Estimating the Theoretical Limit of the Power Conversion Efficiency of a Luminescent Solar Concentrator Device from the Perspective of Shockley-Queisser Limit

Yilin Li and Wen-Ji Dong

School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA, 99164, United States

***Abstract* — A model was developed to estimate the theoretical limit of the power conversion efficiency of a luminescent solar concentrator device from the perspective of Shockley-Queisser limit. The modeling results indicated that the theoretical limit of the power conversion efficiency of a luminescent solar concentrator device is always lower than Shockley-Queisser limit. The types of photon energy loss were also analyzed.**

***Index Terms* — absorption, emission, luminescent solar concentrator, model, photophysical properties.**

I. Introduction

A typical luminescent solar concentrator (LSC) device is a planar LSC slab with solar cell attached on its edge. The fraction of high energy photon in the incident light is absorbed by the luminescent molecules in the LSC slab and converted into low energy photon, most of which follows total internal reflection inside the LSC slab and finally reaches to the edge of the LSC slab. The concentrated emission light is then utilized by the solar cell to generate electrical power [1].

As a photovoltaic device, the power conversion efficiency of a LSC device is the most important parameter to describe the performance of a LSC device. However, different from the theoretical limit calculation of the power conversion efficiency of a solar cell that is dependent on the bandgap of semiconductor [2], the theoretical limit of the power conversion efficiency of a LSC device is not easy to be determined because the properties of the attached solar cell, the properties of the LSC slab as well as the photophysical properties of the luminescent molecules in the LSC slab all make contributions [3].

Currently, the most popular approach to calculating the power conversion efficiency of a LSC device is ray-tracing Monte-Carlo simulation [4]. However, it involves complicated variables and requires intensive numerical calculation [5]. Moreover, the most disadvantage of this approach is the lack of direct mathematical descriptions fully related to the photophysical properties of the luminescent molecules.

In this report, we proposed a theoretical model that links the photophysical properties of the luminescent molecules to the theoretical limit of the power conversion efficiency of the LSC device. We concluded that the theoretical limit of the power conversion efficiency of a LSC device is always lower than Shockley-Queisser limit. Types of photon energy loss were also analyzed. We believed that our study would be helpful for the further development of efficient LSC devices.

II. Theoretical Background

A. Shockley-Queisser Limit

Shockley-Queisser limit provides the theoretical limit of the power conversion efficiency of a single-junction solar cell ($\eta_{cell,max}$, in %) [2]. This limit can be calculated by the spectral irradiance of the incident light ($F_{in}(\lambda)$, in $W \cdot m^{-2} \cdot nm^{-1}$) and the bandgap of semiconductor (E_g, in eV):

$$\eta_{cell,max} = f_{SQL}\left(F_{in}(\lambda), E_g\right) \qquad (1)$$

where f_{SQL} is defined as Shockley-Queisser function. The graph of $\eta_{cell,max}$ vs. E_g is defined as Shockley-Queisser plot.

B. Photophysical Properties of Luminescent Molecules

In most cases, the photophysical properties of the luminescent molecules including absorption properties, emission properties and photoluminescence quantum yield are different when the luminescent molecules are in different conditions such as their solution in organic solvents or in solid states. In our study, the photophysical properties of the luminescent molecules is defined as that in the condition of their mixture with the host polymer of the LSC slab in powder form. The normalized absorption and emission spectra of the luminescent molecules are assumed to follow Gaussian type distribution at the absorption and emission maximums (λ_{abs} and λ_{em}, in nm):

$$P_{abs/em,lum}(\lambda) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{\left(\lambda-\lambda_{abs/em}\right)^2}{2\sigma^2}} \qquad (2)$$

In equation (2), σ (in nm) is the standard deviation of the Gaussian distribution. It can be calculated by $\sigma = \frac{W_{2/h}}{2\sqrt{2\ln 2}}$, where $W_{2/h}$ (in nm) is the full width of the half maximum of this Gaussian distribution. Here we set $W_{2/h}$ = 100 nm as an average value for most luminescent molecules.

C. Light Absorption and Emission by a LSC Slab

According to Franck-Condon principle [6], the absorption properties of the luminescent molecules are less environmentally sensitive than the emission properties. Therefore, the absorption properties of the LSC slab can be considered the same as that of the luminescent molecules. In our model, the absorption spectrum of a LSC slab is assumed to have strong absorbance at its optical density (OD, dimensionless) before λ_{abs}, while after λ_{abs}, follows Gaussian

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distribution. Therefore, the absorption spectrum of the LSC slab ($Abs_{LSC}(\lambda)$, dimensionless) is:

$$Abs_{LSC}(\lambda) = \begin{cases} OD & (\lambda \leq \lambda_{abs}) \\ OD \cdot e^{-\frac{(\lambda-\lambda_{abs})^2}{2\sigma^2}} & (\lambda > \lambda_{abs}) \end{cases} \quad (3)$$

According to Beer-Lambert law, the transmission spectrum of the LSC slab ($T_{LSC}(\lambda)$, dimensionless) is:

$$T_{LSC}(\lambda) = 10^{-Abs_{LSC}(\lambda)} \quad (4)$$

Therefore, the photon flux that is absorbed by the LSC slab ($\phi_{abs,LSC}(\lambda)$ in $m^{-2}\cdot s^{-1}\cdot nm^{-1}$) can be calculated:

$$\phi_{abs,LSC}(\lambda) = [1 - T_{LSC}(\lambda)]\phi_{in}(\lambda) \quad (4)$$

where $\phi_{in}(\lambda)$ (in $m^{-2}\cdot s^{-1}\cdot nm^{-1}$) is the incident photon flux, which can be calculated by $\phi_{in}(\lambda) = F_{in}(\lambda)\frac{\lambda}{hc}$ (h is Planck's constant and c is speed of light).

Re-absorption means that the emitted light from one luminescent molecule can be absorbed by another inside the LSC slab. Therefore, the emission properties of the LSC slab is not the same as that of the luminescent molecules. The normalized emission spectrum of the LSC slab is given by:

$$P_{em,LSC}(\lambda) = \frac{T_{reA}(\lambda)P_{em,lum}(\lambda)}{\int T_{reA}(\lambda)P_{em,lum}(\lambda)\,d\lambda} \quad (5)$$

In equation (5), $T_{reA}(\lambda)$ is defined as re-absorption transmission spectrum of the LSC slab, which is related to $T_{LSC}(\lambda)$ by the re-absorption coefficient (k, dimensionless):

$$T_{reA}(\lambda) = [T_{LSC}(\lambda)]^k \quad (6)$$

In equation (6), k is related to the geometric factor of the LSC slab (G_{LSC}, dimensionless). In our study, the relationship can be described by a linear numerical equation:

$$k = 0.1920 + 1.6714G_{LSC} \quad (7)$$

If there is no white diffuser attached on the back of the LSC slab, the theoretical maximum fraction of the emitted light that reaches the edge of the LSC slab (P_{LSC}, dimensionless) can be calculated by the refractive index (n, dimensionless) of host polymer of the LSC slab by Snell's law [7]:

$$P_{LSC} = \sqrt{1 - \frac{1}{n^2}} \quad (8)$$

Therefore, the photon flux that is emitted on the edge of the LSC slab ($\phi_{em,LSC}(\lambda)$ in $m^{-2}\cdot s^{-1}\cdot nm^{-1}$) can be calculated:

$$\phi_{em,LSC}(\lambda) = P_{LSC}G_{LSC}P_{em,LSC}(\lambda)\Phi_{LSC}\int \phi_{abs,LSC}(\lambda)\,d\lambda \quad (9)$$

In equation (9), Φ_{LSC} (dimensionless) is the photoluminescence quantum yield of the LSC slab. In our study, it is found to be related to that of the luminescent molecules (Φ_{lum}, dimensionless):

$$\Phi_{LSC} = \frac{\int T_{reA}(\lambda)P_{em,lum}(\lambda)\,d\lambda}{\left(\frac{1-\Phi_{lum}}{\Phi_{lum}}\right) + \int T_{reA}(\lambda)P_{em,lum}(\lambda)\,d\lambda} \quad (10)$$

In equation (10), if $\Phi_{lum} = 1.00$ (refers to ideal luminescent molecules), $\Phi_{LSC} = 1.00$. But if $\Phi_{lum} < 1.00$ (refers to non-ideal luminescent molecules), $\Phi_{LSC} \leq \Phi_{lum} < 1.00$.

D. Power Conversion Efficiency of a LSC device

Since the emitted photon flux on the edge of the LSC slab is known from equation (9), the spectral irradiance of the emitted light on the edge of the LSC slab is:

$$F_{em,LSC}(\lambda) = \phi_{em,LSC}(\lambda)\frac{hc}{\lambda} \quad (11)$$

According to equation (1), the theoretical limit of the power conversion efficiency of the LSC device ($\eta_{LSC,max}$) is:

$$\eta_{LSC,max} = \frac{f_{SQL}(F_{em,LSC}(\lambda),E_g)\int F_{em,LSC}(\lambda)\,d\lambda}{G_{LSC}\int F_{in}(\lambda)\,d\lambda} \quad (12)$$

According to above equations, $\eta_{LSC,max}$ can be considered as a function of several parameters. They are F_{in} as the properties of incident light; λ_{abs}, λ_{em} and Φ_{lum} as the photophysical properties of luminescent molecules; n, OD and G_{LSC} as the properties of the LSC slab; and E_g as the properties of the solar cell. Here, in this study, we take AM1.5G sunlight as incident light and set n = 1.49 and OD = 4 for a LSC slab made of poly(methyl methacrylate) (PMMA) that can absorbed 99.99 % of the incident light before λ_{abs}; and G_{LSC} = 10 for a prototype LSC slab with dimensions of 20 cm × 20 cm × 0.5 cm. Thus, $\eta_{LSC,max}$ will only be the function of λ_{abs}, λ_{em}, Φ_{lum} and E_g. For specific values of λ_{abs}, λ_{em} and Φ_{lum}, $\eta_{LSC,max}$ can be consider a function of E_g and can be graphed as Shockley-Queisser plot.

Furthermore, the overall maximum of $\eta_{LSC,max}$ ($[\eta_{LSC,max}]_{max}$, in %) at each level of Φ_{lum} can be found by optimizing the value of λ_{abs} and λ_{em}. It is obvious that the optimal values of λ_{abs} and λ_{em} should meet the following conditions:

1. $P_{em,LSC}$ should show the best match with the external quantum efficiency (EQE) of the solar cell;
2. If no re-absorption is inside the LSC slab, $P_{abs,lum}$ should be 1 nm away from $P_{em,lum}$ to ensure the most incident light to be absorbed by the LSC slab;
3. If re-absorption is inside the LSC slab, $P_{abs,lum}$ should be separated from $P_{em,lum}$ to ensure the most incident light to be absorbed and the least spectral overlap.

Therefore, $[\eta_{LSC,max}]_{max}$ is a function of E_g at each level of Φ_{lum} and can be graphed as Shockley-Queisser plot.

III. Results and Discussion

A. Conditions of Calculation

Based on the LSC model we developed above as well as the re-absorption model we proposed, here, we are going to investigate the theoretical limit of the power conversion efficiency of a LSC device ($[\eta_{LSC,max}]_{max}$ or $\eta_{LSC,max}$) under the following conditions:

1. Perfect: no re-absorption inside the LSC slab (k = 0) and ideal luminescent molecules (Φ_{lum} = 1.00);
2. Ideal: re-absorption inside the LSC slab (k = 17) and ideal luminescent molecules (Φ_{lum} = 1.00);
3. General: re-absorption inside the LSC slab (k = 17) and non-ideal luminescent molecules (Φ_{lum} = 0.90);
4. Specific: re-absorption inside the LSC slab (k = 17) and a common luminescent molecule for LSC application – DCJTB (4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7 tetramethyljulolidyl-9 enyl)-4H-pyran) (λ_{abs} = 510 nm, λ_{em} = 626 nm and Φ_{lum} = 0.90).

B. Modeling Results

Fig.1 depicts the theoretical results for the above conditions (perfect, ideal, general and specific) associated with Shockley-

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Queisser limit (SQL). TABLE I listed the values of $[\eta_{LSC,max}]_{max}$ for perfect, ideal and general conditions and $\eta_{LSC,max}$ for specific condition at E_g = 1.1 eV and 1.5 eV as well as their maximum points.

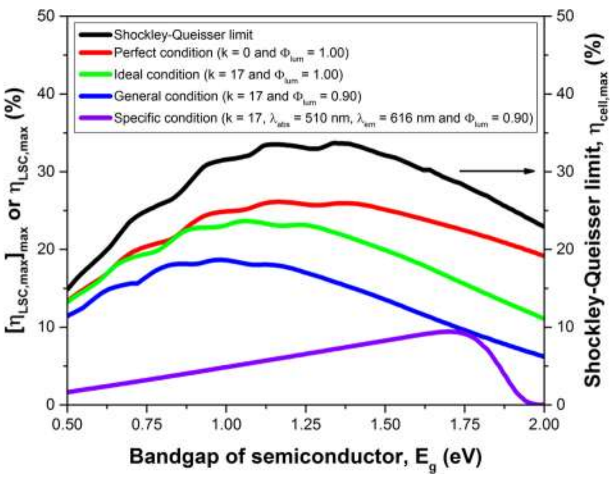

Fig. 1. Shockley-Queisser plots for a LSC device under perfect, ideal, general and specific conditions.

TABLE I
VALUES OF $[\eta_{LSC,max}]_{max}$ FOR PERFECT, IDEAL AND GENERAL CONDITIONS AND $\eta_{LSC,max}$ FOR SPECIFIC CONDITION AT E_g = 1.1 eV AND 1.5 eV AS WELL AS THEIR MAXIMUM POINTS

Condition	E_g = 1.10 eV	E_g = 1.50 eV	maximum point (E_g)
SQL	32.8 %	32.1 %	33.7 % (1.34 eV)
1 (perfect)	25.7 %	25.1 %	26.1 % (1.17 eV)
2 (ideal)	23.5 %	19.9 %	23.7 % (1.06 eV)
3 (general)	18.0 %	13.5 %	18.6 % (0.98 eV)
4 (specific)	5.5 %	8.3 %	9.4 % (1.70 eV)

First, all LSC devices are subject to photon energy loss due to the top and bottom escape of the emission light.

For the perfect condition, because no re-absorption is inside the LSC slab, the photophysical properties of the LSC slab exhibit the same as that of the luminescent molecules. $[\eta_{LSC,max}]_{max}$ in Fig. 1 is lower than SQL by a magnitude of 1.6 – 7.8 %. It is because the LSC slab is not able to convert long-wavelength light. Photon energy between λ_{abs} and E_g is lost.

For the ideal condition, because re-absorption is inside the LSC slab, $P_{em,LSC}$ exhibits red-shift with respect to $P_{em,lum}$. Therefore, in order to match the EQE of the solar cell, $P_{em,lum}$ should shift to blue. However, this blue-shift of $P_{em,lum}$ will causes the blue-shift of $P_{abs,lum}$, which further causes more photon energy loss between λ_{abs} and E_g.

For the general condition, because non-ideal luminescent molecules are used. Besides the photon energy loss between λ_{abs} and E_g, photon energy loss during photon conversion process of the luminescent molecules should also be counted. Furthermore, re-absorption makes an even lower value of $[\eta_{LSC,max}]_{max}$.

For the specific conditions, the LSC device with DCJTB can only have a maximum power conversion efficiency at 9.4 %. The value of $\eta_{LSC,max}$ at E_g = 1.1 eV and E_g = 1.5 eV are pretty low at 5.5 % and 8.3 %, respectively. These values are consistent with the reported experimental results [8]. The photon energy loss can be attributed to the loss between λ_{abs} and E_g, re-absorption and non-unity Φ_{lum}.

III. Conclusions

In conclusion, it is important to note that the theoretical limit of the power conversion efficiency of a LSC device is always lower than Shockley-Queisser limit. Besides the top and bottom escape, the other types of photon energy loss are concluded in TABLE II.

TABLE II
TYPES OF PHOTON ENERGY LOSS IN A LSC DEVICE

Condition	between λ_{abs} and E_g	re-absorption	non-unity Φ_{lum}
1 (perfect)	X		
2 (ideal)	X	X	
3 (general)	X	X	X
4 (specific)	X	X	X

Based on TABLE II, solving the photon energy loss between λ_{abs} and E_g and its loss due to re-absorption are important for developing LSC devices with high power conversion efficiencies. Moreover, developing luminescent molecules with high photoluminescence quantum yield is important as well.

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