THERMODYNAMICS OF PHOTOVOLTAIC AND CONCENTRATOR PHOTOVOLTAIC SYSTEMS AND DETERMINATION OF THEIR ENERGY AND EXERGY EFFICIENCIES

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Summary

The thermodynamic analysis of energy conversion system provides insight understanding that can be used to improve efficiency and performance of the system. The photovoltaic energy conversion system is a complex hybrid process of converting incident solar radiation energy into electrical and thermal energy simultaneously. The process is based on absorption of incident solar radiation by semiconductor materials to generate electron-hole pair and flow of electrons in the external electrical circuits. The energy and exergy flow during the photovoltaic energy conversion process are determined on the basis of first and second law of thermodynamics respectively and can be used for quantitative and qualitative analysis of the process.
The chapter aims to provide an overview of thermodynamics of solar photovoltaic (PV) energy conversion process, along with PV thermal and concentrated PV, through derivation of energy and exergy balance equations and discussion of different thermodynamic models/theories. It begins with an introduction to the photovoltaic phenomenon and the laws of thermodynamics to provide the background for the topic and to understand the basic physics and working principles. Section 2 deals with thermodynamic analysis of PV energy conversion process, derivation of energy and exergy balance equations and efficiencies of PV systems, PV thermal and concentrated PV systems. It includes exergy of incident solar irradiation, different thermodynamic losses, exergy output and irreversibilities. The theoretical upper limit derived by different researchers using different thermodynamic models/theories on the basis of certain assumptions are discussed in Section 3, followed by summary of theoretical upper limit efficiencies of PV in comparison with the practical achievable efficiencies. Finally, the chapter ends with a few concluding remarks.

1. Introduction

The Sun is the primary resource of energy for our planet; produces thermal energy due to nuclear fusion reaction with approximately 15.7 million Kelvin and 5800 Kelvin temperatures at its core and surface respectively. At these temperatures, the Sun emits around $3.845 \times 10^{26}$ Watt of thermal radiation in all directions, known as solar radiation. The earth receives around $1.8 \times 10^{11}$ Megawatt of solar radiation. The term global solar radiation is used for total solar radiation reaching earth’s surface, which is sum of beam and diffuse radiation. The beam radiation, also known as direct radiation, reaches earth’s surface without scatter or interaction with atmospheric gases/particles. It is directional radiation which reaches a particular location directly from the Sun; therefore it can be guided or concentrated through reflection or refraction. The diffuse radiation is scattered or re-radiated in all direction after interacting with atmospheric gases/particles. The presence in cloud coverage, dust particles and polluting gases decreases the beam radiation of the location and increases the diffuse radiation.

Solar radiation can be considered as electromagnetic waves having different wavelength ranges as well as photon gas having photons of different values of energy content, i.e. it has dual nature (wave and particle nature), in accordance with the purpose of investigation. The interaction of solar radiation with material and exchange of energy converts solar radiation into useful form of energy, such as thermal energy and electrical energy through photothermal and photovoltaic conversion processes respectively. In the case of photothermal conversion, the absorption of solar radiation increases the kinetic energy of atoms, which leads to heat generation, while it increases potential energy of the atoms during photovoltaic energy conversion leading to current flow to the load. The conversion process or energy exchange by solar radiation depends upon the absorber material. This energy conversion process occurs in accordance with the Laws of Thermodynamics. The Zeroth Law of Thermodynamics deals with concept of temperature and thermal equilibrium. The First Law of Thermodynamics states that the net energy of a physical system remains conserved and is the basis for the system’s quantitative analysis and energy efficiency. The Second Law of Thermodynamics deals with the directional and qualitative approach of system analysis in terms of the entropy and exergy efficiency. The system exergy is defined as the maximum possible available
energy within the system during its interaction with corresponding surroundings, while system entropy is the measure of associated irreversibility responsible for exergy loss. The term ‘exergy efficiency’ is used to compute the comparative system performance with respect to corresponding performance in reversible conditions. In other words, it reflects the system’s effectiveness in practical working circumstances. The Third Law of Thermodynamics deals with entropy at absolute zero temperature.

There are two concepts of thermodynamics to understand energy conversion processes—, phenomenological and statistical. The phenomenological analysis is based on macroscopic energetic processes, while the statistical analysis is based on microstructure, assuming the particle nature, of matter. These two concepts can be applied to assess the energy exchange by solar radiation. The phenomenological thermodynamic analysis considers electromagnetic waves of solar radiation traveling from one body to another through a medium and exchange energy, while the statistical thermodynamics considers the exchange of energy taking place through emission and absorption of photons between the atoms.

The thermodynamics of solar photovoltaic energy conversion is to understand the photo-thermo-electrical processes and to assess the irreversibilities, losses, performance and upper limit efficiencies of solar PV cell. This chapter deals with thermodynamic analysis of photovoltaic (PV), photovoltaic thermal (PVT) and concentrator photovoltaic (CPV) systems using first and second law of thermodynamics, in order to determine energy and exergy conversion efficiencies of the systems.

1.1. Solar Photovoltaic Energy Conversion

The solar photovoltaic energy conversion is a process of converting solar radiation directly into electricity, in which the potential energy of absorber material increases due to absorption of solar radiation and causes flow of charges. A solar photovoltaic cell absorbs solar radiation having energy, equal to or higher than, the energy bandgap of PV material to generate electron-hole pairs, i.e., charge carriers. The excitation of electron (negative charge carrier) from valence band to conduction band, leaves a hole (positive charge carrier) in valence band, known as electron-hole pair generation. The energy equivalent to the bandgap is required for excitation of charge carrier and electricity generation. If the excited electron exhibits energy higher than the energy bandgap of PV material, then the electron loses the excess energy to reach conduction band minima. These losses of energy are mainly in the form of thermal losses. Considering wave nature of solar radiation, the solar radiation of a particular range of wavelength (i.e. mostly visible range from 0.38 µm to 0.72 µm) is mainly used for electricity generation using photovoltaic energy conversion process and the absorption of infrared range (0.72 µm to 4 µm) generates thermal energy and increases the temperature of PV module. If particle nature of solar radiation is considered, the photons of different energy levels are incident on the PV module. The photons of energy level equal to or higher than energy bandgap of PV material contribute to electricity generation. Based on the position of valence and conduction bands, the semiconductors are divided into two types, i.e. direct and indirect bandgap semiconductors. In the case of direct band gap, the minimum and maximum energy levels of conduction and valence bands are exactly in the same axis, therefore, it
requires absorption of only photons for excitation to conduction band, while, in the case of indirect bandgap semiconductors, since the minimum and maximum energy levels of conduction and valence bands are not in the same axis, it requires absorption of phonons (particle having low energy and high momentum) also along with the photons for excitation to conduction band.

Both the direct and indirect bandgap semiconductors are used for photovoltaic applications, such as Silicon (Si), Germanium (Ge), Cadmium Telluride (CdTe), and Copper Indium Gallium Selenide (CIGS). These materials are used in commercial PV modules. The photovoltaic phenomenon has also been reported in organic materials, such as organic polymers, Dye-Sensitized and Pervoskite Solar Cell. The PV technologies using organic material are currently at research stage, yet to demonstrate long term stable performance with reasonable efficiency. The energy band gaps of different PV materials are given in Table 1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>PV Material</th>
<th>Energy Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Indium Arsenide (InAs)</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>Germanium (Ge)</td>
<td>0.66</td>
</tr>
<tr>
<td>3</td>
<td>Silicon (Si)</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
<td>Copper Indium Gallium di-selenide (Cu(InGa)Se$_2$ or CIGS)</td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td>Gallium Arsenide (GaAs)</td>
<td>1.42</td>
</tr>
<tr>
<td>6</td>
<td>Cadmium Telluride (CdTe)</td>
<td>1.45</td>
</tr>
<tr>
<td>7</td>
<td>Cadmium Sulfide (CdS)</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Table 1. Energy bandgap of PV materials

These semiconductor materials, after doping with $p$-type and $n$-type impurities, are used to make a $p$-$n$ junction device. The junction (also known as space charge region and depletion region) is made by doping of $n$-type impurities or depositing a layer of $n$-type material on $p$-type material, or vice versa. Due to recombination, the opposite charges are accumulated near $n$-type and $p$-type regions, and generate a potential barrier (electric field) in the space charge region. The $p$-type semiconductors have holes in majority and electrons in minority, and the situation is reversed in the case of $n$-type semiconductors. The illumination by solar radiation generates electron-hole pairs in $n$-type, $p$-type and depletion region of photovoltaic device. These charge carriers experience diffusion and drift forces due to concentration difference of charge carriers and electric field of the junction. The majority and minority charge carriers move across the junction due to the diffusion and drift forces respectively, resulting in generation of diffusion and drift current respectively. The electron and hole generated in the depletion region experience maximum drift force and are instantly swept away to $n$-type and $p$-type regions respectively. The drift force is negligible on minority charge carriers generated in the farthest part of $n$-type and $p$-type regions, and therefore these charge carriers move randomly and during random movement they either experience the drift force for being swept away across the junction or recombine with the majority charge carrier. During the equilibrium mode (i.e., when PV device is not illuminated), the diffusion and drift currents are equal and opposite in direction, making net current zero.
During the illuminated condition, the drift current is more than the diffusion current. Thus, the concentrations of electrons and holes increase in n-type and p-type regions respectively. This results in generation of potential difference and flow of charge carriers in the outer circuit. This potential difference generated by illumination by solar radiation is also known as photo-voltage and the drift current is known as light generated current. The working principle of photovoltaic energy conversion is shown in Figure 1.

![Figure 1. Working of photovoltaic energy conversion showing p-n junction solar cell and band to band transition of electron (Left) and current voltage characteristics of output electrical energy (Right).](image)

The solar photovoltaic energy conversion is a thermodynamic process which generates dual output, i.e. electrical and thermal energy, from single input, i.e., solar radiation. In the ideal condition, the entire incident solar radiation shall be absorbed by the PV cell and each photon (entire wavelength spectrum) shall contribute to electricity generation without any losses. The ideal solar cell also implies zero series resistance and infinite shunt resistance. However, in a practical PV cell, there are finite series and shunt resistances, besides other optical and thermal losses. The series current is the sum of resistance offered in the path of current in emitter and base of solar cell, semiconductor-metal contacts and metal-metal contacts. The shunt resistance is the resistance offered in the path of leakage current flowing in the opposite direction of light generated current. The higher shunt resistance indicates lower leakage current, which is desirable in PV power generation. The PV cell generates direct current and the power output is equal to multiplication of voltage and current output \((P=VI)\). The current-voltage characteristic (I-V curve) of solar PV power generation is non-linear (as shown in Figure 1), which shows that the maximum generated current (short circuit current) and voltage (open circuit voltage) cannot be extracted from the device. The ratio of maximum power that can be extracted from solar PV module \((P=V_MI_M)\) to the
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The theoretical maximum generated power, i.e. multiplication of short circuit current \( I_{SC} \) and open circuit voltage \( V_{OC} \), is known as fill factor \( F = V_{M}I_{M} / V_{OC}I_{SC} \). Here, and are known as voltage and current at maximum power point. The mathematical model of a practical PV power generation includes, short circuit current, series and shunt resistances, ideality factors of two diodes \( \eta_{d1} \) and \( \eta_{d2} \) representing the recombination losses due to recombination of electron- hole pairs, as given by

\[
I = I_{SC} - I_{01} \left[ \exp \left( \frac{q(V - IR_s)}{\eta_{d1}kT} \right) - 1 \right] - I_{02} \left[ \exp \left( \frac{q(V - IR_s)}{\eta_{d2}kT} \right) - 1 \right] - \frac{V - IR_s}{R_{sh}}
\]

The different optical, thermal and electrical losses involved in the photovoltaic energy conversion process are as follows:

- **Optical loss:** It involves partial reflection of solar radiation from PV module surface.
- **Radiation mismatch loss:** It involves the loss of energy due to wavelength or photons which are not absorbed by the PV material.
- **Thermal loss:** It involves loss of generated thermal energy through radiative and convective heat transfer. The thermal energy loss can be reduced partially by using photovoltaic thermal devices.
- **Resistive loss:** It involves loss of electrical energy due to series and shunt resistances.
- **Fill Factor loss:** It involves loss of energy due to non-linear \( I-V \) characteristics. PV module operating at voltage and current that are less than open circuit voltage and short circuit current respectively.
- **Irreversibilities:** Energy loss due to entropy generation during the process.

The \( p-n \) junction PV cells having front and back contacts for extraction of power are connected in series and parallel to generate higher voltage and current output respectively. This group of interconnected PV cells makes a PV module, which is then encapsulated and covered by glass in order to protect it from environmental stresses. The PV module also employs different technologies to reduce optical losses, such as anti-reflective coating, texturing and light trapping. The PV module undergoes a series of testing procedures in simulated extreme environmental conditions to ensure its robustness and capability to withstand outdoor environment over its lifetime (i.e., 25 years). The PV modules are rated under standard test conditions, which are 1000 W/m² solar irradiance, 25°C module temperature and 1.5 Air Mass. The PV cells and modules are used for a variety of applications, which range from small PV cells used in calculators and wrist watches for battery charging to Mega Watt scale PV power generation plants supplying power to a grid. The PV modules are also interconnected for generating higher power. Besides PV modules, the systems also include other devices such as converter (for DC to DC conversion), maximum power point tracker (to enable the system to operate at maximum power point), inverter (for converting DC to AC) and battery storage. The off-grid applications are streetlighting, water pumping, home lighting, etc. while grid connected applications include large scale commercial PV plants for sale of electricity and small-scale rooftop PV plants of a few kilo Watts nominal capacity.
1.2. Laws of Thermodynamics

Thermodynamics is the branch of science that deals with the effects of energy transfer on a system and its surroundings. The first law of thermodynamics is used for quantitative analysis of any thermodynamic process. The energy balance equation is developed on the basis of law of energy conservation to solve and understand the thermodynamic process. It states that the energy input to any system will always be equal to the sum of energy gained by the system and energy output and is given by

\[ E_{\text{in}} = \Delta E + E_{\text{out}} \]  

(2)

In the case of energy conversion devices, such as heat engines that convert thermal energy into power or work, the power \( P \) generated will always be the difference between the thermal energy of the heat source \( (Q_h) \) and that of heat sink \( (Q_s) \), i.e., received heat from source and the remaining heat released to the sink after power generation. The energy balance equation of such system is given by

\[ P = Q_h - Q_s. \]  

(3)

The second law of thermodynamics provides qualitative as well as quantitative analysis of a thermodynamic process. It includes irreversibility associated with the process and exergy balance equation is developed accordingly to assess the process. It introduces the concept of exergy, which is qualitative and shows the useful part of energy. The part of energy that cannot be used is known as anergy. The exergy balance of system states that the exergy input will be equal to the sum of exergy lost, exergy output and irreversibility, as given by

\[ \text{Exergy}_{\text{in}} = \text{Exergy}_{\text{lost}} + \text{Exergy}_{\text{out}} + \text{Irreversibilities} \]  

(4)

The exergy balance equation of a heat engine states that the exergy input \( (B_h) \) from the heat source is equal to the sum of the exergy lost to the heat sink \( (B_s) \), the exergy output (power, \( 'P' \)) and the exergy loss due to irreversibility \( (\delta B) \), as:

\[ B_h = B_s + P + \delta B. \]  

(5)

The exergy loss due to irreversibility is non recoverable loss of exergy within the system or process and also known as internal exergy loss or exergy destruction. The Gouy-Stodola law States that the exergy destruction due to irreversibility depends on the entropy generation \( (S_{\text{gen}}) \) and the temperature of the surroundings \( (T_E) \), as given by

\[ \delta B = T_E S_{\text{gen}}. \]  

(6)

Entropy generation during the process will always be positive for an irreversible system and zero for a reversible system. In any system or process negative entropy generation
is not possible in nature. The total entropy generated is equal to the sum of entropy generated by the system and surroundings, as given by

\[ S_{\text{gen}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) = -\frac{Q_h}{T_s} + \frac{Q_h}{T_s} \geq 0. \]  

(7)

2. Thermodynamics of Solar Photovoltaic Conversion

2.1. Energy and Exergy of Solar Radiation

Solar radiation is a source of low-grade input energy to the system that can be converted into high grade electrical energy as well as low grade thermal energy through photovoltaic energy conversion process. The solar radiation is measured using pyranometer in terms of power, i.e., Watts per meter square (W/m²), at a particular location at an instant time, that can be integrated to obtain energy for over a definite period such as a day or a month or a year, i.e., Wh/m². The energy received at the PV module surface can be used for energy balance equation, while the exergy of solar radiation is required for exergy balance analysis. In an established environmental condition, the maximum limit up to which the solar radiation can be utilized or converted into useful form of energy is known as exergy of solar radiation.

Petela (1964) derived a formula to calculate exergy of solar radiation considering arbitrary radiation is emitted from the Sun and approaching Earth’s surface. He proposed a relation on the basis of temperature of both the surfaces. The energy flux emitted from a black body at temperature \( T_s \) is given by

\[ E_s = \frac{a c}{4} T_s^4, \]  

(8)

where \( a \) is universal constant \( (7.561 \times 10^{-19} \text{ kJ/m}^3\text{K}^4) \) and \( c \) is speed of light in vacuum \( (2.998 \times 10^8 \text{ m/s}) \). The exergy of the above black body emission (solar radiation) can be calculated by

\[ B_s = \frac{ac}{12} \left( T_s^4 + T_e^4 - 4T_e T_s^2 \right). \]  

(9)

The ratio of exergy of emission to the total blackbody emission, i.e. ratio of exergy to energy of solar radiation, is the work conversion efficiency of solar radiation and can be used for calculation exergy of measured solar radiation, as given by

\[ \frac{B_s}{E_s} = 1 - 4 \left( \frac{T_e}{T_s} \right)^4 + \frac{1}{3} \left( \frac{T_e}{T_s} \right)^4. \]  

(10)

Parrott (1978) had included sun-earth geometry (as half angle of the cone subtended by disc of Sun) of incoming radiation and partially modified Eq. (10) to the following
Some other researchers have also proposed methods to determine exergy of solar radiation. Spanner (1964) has considered that the exergy of solar radiation would be equal to its work potential and proposed the following relation for determining solar radiation exergy:

$$\frac{B_S}{E_S} = 1 - \frac{4}{3} \left( \frac{T_E}{T_S} \right)^4 \left(1 \cos \delta \right)^3 + \frac{1}{3} \left(1 - \cos \delta \right) \left( \frac{T_E}{T_S} \right)^4 \]$$

(11)

Jeter (1981) applied Carnot heat engine model to solar radiation and accordingly proposed the formula for calculating exergy of solar radiation, as given by

$$\frac{B_S}{E_S} = 1 - \frac{4}{3} \left( \frac{T_E}{T_S} \right)^4$$

(12)

After examining the theories of calculation of solar radiation exergy proposed by Petela (2010), Spanner (1964) and Jeter (1981), some researchers concluded that all the theories are correct as per their assumptions, while majority have recommended theories of Petela and Jeter. Equation (10) given by Petela has most widely been accepted and recommended for calculating the exergy of solar radiation.


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Biographical Sketch

Dr. Rahul Rawat is a Scientist at the Ministry of New and Renewable Energy (MNRE), Government of India. He received PhD in solar photovoltaics from the Centre for Energy Studies, Indian Institute of Technology Delhi (IIT Delhi) in 2018. After 2.5 years in research as full time PhD scholar, he joined the MNRE as a Scientist in July, 2016, while continuing research for PhD Part time. At MNRE, he has been part of the team responsible for overall policy planning of the Renewable Energy sector-manufacturing sector of solar photovoltaic, canal top solar PV projects and wind energy sector. Prior to the PhD, he completed M.Tech. in Energy Technology from Centre for Energy and Environment, National Institute of Technology Hamirpur (H.P.) and B. Tech in Electronics and Communication Engineering from Rajasthan Technical University, Kota (Rajasthan). His research area is solar photovoltaic technologies, thermodynamics of solar photovoltaics and policy planning of renewable energy sectors includes solar and wind energy. He has published 10 papers in international journals of high repute including Renewable & Sustainable Energy Reviews (Elsevier), Renewable Energy (Elsevier), Solar Energy (Elsevier), Energy (Elsevier), Energy Conversion & Management (Elsevier), Energy Technology (Wiley), etc. and presented his research work in several international conferences. He is also a member of the technical committee of Bureau of Indian Standards (BIS) responsible for the standards related to solar photovoltaics.