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Theoretical Calculation of the Efficiency Limit for Solar Cells

Abderrahmane Belghachi

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1. Introduction

In recent years there has been intense research work into the development of high efficiency solar cells relying on emerging novel materials and structures. All this has lead to a continuous record breaking of highest achievable efficiencies using different technologies. Since the first photovoltaic devices were developed the most prevalent concern is to hem in all sorts of efficiency losses preventing from reaching the physical limits [1-3]. To overcome this impediment, thorough investigations have been carried out to control and unearth their origins in order to identify potential efficiency advantages. Numerous thermodynamic approaches were employed to calculate solar cell efficiency limit, starting from the ideal Carnot engine to the latest detailed balance with its improved approach.

The aim of this chapter is to present a review of the techniques used to calculate the energy conversion efficiency limit for solar cells with detailed calculation using a number of numerical techniques. The study consists of analyzing the solar cell intrinsic losses; it is these intrinsic losses that set the limit of the efficiency for a solar energy converter. Several theoretical approaches were used in order to obtain the thermodynamic limit for energy conversion.

In the first place a solar cell could be considered as a simple energy converter (engine) able to produce an electrical work after the absorption of heat from the sun. In this fundamental vision the solar cell is represented by an ideally reversible Carnot heat engine in perfect contact with high temperature reservoir (the sun) and low temperature reservoir representing the ambient atmosphere. If the sun is at a temperature of $6000K$ and the ambient temperature is $300K$, the maximum Carnot efficiency is about 95% this value constitutes an upper limit for all kind of solar converters.

When the solar cell is supposed a blackbody converter absorbing radiation from the sun itself a blackbody, without creating entropy, we obtain an efficiency of about 93 % known as the Landsberg efficiency limit, which is slightly lower than Carnot efficiency.

Whilst a solar cell is assumed as an endoreversible system [4], the energy conversion efficiency is limited to 85.7% this figure is obtained where the sun is assumed fully surrounding the cell (maximum concentration). If we bear in mind that in a real situation the solar cell does not operate always in maximum concentration and the solid angle under which the cell sees the sun is in fact only a minute fraction of a hemisphere, the maximum efficiency is not larger than 12.79%, which is actually lower than most recently fabricated solar cells. However, we can conclude that solar cell is a quantum converter and cannot be treated as a simple solar radiation converter [5].

Semiconductor *pn* junction solar cell is a quantum converter where the energy band-gap of semiconductor material is the most important and critical factor controlling efficiency. Incident photons with energy higher than the energy gap can be absorbed, creating electron-hole pairs, while those with lower energy are not absorbed, either reflected or transmitted.

In the ideal model of a monochromatic cell incident photons are within a narrow interval of energy, while the cell luminescence outside this range is prevented. The overall resulting efficiency upper limit for an infinite number of monochromatic cells is 86.81% for fully concentrated sun radiation.

The ultimate efficiency of a single band gap *pn* junction for an AM1.5 G solar spectrum gives a value of 49%, this maximum efficiency, if compared to Carnot efficiency limit, is substantially lower. Therefore in quantum converters it is obvious that more than 50% of the solar radiation is lost because of spectral mismatch.

To represent a more realistic picture of a solar cell, three other fundamental factors should be taken into account, namely; the view factor of the sun seen from the solar cell position, the background radiation which could be represented as a blackbody at ambient temperature, and losses due to recombination, radiative and non-radiative.

In the detailed balance efficiency limit calculation first suggested in 1961 by Shockley and Queisser (SQ) in their seminal paper [6]. It is assumed that illumination of semiconductor *pn* junction by a blackbody source creates electron-hole pairs due to the fundamental absorption of photons with energies greater than the band-gap. These pairs either recombine locally if they are not separated and extracted along different paths to perform work in an external circuit. They assumed that recombination in the semiconductor is partly radiative and the maximum efficiency is attained when radiative recombination in dominant. The Shockley-Queisser model has been extended and completed to account for more physical phenomena [7-13]. For instance, the generalised Planck radiation law introduced by Würfel [7], the effect of background radiation has been included and elaborate numerical techniques has been used in order avoid mathematical approximations which would yield erroneous results.

The currently achieved short-circuit current densities for some solar cells are very close to predicted limits [14]. Nevertheless, further gain in short-circuit current can therefore still be

obtained, mainly by minimising the cell surface reflectivity, while increasing the thickness, so as to maximize the photons absorption. For thin film solar cells gain in photocurrent can be obtained by improving light trapping techniques to enhance the cell absorption.

Radiative recombination and the external fluorescence efficiency have a critical role to play, if the created photons are re-emitted out of the cell efficiently, which corresponds to low optical losses, the open circuit voltage and consequently the cell efficiency approach their limits [15]. Concentrating solar radiation onto a solar cell improves remarkably its performance. Comparable effect could be obtained if the solar cell emission and acceptance angles were made equal.

2. Solar cell as a heat engine

2.1. Solar cell as a reversible heat engine

Thermodynamics has widely been used to estimate the efficiency limit of energy conversion process. The performance limit of solar cell is calculated either by thermodynamics or by detailed balance approaches. Regardless of the conversion mechanism in solar cells, an upper efficiency limit has been evaluated by considering only the balances for energy and entropy flux rates. As a first step the solar cell was represented by an ideally reversible Carnot heat engine in perfect contact with high temperature T_s reservoir (the sun) and low temperature T_a reservoir representing the ambient atmosphere. In accordance with the first law of thermodynamics the extracted work, the cell electrical power output, is represented as the difference between the net energy input from the sun and the energy dissipated to the surrounding environment. The model is illustrated in figure 1. Where Q_1 is the incident solar energy impinging on the cell, Q_2 is the amount of energy flowing from the converter to the heat sink and W is the work delivered to a load in the form of electrical energy ($W = Q_1 - Q_2$). The efficiency of this system is defined using the first thermodynamic law as:

$$\eta_c = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \tag{1}$$

for a reversible engine the total entropy is conserved, $S = S_1 - S_2 = 0$, then;

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \tag{2}$$

Hence the Carnot efficiency could be represented by:

$$\eta_c = 1 - \frac{T_a}{T_s} \tag{3}$$

This efficiency depends simply on the ratio of the converter temperature, which is equal to that of the surrounding heat sink, to the sun temperature. This efficiency is maximum (η_c=1) if the converter temperature is *0 K* and the solar energy is totally converted into electrical work, while η_c=0 if the converter temperature is identical to that of the sun T_s the system is in thermal equilibrium so there is no energy exchange. If the sun is at a temperature of *6000K* and the ambient temperature is *300K*, the Carnot efficiency is *95%* this value constitutes an upper limit for all solar converters.
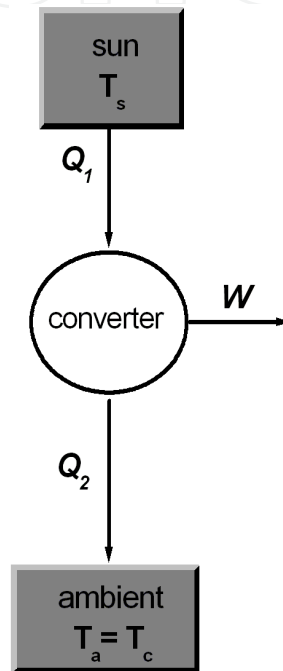

Figure 1. A schematic diagram of a solar converter represented as ideal Carnot engine.

Another way of calculating the efficiency of a reversible heat engine where the solar cell is assumed as a blackbody converter at a temperature T_c, absorbing radiation from the sun itself a blackbody at temperature T_s, without creating entropy, this efficiency is called the Landsberg efficiency[16].

Under the reversibility condition the absorbed entropy from the sun S_{abs} is given off in two ways one is emitted back to the sun S_{emit} and the second part goes to the ambient thermal sink S_a. Under this condition, the solar cell is called reversible if:

$$S_{abs} - S_{emit} - S_a = 0 \tag{4}$$

In accordance with the Stefan–Boltzmann law of black body, the absorbed heat flow from the sun is:

$$Q_{abs} = \sigma T_s^4 \tag{5}$$

For a blackbody radiation, the absorbed density of entropy flow is:

$$S_{abs} = \frac{4}{3} \sigma T_s^3 \tag{6}$$

The energy flow emitted by the converter at a temperature T_c is:

$$Q_{emit} = \sigma T_c^4 \tag{7}$$

And the emitted entropy flow is:

$$S_{emit} = \frac{4}{3} \sigma T_c^3 \tag{8}$$

In this model the blackbody source (sun) surrounds entirely the converter at T_c which is assumed in a contact with a thermal sink at T_a then $T_c = T_a$. Therefore the entropy transferred to the thermal sink is:

$$S_a = S_{abs} - S_{emit} = \frac{4}{3} \sigma (T_s^3 - T_c^3) \tag{9}$$

And the transferred heat flow is:

$$Q_a = T_c S_a = \frac{4}{3} \sigma T_c (T_s^3 - T_c^3) \tag{10}$$

The entropy-free, utilizable work flow is then:

$$W = Q_{abs} - Q_{emit} - Q_a \tag{11}$$

Therefore the Landsberg efficiency can be deduced as:

$$\eta_L = \frac{W}{Q_{abs}} = 1 - \frac{4}{3}\frac{T_c}{T_s} + \frac{1}{3}\left(\frac{T_c}{T_s}\right)^4 \tag{12}$$

The actual temperature of the converter T_c depends on the operating point of the converter and is different from the ambient temperature T_a, ($T_c \neq T_a$). To maintain the same assumption as the Landsberg efficiency calculation, the entropy transferred to the ambient thermal sink is rewritten as:

$$Q_a = T_a S_a = \frac{4}{3}\sigma T_a(T_s^3 - T_c^3) \tag{13}$$

We arrive to a more general form of the Landsberg efficiency η':

$$\eta'_L = 1 - \left(\frac{T_c}{T_s}\right)^4 - \frac{4}{3}\frac{T_a}{T_s}\left(1 - \frac{T_c^3}{T_s^3}\right) \tag{14}$$

Both forms of Landsberg efficiency (η_L and η'_L) are plotted in Figure 2, Carnot efficiency curve is added for comparison. At 300K η_L and η'_L coincide at 93.33 % which is slightly lower than Carnot efficiency. When the temperature of the converter is greater than the ambient temperature ($T_c > T_a$) there is less heat flow from the converter to the sun (in accordance with Landsberg model). This means that much work could be extracted from the converter leading to a higher efficiency. As T_c approaches the sun temperature, the net energy exchange between the sun and the converter drops, therefore the efficiency is reduced and finally goes to zero for $T_c = T_s$.
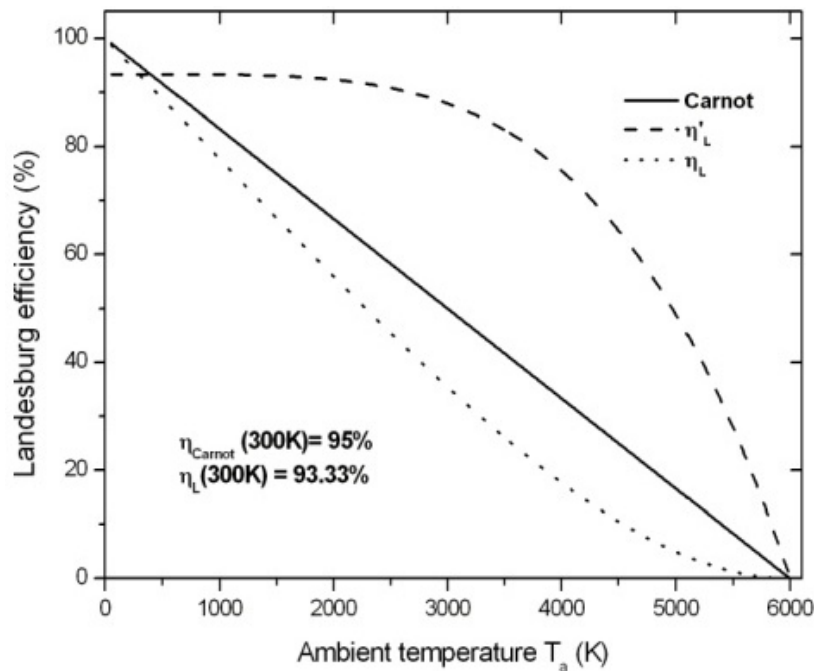

Figure 2. Landsberg and Carnot Efficiency limits of a solar converter versus ambient temperature.

In the Landsberg model the blackbody radiation law for the sun and the solar cell has been included, unlike the previous Carnot engine.

This figure represents an upper bound on solar energy conversion efficiency, particularly for solar cells which are primarily quantum converters absorbing only photons with energies higher or equal to their energy bandgap. On the other hand in the calculation of the absorbed solar radiation the converter was assumed fully surrounded by the source, corresponding to a solid angle of 4π.

Using the same approach it is possible to split the system into two subsystems each with its own efficiency; the Carnot engine that include the heat pump of the converter at T_c and the ambient heat sink at T_a, with an efficiency η_c (ideal Carnot engine).

$$\eta_c = 1 - \frac{T_a}{T_c} \tag{15}$$

The ambient temperature is assumed equal to 300 K, therefore high efficiency is obtained when the converter temperature is higher then the ambient temperature.

The second part is composed of the sun as an isotropic blackbody at T_s and the converter reservoir assumed as a blackbody at a temperature T_c. The energy flow falling upon Q_{abs} and emitted by the solar converter Q_{emit} are given by:

$$Q_{abs} = C f \sigma T_s^4 \text{ and } Q_{emit} = \sigma T_c^4 \tag{16}$$

In which f is a geometrical factor taking into account the limited solid angle from which the solar energy falls upon the converter. In accordance with the schematic representation of figure 3, where the solar cell is represented as a planar device irradiated by hemisphere surrounding area and the sun subtending a solid angle ω_s at angle of incidence θ, f is defined as the ratio of the area subtended by sun to the apparent area of the hemisphere:

$$f = \frac{\int_{\omega_s} \cos\theta \, d\omega}{\int_{2\pi} \cos\theta \, d\omega} = \frac{\omega_s}{\pi} \tag{17}$$

ω_s being the solid angle subtended by the sun, where $\omega_s = 6.85 \times 10^{-5}$ sr. The concentration factor C ($C > 1$) is a measure of the enhancement of the energy current density by optical means (lens, mirrors…).The maximum concentration factor is obtained if we take $T_s = 6000°K$:

$$\sigma T_s^4 = C_{max} f \sigma T_s^4 \tag{18}$$

Then

$$C_{max} = 1 / f \approx 46200$$

The case of maximum concentration also corresponds to the schematic case where the sun is assumed surrounding entirely the converter as assumed in previous calculations.

Similar situation can be obtained if the solid angle through which the photons are escaping from the cell (emission angle) is limited to a narrow range around the sun. This can be achieved by hosing the cell in a cavity that limits the angle of the escaping photons.
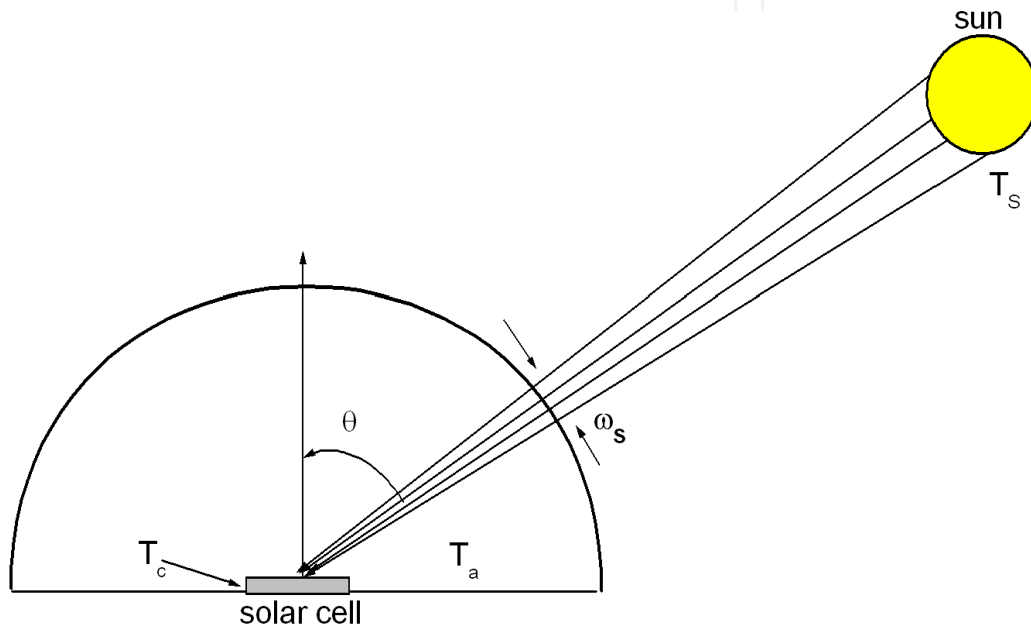

Figure 3. A schematic representation of a solar converter as a planar cell irradiated by the sun subtending a solid angle ω_s at angle of incidence θ.

The efficiency of this part of the system (isolated) is given by:

$$\eta_{abs} = 1 - \frac{Q_{emit}}{Q_{abs}} \tag{19}$$

the resulting efficiency is simply the product:

$$\eta_{ac} = \eta_c . \eta_{abs} = \left(1 - \frac{T_c^4}{C f T_s^4}\right)\left(1 - \frac{T_a}{T_c}\right) \tag{20}$$

This figure represents an overall efficiency of the entropy-free energy conversion by blackbody emitter-absorber combined with a Carnot engine. The temperature of the surrounding ambient

T_a is assumed equal to 300K. When f is taken equal to ω_s/π=2.18×10^{-5} and without concentration (C=1) we obtain a very low efficiency value (about 6.78%), as shown in figure 4. The efficiency for concentrations of 10, 100 and full concentration (46200) is found respectively 31.36, 53.48 and 85.38%. In this model the solar cell is not in thermal equilibrium with its surrounding ($T_c \neq T_a$), then it exchanges radiation not only with the sun but also with the ambient heat sink. Therefore, energy can be produced or absorbed from the surrounding acting as a secondary source. Neglecting this contribution naturally decreases the efficiency of the converter, particularly at C=1. The second explanation of the low efficiency value is the under estimation of the re-emitted radiation from the cell, at operating conditions the solar cell re-emits radiation efficiently especially at open circuit point.
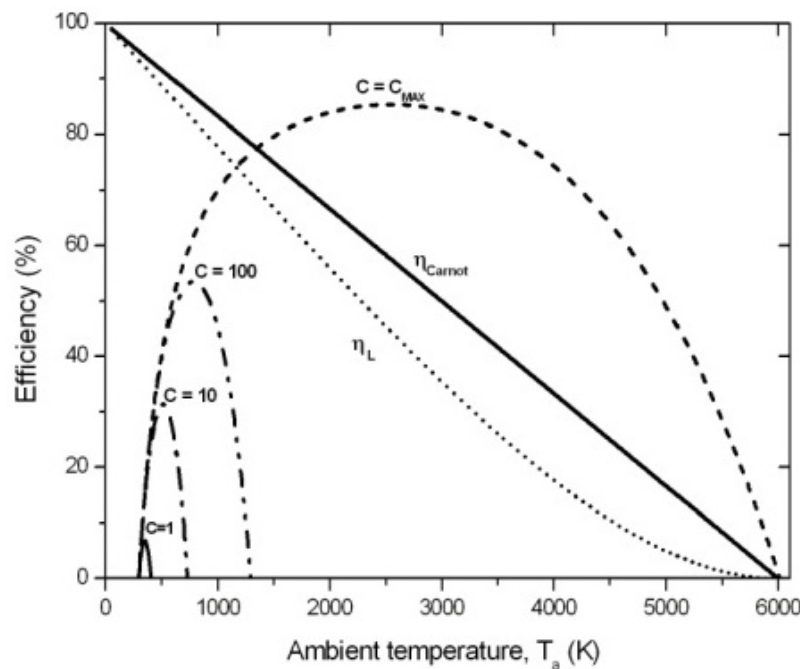

Figure 4. Efficiency η_{ac} for different concentration rates (C=1, 10, 100 and C_{max}) with Landsberg and Carnot Efficiency limits of a solar converter as a function of ambient temperature.

2.2. Solar cell as an endoreversible heat engine

A more realistic model has been introduced by De Vos et al. [8] in which only a part of the converter system is reversible, endoreversible system. An intermediate heat reservoir is inserted at the temperature of the converter T_c, this source is heated by the sun at T_s (blackbody radiation) and acting as a new high temperature pump in a reversible Carnot engine. In this system the entropy is generated between the T_s reservoir and the converter, the temperature T_c is fictitious and is different from the ambient temperature T_a. The effective temperature T_c depends on the rate of work production. In this model the solar converter is assumed to behave like the Müser engine, itself a particular case of the Curzon-Ahlborn engine, as shown in Fig. 5, the sun is represented by blackbody source at temperature T_1=T_s the solar cell includes a heat reservoir assumed as blackbody at T_3=T_c (the converter temperature) and an ideal Carnot

engine capable of producing utilizable work (electrical power), however T_c is related to the converter working condition. This engine is in contact with an ambient heat sink at T_2 representing the ambient temperature $T_2=T_a$. In addition to the absorbed energy from the sun, the converter absorbs radiation from ambient reservoir assumed as a blackbody at T_a.
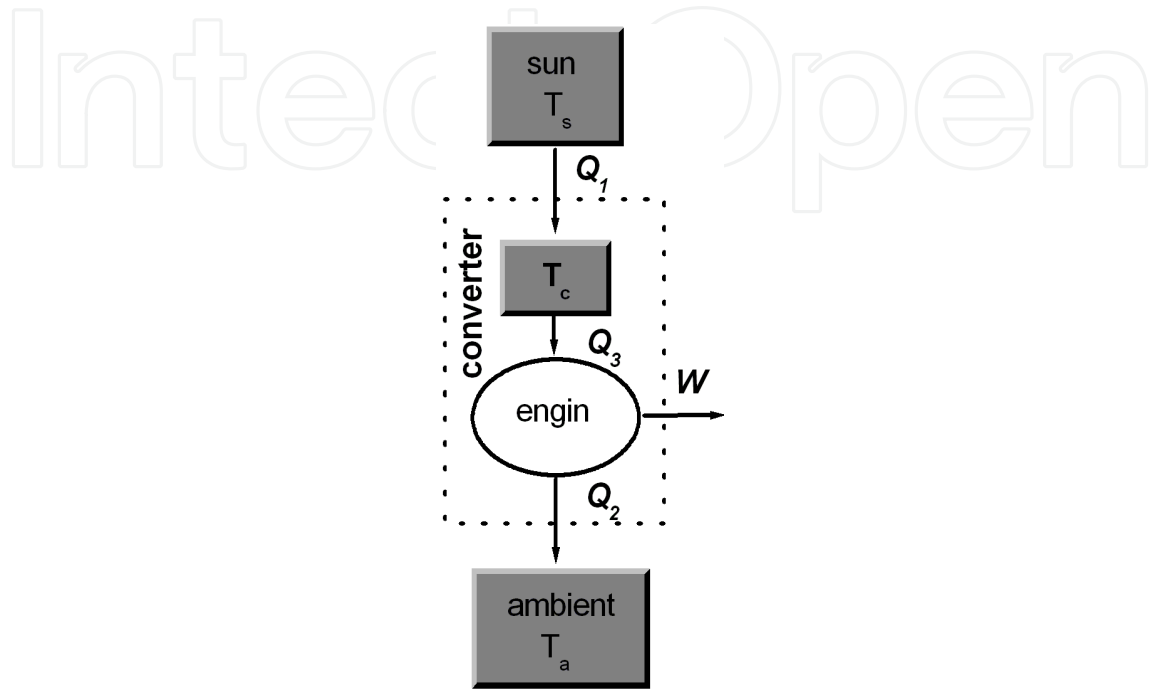

Figure 5. A schematic diagram of a solar converter represented as an endoreversible system.

The net energy flow input to the converter, including the incident solar energy flow $f \sigma T_s^4$, the energy flow $(1-f)\sigma T_a^4$ from the surrounding and the energy flow emitted by the converter is then:

$$Q_1 = f\sigma T_s^4 + (1-f)\sigma T_a^4 - \sigma T_c^4 \qquad (21)$$

The Müser engine efficiency (Carnot engine):

$$\eta_M = \frac{W}{Q_1} = 1 - \frac{T_a^4}{T_c^4} \qquad (22)$$

The converter temperature can be extracted from η_M:

$$T_c = \frac{T_a}{1-\eta_M} \qquad (23)$$

And the solar efficiency is defined as ratio of the delivered work to the incident solar energy flux:

$$\eta_S = \frac{W}{f\sigma T_s^4} \tag{24}$$

hence

$$\eta_S = \eta_M \left[1 + \frac{(1-f)(1-\eta_M)^4 - 1}{(1-\eta_M)^4} \frac{T_a^4}{f T_s^4} \right] \tag{25}$$

The maximum solar efficiency is then a function of two parameters; the Müser efficiency and the surrounding ambient temperature. From the 3d representation at figure 6 of the solar efficiency (η_s) against Müser efficiency η_M and the surrounding temperature T_a, the efficiency is high as the temperature is very low and vanishes for very high temperature (as T_a approaches the sun temperature). For T_a=289.23K the efficiency is 12.79% if the sun's temperature is 6000°K.

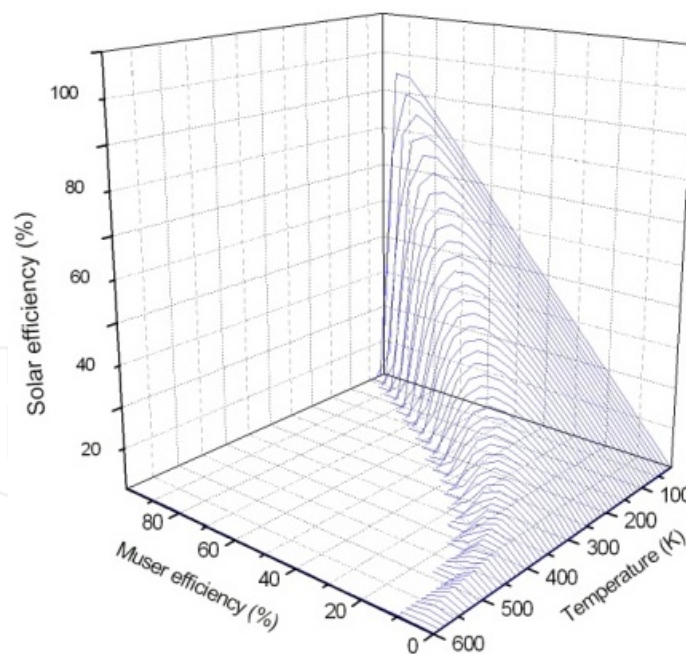**Figure 6.** The solar efficiency surface η_s (η_M, T_a), the sun as a blackbody at T_s=6000°K.

A general expression of solar efficiency of the Müser engine is obtained when the solar radiation concentration factor C is introduced:

$$\eta_S = \eta_M \left[1 + \frac{(1-Cf)(1-\eta_M)^4 - 1}{(1-\eta_M)^4} \frac{T_a^4}{CfT_s^4} \right] \qquad (26)$$

Compared to Carnot efficiency engine the Müser engine efficiency, even when C is maximal, remains low.

If the ratio $T_a^4 / f\, T_s^4$ is fixed to 1/4, as in [5], which gives a good approximation for ambient temperature, T_a=289.23K, with T_s=6000K.

Hence, the corresponding η_S becomes:

$$\eta_S = \eta_M \left[1 + \frac{(1-Cf)(1-\eta_M)^4 - 1}{4(1-\eta_M)^4} \right] \qquad (27)$$

In the assumption of T_a=289.23K the maximum efficiency without concentration, i.e. the solar cell sees the sun through a solid angle ω_s is 12.79% which is better than the predicted value of Würfel [7] but still very low, as shown in figure 8. For concentration equal to 10, 100 and C_{MAX}, the efficiency reaches 33.9, 54.71 and 85.7% respectively.
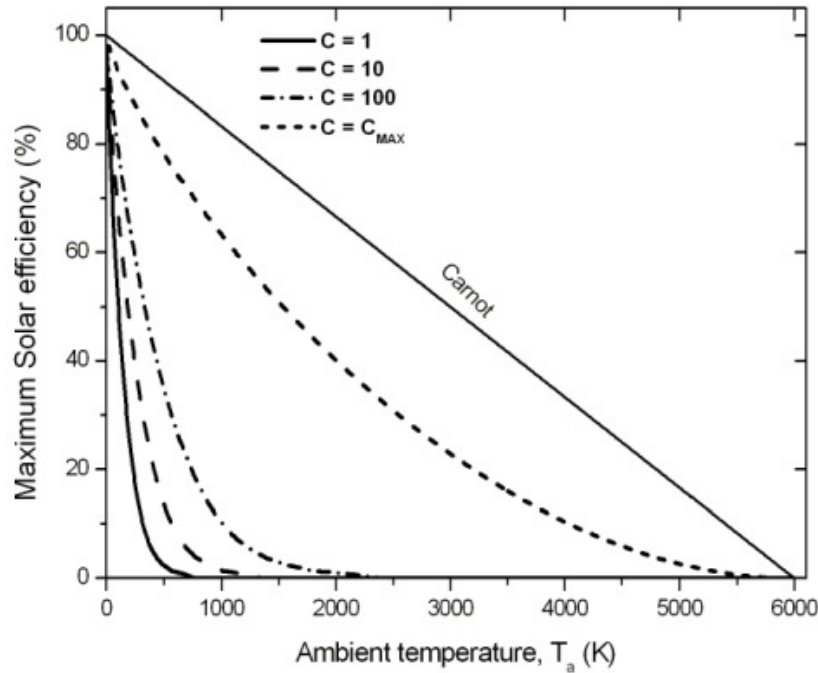

Figure 7. The maximum solar efficiency using Müser engine for different concentration rates (C=1, 10, 100 and $C_{max)}$ with Carnot Efficiency limit as a function of ambient temperature.
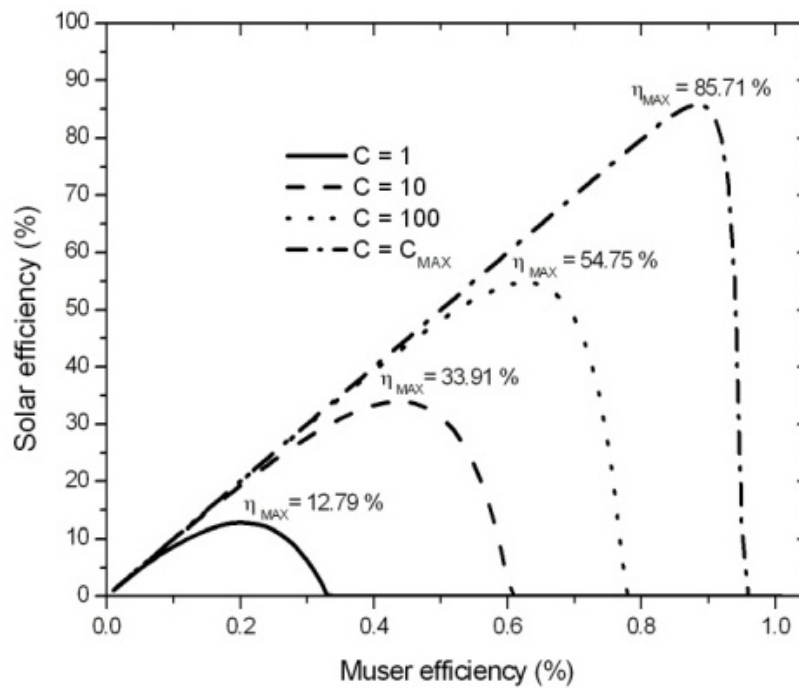
Figure 8. The solar efficiency using Müser engine for different concentration rates (C=1, 10, 100 and C_{max}) as a function of Müser efficiency.

3. Solar cell as a quantum converter

3.1. Introduction

In a quantum converter the semiconductor energy band-gap, of which the cell is made, is the most important and critical factor controlling efficiency losses. Although what seems to be fundamental in a solar cell is the existence of two distinct levels and two selective contacts allowing the collection of photo-generated carriers [2].

Incident photons with energy higher than the energy gap can be absorbed, creating electron-hole pairs, while those with lower energy are not absorbed, either reflected or transmitted. The excess energy of the absorbed energy greater than the energy gap is dissipated in the process of electrons thermalisation, resulting in further loss of the absorbed energy. Besides, only the free energy (the Helmholtz potential) that is not associated with entropy can be extracted from the device, which is determined by the second law of thermodynamics.

3.2. Monochromatic solar cell

It is interesting to examine first an ideal monochromatic converter illuminated by photons within a narrow interval of energy around the bandgap $h\,v_g = E_g$. In the ideal case each absorbed photon yields an electron-hole pair. This cell also prevents the luminescent radiation of energy outside this range from escaping. According to the blackbody formula of the Plank distribu-

tion, the number of photons incident from the sun within an interval of frequency dv per unit area per second is:

$$dN_S = \frac{2\pi}{c^2} \frac{v_g^2}{\exp\left(\frac{hv_g}{kT_s}\right) - 1} dv \tag{28}$$

The number of created electron-hole pairs, in the assumption that each absorbed photon yields an electron-hole pair, could be simply represented by: $C f A_c dN_S$, where C is the solar radiation concentration factor, f is a geometrical factor, taking into account the limited angle from which the solar energy falls upon the solar converter and A_c is the converter projected area. In monochromatic cell only photons with proper energy are allowed to escape from the cell ($hv_g \approx E_g$) as a result of recombination. To obtain the efficiency of monochromatic ideal quantum converter we assume that only radiative recombination is allowed. Using the generalised Planck radiation law introduced by Würfel [7], the number of photons emitted by the solar cell per unit area per second within an interval of frequency dv is:

$$dN_c = \frac{2\pi}{c^2} \frac{v_g^2}{\exp\left(\frac{hv_g - \mu_{eh}}{kT_c}\right) - 1} dv \tag{29}$$

Where μ_{eh} is the emitted photon chemical potential, with $\mu_{eh} = F_n - F_p$, (F_n, F_p are the quasi Fermi levels of electrons and holes respectively). The cell is assumed in thermal equilibrium with its surrounding ambient, then $T_c = T_a$.

This expression describes both the thermal radiation (for $\mu_{eh} = 0$) and emission of luminescence radiation (for $\mu_{eh} \neq 0$). The number of emitted photons from the cell is then: $f_c A_c dN_c$, f_c is a geometrical factor depending on the external area from which the photons are leaving the solar converter and is equal to 1 if only one side of the cell is allowed to radiate and 2 if both sides of the cell are luminescent (f_c is chosen equal to one in the following calculation). For a spatially constant chemical potential of the electron-hole pairs $\mu_{eh} = Const.$, the net current density of extracted electron-hole pairs, in the monochromatic cell, dJ, (the area of the cell is taken equal to unity, $A_c = 1$) is:

$$dJ = q \frac{2\pi}{c^2} \left(\frac{C f}{\exp\left(\frac{hv_g}{kT_s}\right) - 1} - \frac{1}{\exp\left(\frac{hv_g - \mu_{eh}}{kT_c}\right) - 1} \right) v_g^2 dv \tag{30}$$

This equation allows the definition of an equivalent cell temperature T_{eq} from:

$$\frac{hv_g - \mu_{eh}}{kT_c} = \frac{hv_g}{kT_{eq}} \Rightarrow \mu_{eh} = hv_g \left(1 - \frac{T_c}{T_{eq}}\right) \tag{31}$$

When a solar cell formed by a juxtaposition of two semiconductors p- and n-types is illuminated, an electrical voltage V between its terminals is created. This voltage is simply the difference in the quasi Fermi levels of majority carriers at Ohmic contacts for constant quasi Fermi levels and ideal Ohmic contacts, this voltage is equal to the chemical potential: $qV = \mu_{eh} = F_n - F_p$.

At open circuit condition, the voltage V_{oc} is given by a simple expression (deduced from (31)):

$$V_{oc} = \frac{E_g}{q} \left(1 - \frac{T_c}{T_{eq,oc}}\right) \tag{32}$$

The density of work delivered to an external circuit (density of extracted electrical power) dW is:

$$dW = dJ.V = \frac{2\pi}{c^2} \left(\frac{Cf}{\exp\left(\frac{hv_g}{kT_s}\right) - 1} - \frac{1}{\exp\left(\frac{hv_g}{kT_{eq}}\right) - 1} \right) v_g^2 dv \; hv_g \left(1 - \frac{T_c}{T_{eq}}\right) \tag{33}$$

The incoming energy flow from the sun can be written as:

$$dQ_1 = \frac{2\pi}{c^2} \left(\frac{Cf}{\exp\left(\frac{hv_g}{kT_s}\right) - 1} \right) v_g^2 dv \; hv_g \tag{34}$$

The emitted energy density from the solar cell in a radiation form (radiative recombination) is:

$$dQ_2 = \frac{2\pi}{c^2} \left(\frac{1}{\exp\left(\frac{hv_g}{kT_{eq}}\right) - 1} \right) v_g^2 dv \; hv_g \tag{35}$$

The efficiency of this system is:

$$\eta = \frac{dW}{dQ_1} = \frac{dQ_1 - dQ_2}{dQ_1} = \left(1 - \frac{T_c}{T_{eq}}\right) \qquad (36)$$

The work extracted from a monochromatic cell is similar to that extracted from a Carnot engine. The equivalent temperature of this converter is directly related to the operating voltage. At short-circuit condition it corresponds to the ambient temperature ($\mu_{eh}=0$ then $T_{eq,sc}=T_c=T_a$) whereas at open circuit condition and for fully concentrated solar radiation, the equivalent temperature is that of the sun, ($dJ=0$ then $T_{eq,oc}=T_s$). For non-concentrated radiation ($C \neq C_{Max}$) at open circuit voltage $T_{eq,oc}$ is obtained by solving the equation $dJ =0$, neglecting the 1 compared to the exponential term, we find then:

$$\frac{1}{T_{eq,oc}} = \frac{1}{T_s} - \frac{k}{h\nu_g}\ln(C.f) \qquad (37)$$

It is therefore possible to consider a monochromatic solar cell as reversible thermal engine (Carnot engine) operating between $T_{eq,oc}$ and T_a.

We can see that an ideal monochromatic cell, which only allows radiative recombination, represents an ideal converter of heat into electrical energy.

In order to find the maximum efficiency of such a cell as a function of the monochromatic photon energy ($h\nu_g$), the $dW=dJ\times V$ versus V characteristic is used. We search for the point (dJ_{mp}, V_{mp}) corresponding to the maximum extracted power. The maximum chemical energy density ($dW_{mp}=dJ_{mp}\times V_{mp}$) is divided by the absorbed monochromatic energy gives the efficiency $\eta_{mono}(E_g)$ as a function of the bandgap.

The monochromatic efficiency is considerable, particularly in the case of fully concentrated radiation ($C=C_{Max}$), and rises with the energy bandgap, as shown in figure 9. In theory the connection of a large number of ideal monochromatic absorbers will produce the best solar cell for the total solar spectrum. To calculate the overall efficiency numerically, a fine discretization of the frequency domain is made; the sum of the maximum power density over the solar spectrum divided by the total absorbed energy density. The efficiencies resulting from this calculation are respectively 67.45% and 86.81% for non-concentrated and fully concentrated radiation.

To cover the whole solar energy spectrum an infinite number of monochromatic absorbers, each for a different photon energy interval, are needed. Each absorber would have its own Carnot engine and operate at its own optimal temperature, since for a given voltage the cell equivalent temperature depends on the photon energy ($h\nu_g$). Finally this model can not be directly used to describe semiconductor solar cells where the electron-hole pairs are generated in bands and not discrete levels, besides if the cell is considered as a cascade of tow-level

converters; the notion of effective or equivalent temperature is no longer valid, since for each set of levels a different equivalent temperature is defined.
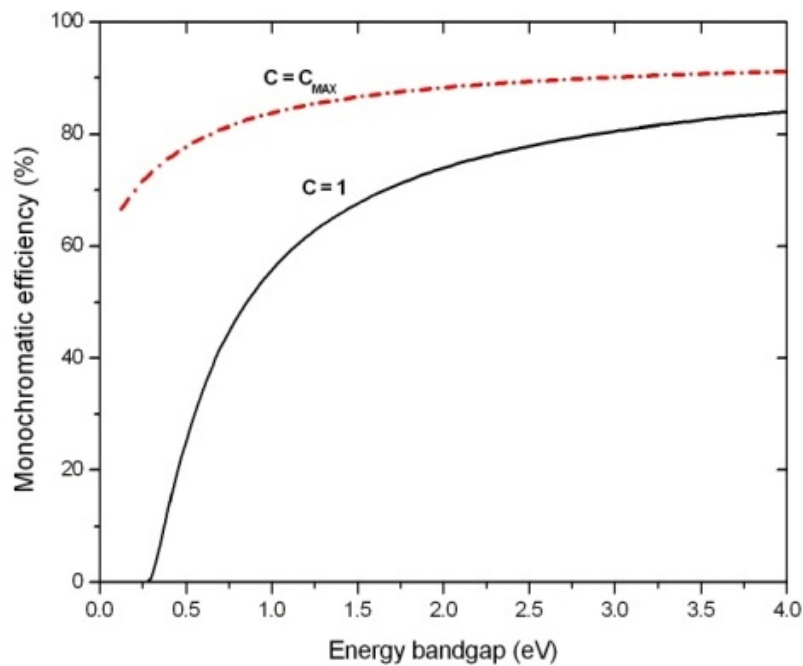

Figure 9. The monochromatic efficiency against the photon energy corresponding to the energy band-gap of the cell for non-concentrated (C=1) and fully concentrated (C=C_{max}) solar spectrum.

3.3. Ultimate efficiency

The total number of photons of frequency greater than v_g (E_g=hv_g) impinging from the sun, assumed as a blackbody at temperature T_s, in unit time and falling upon the solar cell per unit area N_s is given by:

$$N_s = \left(2\pi / c^2\right)\int_{v_g}^{\infty} \frac{v^2 dv}{\exp(hv / kT_s) - 1} \tag{38}$$

This integral could be evaluated numerically.

In the assumption that each absorbed photon will produce a pair of electron-hole, the maximum output power density that could be delivered by a solar converter will be:

$$P_{out} = hv_g \times N_s \tag{39}$$

The solar cell is assumed entirely surrounded by the sun and maintained at $T_c=0K$ as a first approximation and to get the maximum energy transfer from the sun. The total incident energy density coming from the sun at T_s and falling upon the solar cell, P_{in} is given by

$$P_{in} = \left(2\pi / c^2\right)\int_0^\infty \frac{v^3 dv}{\exp(hv / kT_s)-1} = 2\pi(kT_s)^4 / h^3c^2 \int_0^\infty \frac{x^3 dx}{\exp(x)-1} \tag{40}$$

$$P_{in} = 2\pi^5(kT_s)^4 / 15h^3c^2 \tag{41}$$

In accordance with the definition of the ultimate efficiency [6, 17], as the rate of the generated photon energy to the input energy density, its expression can be evaluated as a function of E_g as follows:

$$\eta_u(v_g) = \frac{hv_g N_s}{P_{in}} \tag{42}$$

This expression is plotted in figure 10, so the maximum efficiency is approximately 43.87% corresponding to E_g=1.12 eV, this energy band-gap is approximately that of crystalline silicon. Similar calculation of the ultimate efficiency taking the solar spectrum AM1.5 G (The standard global spectral irradiance, ASTM G173-03, is used [18]) is shown in figure 10 gives a slightly higher value of 49%. If one compares this efficiency to the aforementioned thermodynamic efficiency limits, most of them approach the Carnot limit for the special case where the converter's temperature is absolute zero, this ultimate efficiency limit is substantially lower (44% or 49%) than the Carnot limit (95%). In quantum converters it is obvious that more than 50% of the solar radiation is lost because of the spectral mismatch. Therefore, non-absorption of photons with less energy than the semiconductor band-gap and the excess energy of photons, larger than the band-gap, are the two main losses.

3.4. Detailed balance efficiency limit

The detailed balance limit efficiency for an ideal solar cell, consisting of single semiconducting absorber with energy band-gap E_g, has been first calculated by Shockley and Queisser (SQ) [6]. The illumination of a *pn* junction solar cell creates electron-hole pairs by electronic transition due to the fundamental absorption of photons with $hv > E_g$, which is basically a quantum process. The photogenerated pairs either recombine locally or circulate in an external circuit and can transfer their energy. Their approach reposes on the following main assumptions; the probability that a photon with energy $hv > E_g$ incident on the surface of the cell will produce a hole-electron pair is equal to unity, while photons of lower energy will produce no effect, all photogenerated electrons and holes thermalize to the band edges (photons with energy greater than E_g produce the same effect), all the photogenerated charge carriers are collected at short-
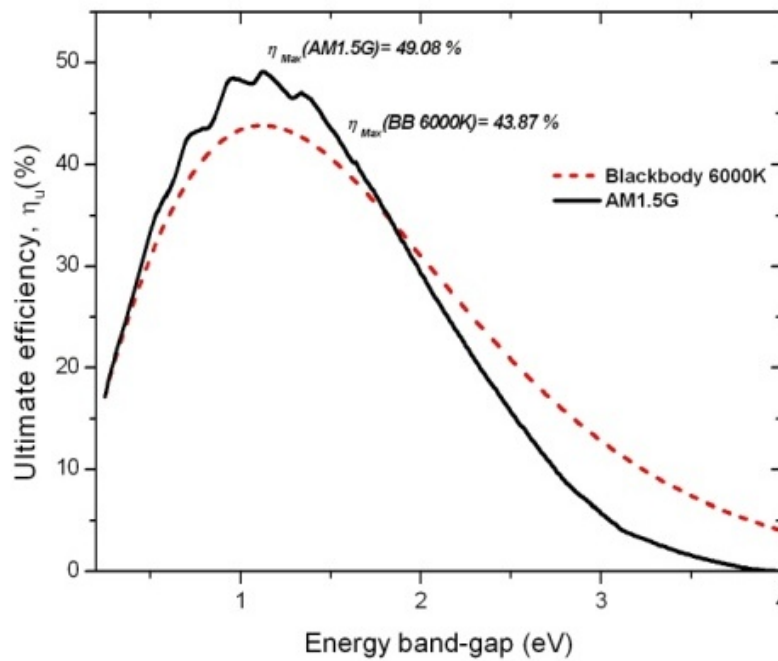
Figure 10. The ultimate efficiency against the energy band-gap of the solar cell, using the AM1.5G spectrum with the blackbody spectrum at T_s=6000°K.

circuit condition and the upper detailed balance efficiency limit is obtained if radiative recombination is the only allowed recombination mechanism.

The model initially introduced by SQ [6] has been improved by a number of researchers, by first introducing a more exact form of radiative recombination. The radiative recombination rate is described using the generalised Planck radiation law introduced by Würfel [7], where the energy carried by emitted photons turn out to be the difference of electron-hole quasi Fermi levels. While for non-radiative recombination the released energy is recovered by other electrons, holes or phonons.

In the following sub-section the maximum achievable conversion efficiency of a single band-gap absorber material is determined.

3.4.1. Short-circuit current density (J_{sc}) calculation

Now we consider a more realistic situation of a solar cell, depicted in figure 3. Three factors will be taken into account, namely; the view factor of the sun seen from the solar cell, the background radiation is represented as a blackbody at ambient temperature T_a, and losses due to recombination (radiative and non-radiative).

In steady state condition the current density $J(V)$ flowing through an external circuit is the algebraic sum of the rates of increase of electron-hole pairs corresponding to the absorption of incoming photons from the sun and the surrounding background, in addition to recombination (radiative and non-radiative). This leads to a general current voltage characteristic formula:

$$J(V) = q(2\pi / c^2) \left[C f \times \int_{v_g}^{\infty} \frac{v^2 dv}{\exp(hv / kT_s) - 1} + (1 - C f) \times \int_{v_g}^{\infty} \frac{v^2 dv}{\exp(hv / kT_a) - 1} \right.$$

$$\left. - \frac{1}{f_{RR}} \times \int_{v_g}^{\infty} \frac{v^2 dv}{\exp((hv - qV) / kT_c) - 1} \right]$$

(43)

with reference to the solar cell configuration shown in figure 3, T_s, T_a and T_c are the respective temperatures of sun, ambient background and solar cell. As defined previously, C and f are the concentration factor and the sun geometrical factor, while f_{RR} represents the fraction of the radiative recombination rate or radiative recombination efficiency. If U_{NR} and U_{RR} are the non-radiative and radiative recombination rates respectively, f_{RR} is defined by:

$$f_{RR} = \frac{U_{RR}}{U_{RR} + U_{NR}}$$

(44)

The current density formula (43) can be rewritten in a more compact form as follows:

$$J(V) = qCf\phi_s + q(1 - C f)\phi_a - \frac{q}{f_{RR}}\phi_c(V)$$

(45)

With:

$$\varphi_s = (2\pi / c^2)\int_{v_g}^{\infty} \frac{v^2 dv}{\exp(hv / kT_s) - 1} \qquad \text{a}$$

$$\varphi_a = (2\pi / c^2)\int_{v_g}^{\infty} \frac{v^2 dv}{\exp(hv / kT_a) - 1} \qquad \text{b} \qquad (46)$$

$$\varphi_c(V) = (2\pi / c^2)\int_{v_g}^{\infty} \frac{v^2 dv}{\exp((hv - qV) / kT_c) - 1} \qquad \text{c}$$

Under dark condition and zero bias the current density must be null, then:

$$J(0) = 0 \Rightarrow \varphi_a = \frac{1}{f_{RR}}\varphi_c(0)$$

(47)

Therefore the current density expression becomes:

$$J(V) = qCf(\phi_s - \phi_a) - \frac{q}{f_{RR}}\left(\phi_c(V) - \phi_c(0)\right)$$

(48)

From the above J (V) expression we can obtain the short-circuit current density ($J_{sc}=J_{(V=0)}$) as follows:

$$J_{sc} = qCf(\phi_s - \phi_a) \qquad (49)$$

In the ideal case the short-circuit current density depends only on the flux of impinging photons from the sun and the product Cf, recombination has no effect. The term φ_a in J_{sc}, representing the radiation from the surrounding ambient is negligible. The total photogenerated carriers are swept away and do not recombine before reaching the external circuit where they give away their electrochemical energy. Figure 11 illustrates the maximum short-circuit current density to be harvested against band-gap energy according to (49) for a blackbody spectrum at T_s=6000°K normalised to a power density of 1000W/m^2 and a spectral photon flux corresponding to the terrestrial AM1.5G spectrum. Narrow band-gap semiconductors exhibit higher photocurrents because the threshold of absorption is very low, therefore most of the solar spectrum can be absorbed. For power extraction this is not enough, the voltage is equally important and more precisely, the open circuit voltage.

The currently achieved short-circuit current densities for some solar cells are very close to predicted limits. Nevertheless, further gain in short-circuit current can therefore still be obtained, mainly by minimising the cell surface reflectivity, while increasing its thickness, so as to maximize the photon absorption. For thin film solar cells the gain in J_{sc} can be obtained by improving light trapping techniques to enhance the cell absorption.

For instance crystalline silicon solar cells with an energy band-gap of 1.12 eV at 300K has already achieved a J_{sc} of 42.7 mA/cm^2 compared to a predicted maximum value of 43.85 mA/cm^2 for an AM1.5 global spectrum (only 39.52 mA/cm^2 for a normalised blackbody spectrum at 6000°K), while for GaAs with E_g=1.43eV a reported maximum J_{sc} of 29.68 mA/cm^2 compared to 31.76 mA/cm^2 (only 29.52 mA/cm^2 for a normalised blackbody spectrum at 6000°K) [14].

	J_{sc}(mA/cm^2)		V_{oc}(V)		η (%)	
	Limit	record	limit	record	limit	record
Si	43.85	42.7	0.893	0.706	34.37	25.0
GaAs	31.76	29.68	1.170	1.122	33.72	28.8

Table 1. Summary of the reported records [14] and the calculated limits of Si and GaAs solar cells performances under the global AM1.5 spectrum.

3.4.2. Open-circuit voltage (V_{oc}) calculation

At open circuit condition electron-hole pairs are continually created as a result of the photon flux absorption, the only mechanism to counter balance this non-equilibrium condition is
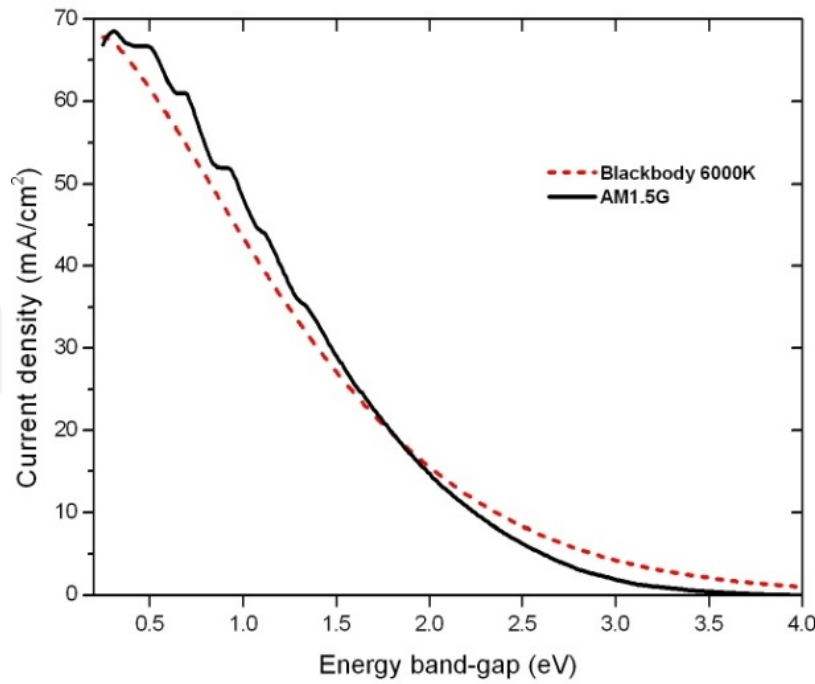
Figure 11. The maximum short-circuit current density against the energy band-gap of the solar cell, using the AM1.5G spectrum with the blackbody spectrum at $T_s=6000°K$.

recombination. Non-radiative recombination could be eliminated, whereas radiative recombination has a direct impact on the cell efficiency and particularly on the open circuit voltage. The radiative current as the rate of radiative emission increases exponentially with the bias subtracts from the current delivered to the load by the cell. At open circuit condition, external photon emission is part of a necessary and unavoidable equilibration process [15]. The maximum attainable V_{oc} corresponds to the condition where the cell emits as many photons as it absorbs. The open circuit voltage of a solar cell can be found by taking the band gap energy and accounting for the losses associated with various sources of entropy increase. Often, the largest of these energy losses is due to the entropy associated with radiative recombination.

In the case where qV is several kT smaller than $h\nu_g$, $\varphi_c(V)$ could be approximated by:

$$\phi_c(V) \cong (2\pi/c^2)\left(\int_{\nu_g}^{\infty}\frac{\nu^2 d\nu}{\exp((h\nu)/kT_c)-1}\right)\exp\left(\frac{qV}{kT_c}\right) = \phi_c(0)\exp\left(\frac{qV}{kT_c}\right)$$ (50)

The current density expression becomes then:

$$J(V) = qCf(\phi_s - \phi_a) - \frac{q}{f_{RR}}\phi_c(0)\left(\exp\left(\frac{qV}{kT_c}\right)-1\right)$$ (51)

The open circuit voltage can be deduced directly from this expression as:

$$0 = Cf(\phi_s - \phi_a) - \frac{1}{f_{RR}} \phi_c(0) \left(\exp\left(\frac{qV_{oc}}{kT_c} \right) - 1 \right) \tag{52}$$

$$V_{oc} = \frac{kT_c}{q} \ln\left(\frac{Cf(\phi_s - \phi_a)}{\phi_c(0)} f_{RR} + 1 \right) \tag{53}$$

The open circuit voltage is determined entirely by two factors; the concentration rate of solar radiation C ($C \geq 1$) and radiative recombination rate f_{RR} ($f_{RR} \leq 1$).

$$\begin{aligned} V_{oc} &\approx \frac{kT_c}{q} \ln\left(\frac{Cf(\phi_s - \phi_a)}{\phi_c(0)} f_{RR} \right) \\ &= \frac{kT_c}{q} \ln\left(\frac{f(\phi_s - \phi_a)}{\phi_c(0)} \right) - \frac{kT_c}{q} \ln\left(\frac{1}{C} \right) - \frac{kT_c}{q} \ln\left(\frac{1}{f_{RR}} \right) \end{aligned} \tag{54}$$

Radiative recombination has a critical role to play, if the created photons are re-emitted out of the cell, which corresponds to low optical losses, the open circuit voltage and consequently the cell efficiency approach the SQ limit. Therefore the limiting factor for high V_{oc} (efficiency) is the external fluorescence efficiency of the cell as far as radiative recombination is concerned. Since the escape cone is in general low, efficient external emission involves repeated escape attempts and this is ensured by perfect light trapping techniques. In this case the created photons are allowed to be reabsorbed and reemitted again until they coincide with the escape cone, reaching high external fluorescence efficiency [15, 18-19].

So dominant radiative recombination is required to reach high V_{oc} and this is not sufficient to reach the SQ limit, the other barrier is to get the generated photons out of the cell and this is limited by the external fluorescence efficiency η_{fex}. Hence, the external fluorescence efficiency η_{fex}, is introduced in the expression of V_{oc} and f_{RR} is multiplied by η_{fex}, ($\eta_{fex} \leq 1$) then:

$$V_{oc} = \frac{kT_c}{q} \ln\left(\frac{f(\phi_s - \phi_a)}{\phi_c(0)} \right) - \frac{kT_c}{q} \ln\left(\frac{1}{C} \right) - \frac{kT_c}{q} \ln\left(\frac{1}{f_{RR}\eta_{fex}} \right) \tag{55}$$

If we define a maximum ideal open circuit voltage value $V_{oc,max}$ for fully concentrated solar radiation ($C = C_{max} = 1/f$) and when the radiative recombination is the only loss mechanism with maximum external fluorescence efficiency (i.e, $f_{RR}\eta_{fex} = 1$), then:

$$V_{oc} = V_{oc,max} - \frac{kT_c}{q} \ln\left(\frac{C_{max}}{C} \right) - \frac{kT_c}{q} \ln\left(\frac{1}{f_{RR}\eta_{fex}} \right) \tag{56}$$

It is worth mentioning that (56) is not an exact evaluation of V_{oc}. As shown in figure 12.b equation (56) for narrow band-gap semiconductors yields wrong values of $V_{oc,max}$ (above E_g/q line), acceptable values are obtained only for E_g greater than 2 eV, where it coincides with the result obtained when solving numerically (45) for $J(V)=0$.

From this figure one can say that taking $V_{oc,max}=E_g/q$ is a much better approximation; thus, instead of (56) we can use the following approximation:

$$V_{oc} = \frac{E_g}{q} - \frac{kT_c}{q}\ln\left(\frac{C_{max}}{C}\right) - \frac{kT_c}{q}\ln\left(\frac{1}{f_{RR}\eta_{fex}}\right) \tag{57}$$

A more accurate value of V_{oc} is obtained after numerical resolution of equation (45) for $J(V)=0$, the results are plotted in figure12a and 12.b.

The other type of entropy loss degrading the open-circuit voltage is the photon entropy increase due to isotropic emission under direct sunlight. This entropy increase occurs because solar cells generally emit into 2π steradian, while the solid angle subtended by the sun is only 6.85×10^{-5} steradian.

The most common approach to addressing photon entropy is a concentrator system. If the concentration factor C of sun radiation is increased, this is generally achieved by optical means, a significant increase of V_{oc} is obtained (as shown in figure 12.b). The calculation is carried out assuming a dominant radiative recombination and with maximum external fluorescence efficiency ($f_{RR}\eta_{fex}=1$). In this case we can notice that as C is increased V_{oc} approaches its ultimate value E_g/q, for example GaAs ($E_g=1.43$ eV) for $C=C_{Max}$ we get $V_{oc}=0.99\times E_g/q=1.41$ V, which corresponds to an efficiency limit of approximately 38.5% (blackbody spectrum at 6000K). This theoretical limit shows the importance of dealing with entropy losses associated with angle of acceptance of photons from the sun and emission of photons from the cell efficiently. This value is well above the predicted SQ limit, where the concentration factor was considered.

With reference to table 1 we can clearly see that the record open circuit voltage under one-sun condition ($C=1$) of gallium arsenide solar cell (1.12 V) is already close to the SQ limit (1.17 V) while silicon solar cell is still behind with a record V_{oc} of 0.706 V compared to a limit of 0.893 V, this difference is due to the fact that GaAs has a direct band gap, which means that it can be used to absorb and emit light efficiently, whereas Silicon has an indirect band gap and so is relatively poor at emitting light. Although Silicon makes an excellent solar cell, its internal fluorescence yield is less than 20%, which prevents Silicon from approaching the SQ limit [20]. On the other hand It has been demonstrated that efficiency in Si solar cells is limited by Auger recombination, rather than by radiative recombination [20-22].

3.4.3. The efficiency calculation

Energy conversion efficiency η is usually known as the most relevant figure for solar cell performance. Solar cell efficiency is calculated by dividing a cell's electrical power output at its maximum power point by the input solar radiation and the surface area of the solar cell.
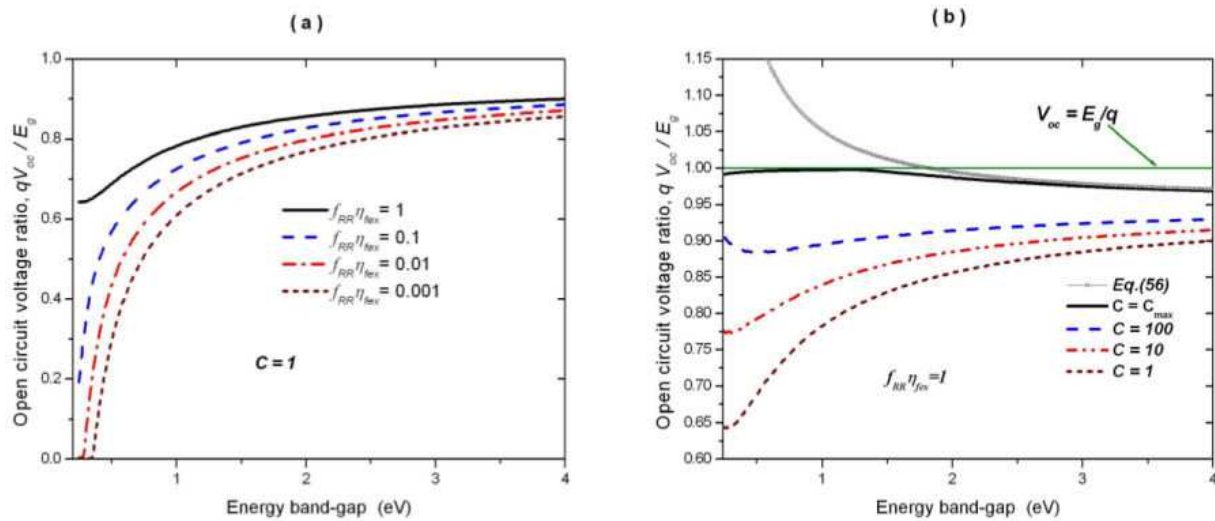
Figure 12. The V_{oc}/E_g against energy band-gap of the solar cell, using a blackbody spectrum at T_s=6000°K; a)-for different radiative recombination rates, b)-for different solar concentrations and a plot of (56) for C=C_{max}.

The maximum power output from the solar cell is obtained by choosing the voltage V so that the product current-voltage (IV) is a maximum. This point corresponds to the situation where a maximum power is extracted from the cell. Using equation 45 we can define the power delivered by a cell as:

$$P(V) = (qCf\phi_s + q(1 - C f)\phi_a - \frac{q}{f_{RR}}\phi_c(V)) \times V \tag{58}$$

The maximum power $P_M = J_M \times V_M$ is obtained numerically from (58) and the efficiency η (if the sun is assumed a blackbody at T_s) is then calculated as:

$$\eta(\%) = \frac{P_M}{P_{in}} = \frac{P_M}{2\pi^5(kT_s)^4 / 15h^3c^2} \times 100 \tag{59}$$

For AM1.5G solar spectrum P_{in} is replaced by 1000.

Figure 13 illustrates efficiency against energy band-gap of a solar cell, using the AM1.5G spectrum and the blackbody spectrum at T_s=6000°K for one sun and full concentration (C=C_{Max}), the only recombination mechanism is radiative and 100% external fluorescence efficiency, which means that all emitted photons from the cell (issue from radiative recombination) are allowed to escape. The maximum efficiency is 34.42% for AM1.5G corresponding to a gap of 1.34 eV, for a blackbody spectrum normalized to 1000 W/m² the maximum efficiency is 31.22% at 1.29 eV, while for a full solar concentration the maximum is 40.60% at 1.11 eV, this confirms the fact that the optimal band gaps decrease as the solar concentration increases.

In figure 14 the product of radiative recombination rate and the external fluorescence efficiency ($f_{RR} \times \eta_{fex}$) is decreased from 1 to 10^{-3} to illustrate the effect radiative recombination and the external fluorescence on the cell efficiency. The maximum efficiency limit dropped from 34.42% to 28.58%.
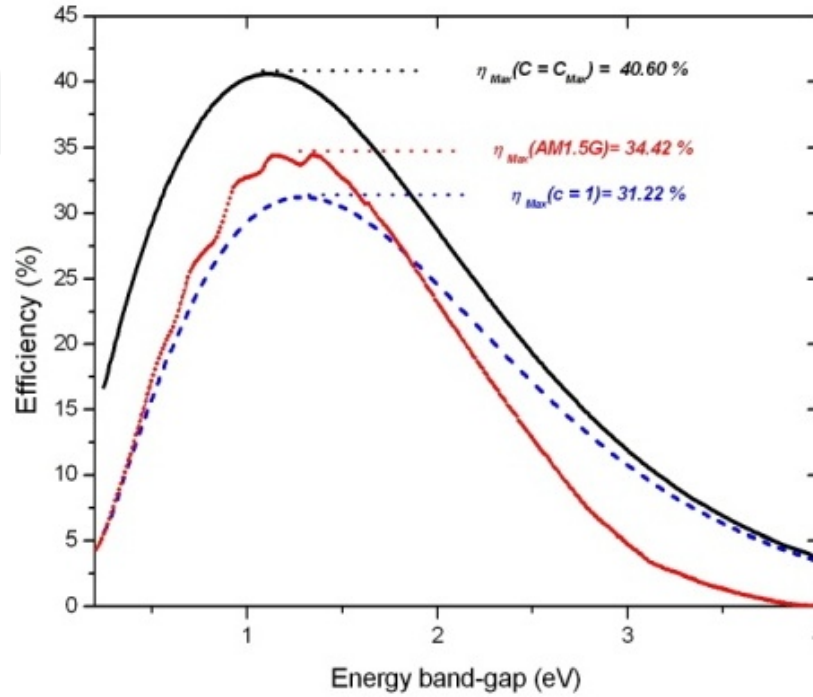

Figure 13. The maximum efficiency against the energy band-gap of the solar cell, using the AM1.5G spectrum with the blackbody spectrum at T_s=6000°K for one sun and full concentration (C=C_{Max}).

Since the power output of the cell is determined by the product of the current and voltage, it is therefore imperative to understand what material properties (and solar cell geometries) boost these two parameters. Certainly, the short-circuit current in the solar cell is determined entirely by both the material absorption property and the effectiveness of photo-generated carriers collection at contacts. As previously mentioned (section 2.4.1), the manufactured solar cells with present technologies and materials have already achieved short-circuit currents close to predicted limits. Therefore the shortfall in efficiency could be attributed to the voltage. We show here that the key to reaching the highest possible voltages is first to have a recombination predominantly radiative with a maximal external emission of photons from the surface of the solar cell. Secondly we need a maximum solar concentration. The second condition could be achieved either by using sun concentrators, there are concentrators with concentration factor from ×2 to over ×1000 [23] or by non-concentrating techniques with emission and acceptance angle limited to a narrow range around the sun [24-26].

At this level we can conclude that the efficiency limit of a single energy gap solar cell is bound by two intrinsic limitations; the first is the spectral mismatch with the solar spectrum which retains at least 50% of the available solar energy. The best known example of how
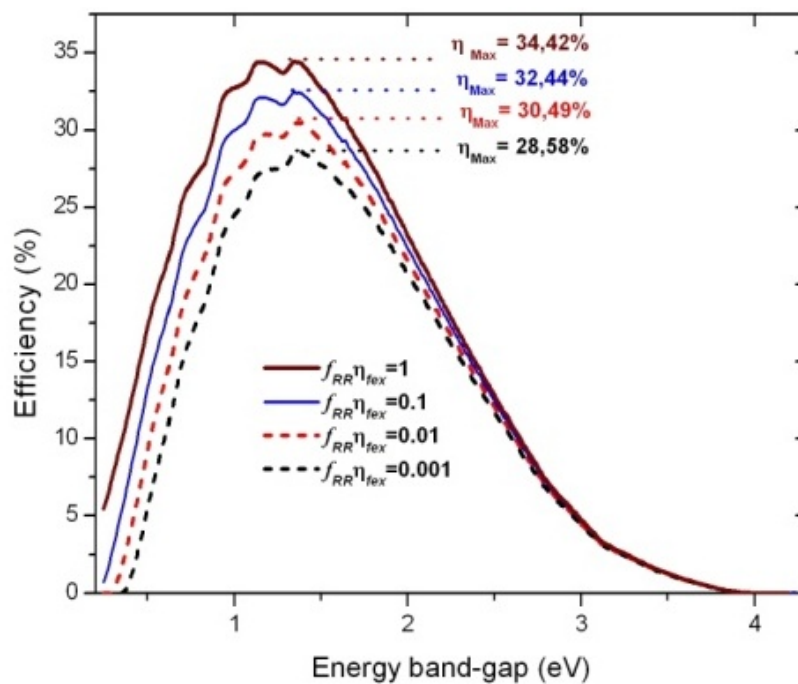
Figure 14. The maximum efficiency against the energy band-gap of the solar cell, using the AM1.5G spectrum with the blackbody spectrum at $T_s=6000°K$ for one sun and full concentration ($C=C_{Max}$)

to surmount such efficiency restraint is the use of tandem or stacked cells. This alternative will become increasingly feasible with the likely evolution of materials technology over the decades to 2020 [27].

The second intrinsic loss is due to the entropy associated with spontaneous emission. To overcame this limitation three conditions should be satisfied, that is: a) – prevailing radiative recombination (to eliminate the non-collected electro-hole pairs), b)-efficient external fluorescence (to maximise the external emission of photons from the solar cell) and c)-using concentrated sun light or restricting the emission and acceptance angle of the luminescent photons to a narrow range around the sun.

4. Conclusion

For single junction cell the record at present is 28.8% (GaAs) [14] compared to the SQ limit of 33.7% which is a significant accomplishment and little room has been left for improvement. Immense experimental research is now directed towards maximizing the external emission of photons from the solar cell. One way of getting beyond the SQ limit for a single junction is the use of concentrated radiation, the current record for concentrator cell is only 29.1% (GaAs) under 117 suns [14], this technology has a number of challenging problems (such as tracking and cooling systems) and there is still a long way to go. The same goal is accomplished by matching the angles under which light impinges from the sun and into which light is emitted from the solar cell. Recently it has been demonstrated that light trapping GaAs solar cell with

limited emission angle efficiencies above 38% may be achievable with a single junction solar cell [25].

To overcome the restrictions of a single junction solar cell several directions were investigated during the last decades (i.e. hot carrier cells, carrier multiplication and down-conversion, impurity photovoltaic and multiband cells, thermophotovoltac and thermophotonic conversion…).

The most widely explored path has been tandem or stacked cells; they provide the best known example of how such high efficiency might be achieved. The present efficiency record for a triple junctions cell (InGaP/GaAs/InGaAs) is 37.9% compared to a predicted value of over 51% for an optimised set of three stacked cells [28, 29]. The major technological challenge with tandem solar cells is to find materials with the desired band gaps and right physical properties (i.e. lattice constant and thermal parameters). The ultimate efficiency target for this kind of configuration is 86.81% (for a set of an infinite number of stacked monochromatic cells under maximum solar concentration) which constitutes an arduous target, corresponding to an infinite number of stacked junctions radiated by a maximum solar concentration. The best performance that the present technology can offer is 44.4% using a triple junction GaInP/GaAs/GaInAs cell under 302 suns [14].

Acknowledgements

Author details

Abderrahmane Belghachi[*]

Address all correspondence to: abelghachi@yahoo.fr

Laboratory of Semiconductor Devices Physics, University of Bechar, Algeria

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