efficiency with respect to the value of the optimum bandgaps is lower as the bandgap of the cell in the stack is higher. In other words, the efficiency is more and more sensitive to the values of the gap of the cells as we consider the cells towards the bottom of the stack. This was pointed out in Ref. [24] for a system with two cells and it is illustrated here, in Fig. 7, for a system up to 4 cells. The sensitivity to the bottom cell gap is higher when AM1.5 direct normal irradiance spectrum is considered, instead of black body radiation at 6000K as illustrated in Fig. 7b.

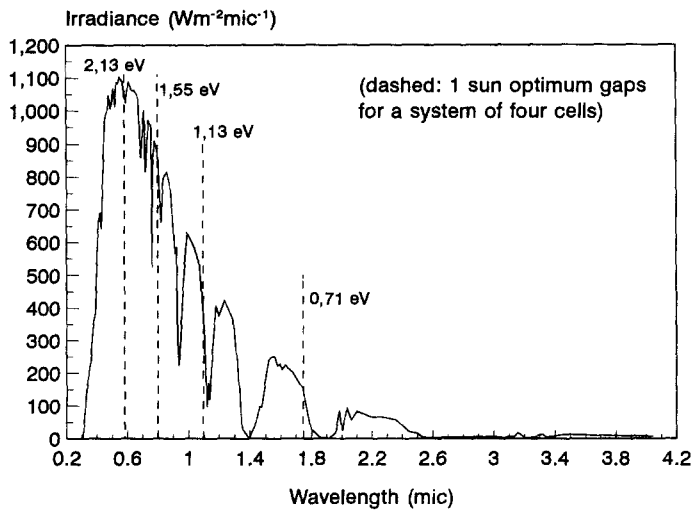


Fig. 8. Plot of the data corresponding to terrestrial direct normal solar spectral irradiance for air mass 1.5 [23]. The vertical lines show the optimum gaps for a system of four cells at one sun.

(d) When the sun is assumed as a black body at 6000K, the values of the optimum gaps depend on the concentration (if no angular restriction is provided) and also on whether reflectors have been placed at the rear side of the cells. The numerical results show that the optimum gaps shift towards values about 10 meV higher when no reflectors are placed in comparison with the case with reflectors. Also, when values at one sun are compared with values at maximum concentration (or total angular restriction) the optimum gaps shifts towards values in the range of 100–200 meV higher. However, when AM1.5 direct normal irradiance is considered, there is no such shift when the cases with reflectors and without reflectors are compared. Also, in the stacked system, when more than one cell is considered, only the optimum gap of the bottom cell is sensitive to concentration. Due to the valleys and crests that appear in the AM1.5 direct normal irradiance as a result of the atmospheric absorption, optimum gaps seems to be locked to them as illustrated in Fig. 8.

5. Conclusions

The limiting efficiency of photovoltaic energy conversion is 86.8% for the sun assumed as black body at 6000K, 85.0% if AM1.5 direct normal irradiance is considered. These results are independent of the concentration providing the emission of photons can be restricted in angle to that strictly necessary to receive the photons from the sun. This limit is attributed to a system consisting of an infinite number of cells. The figures that result differ from the ones obtained from standard thermodynamic approaches (93.3–95%) due to the different assumptions and even the definition of efficiency itself that is used (see Table 1). For systems consisting of a stack of a finite number of cells, the use of back reflectors increases the limiting efficiency slightly when compared to the situation without reflectors. The sensitivity of the optimum efficiency is higher for the bottom cells of the stack. Calculations involving AM1.5 direct normal irradiance have been included and show some peculiarities when compared with results corresponding to black body radiation at 6000K: the sensitivity of the efficiency to the value of the gap of the bottom cell increases and the value of the optimum gap for cells other than the bottom one does not shift significantly with concentration.

6. List of symbols

E'_S	Energy flux that the converter receives from the sun.
E'_O	Energy flux emitted from the converter to the sink.
E'_C	Internal energy variation rate in the converter.
E_n	Energy gap of cell n th in a stacked system.
S'_S	Entropy flux that the converter receives from the sun.
S'_O	Entropy flux emitted from the converter to the sink.
S'_C	Internal entropy variation rate in the converter.
Q'	Rate of heat conduction out of converter.
W'	Work produced per unit of time (power).

T_C	Converter temperature.
T_S	Temperature of the sun.
T_O	Effective temperature for characterizing the photons emitted from the converter.
σ	Stefan-Boltzman constant.
X	Light concentration.
n	Refraction index.
θ_S	Semiangle with which photons from the sun reach the Earth.
θ_X	Maximum semiangle with which photons impinge on the cell.
θ_E	Maximum semiangle for the photons emitted from the cell.
θ	Angle that defines ray trajectories (Fig. 3a).
Ω	Solid angle sustained by θ .
η_1	Efficiency (thermodynamic definition).
η_2	Efficiency (photovoltaic definition).
F_{ABS}	Number of photons absorbed per unit of time in the cell.
F_{EM}	Number of photons emitted per unit of time from the cell.
a	Absorptivity.
e	Emissivity.
V	Voltage.
P_{WR}	Power delivered by a system with reflectors.
P_{NR}	Power delivered by a system without reflectors.
q	Electron electric charge.
h	Planck's constant.
c	Speed of the light in vacuum.
k	Boltzman's constant.

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