Non-Imaging Technologies for Designing a Hybrid Photovoltaic and Solar Thermal Collector

A thesis presented for the degree of
Doctor of Philosophy

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the research is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Maja Gajic

December 2017
The sun is the world’s most abundant energy source and means of harvesting it include photovoltaic cells to create electricity and solar thermal collectors to generate heat. Low temperature heat can be used for domestic applications where in urban environments available space is often limited. By combining solar thermal and photovoltaics in one system, roof space can be saved and potentially efficiency can be increased. Photovoltaic technologies can only convert photons with energies above their bandgap to electricity, with the remainder of the solar spectrum wastefully generating heat. In a hybrid configuration that heat is not wasted but collected instead. The work done in this thesis investigates and then combines two non-imaging types of concentrating solar technologies: the luminescent solar concentrator that generates electricity via photovoltaic cells, conventionally used in the built environment and the compound parabolic concentrator, used for capturing solar thermal energy. LSCs combined with flexible SLIVER solar cells were investigated in a new circular configuration and were found to work well although the manual fabrication nature of these devices limited their efficiency. Various high quantum yield fluorophores were also investigated and it was found that performance of the LSCs was highly dependent on maximising the Stokes-shift of the fluorophore to minimise losses. Following on from this work, the luminescent solar concentrator in a new application of the technology, was used as a cover for the solar thermal collector (the CPC) whilst at the same time concentrating a band of light to its edges where solar cells convert photons to electricity. The capture of a part of the solar spectrum in the LSC is done with fluorescent particles whilst the rest of the solar spectrum can be captured as thermal energy in the CPC, essentially coming up with a new spectral splitting hybrid solar collector. A small prototype hybrid CPC and LSC collector was tested in the lab under a solar simulator. This proof of concept device compared a high transmission and low transmission LSC and demonstrated the experimental basis of the new type of PV-T collector. An outdoors flow experiment was undertaken, measuring instantaneous thermal efficiency and electrical output.
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Journal articles


Gajic, Maja, et al. "Circular luminescent solar concentrators." *Solar Energy*, 150 (2017): 30-37. (This paper is the basis of Chapter 4 of this thesis)

Conference papers

Gajic, M., et al. "Beam Splitting with a Luminescent Solar Concentrator in a Hybrid Photovoltaic/Thermal Collector" (Presented at ISES 2017 Solar World Congress, will be published in *Energy Procedia*. Based on results from Chapter 6 and Chapter 7)

Research not related to this thesis

Gajic, M., et al. “Evaluation of a Solar Home System Program in East Timor - Putting communities first”. (To be presented later this year at the 2017 IEEE conference for Humanitarian Technology)
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Chapter 1

Introduction

1.1 Background

Recently the IPCC’s 5th assessment report stated that “Warming of the climate system is unequivocal, and since the 1950’s, many observed changes are unprecedented over decades to millennia. The atmosphere and oceans have warmed, the amount of snow and ice have diminished, the sea level has risen and the concentration of greenhouse gases has increased.” If we do nothing to curb greenhouse gas emissions into our atmosphere, the outlook for our species and the planet is catastrophic. (IPCC Working Group I 2013).

In Australia in 2010 the stationary energy sector was responsible for 51.4% of our CO$_2$ equivalent emissions (Parliament 2010). These emissions can be reduced and eventually eliminated by making the necessary change from emission intensive forms of generating electricity to generation from renewable energy sources that produce little or no emissions.

As the world starts to shift away from polluting forms of generating electricity to renewable energy sources, the solar energy resource stands out simply due to its sheer size. Approximately 89,000 TW strikes the earth’s surface, providing in an hour and a half more energy than the world consumed from all sources in 2011 (Yam 2010). Our sun is a broad source of energy that is the obvious source to support a renewable energy future. Various technologies that are used to capture the sun’s energy can generally be categorised as either photovoltaic (PV) technologies, that generate electricity, or solar thermal technologies that utilise the energy in the form of heat. Photovoltaic technologies can only convert photons with energies above their
CHAPTER 1. INTRODUCTION

bandgap, as shown in Figure 1.1 for silicon PV cells. These cells have efficiencies between 12 % and 24 % and recent plummeting costs have seen solar PV favoured over other solar technologies.

Across households and industry there is a high demand for heat energy. Solar thermal technologies are mature, well established and able to meet heat demand in areas with a high enough solar resource. Solar collectors can be designed to provide heat over a wide range at reasonable efficiencies. In an attempt to improve overall system efficiency, solar thermal and PV technologies can be combined generating both electricity and useful thermal output, better utilising the solar source for a given physical area and application. To understand how the technologies can be combined we need to understand the solar source.

As the sun's radiation passes through the atmosphere, various effects such as absorption and scattering change the spectrum's shape and intensity, with the amount of change dependent on how much atmosphere the radiation has passed through. It would be computationally expensive to constantly adjust the spectrum for each time of day so a standard called air mass (AM) 1.5 is commonly adopted, shown in Figure 1.1 (NREL 2010).

![Figure 1.1: Solar AM 1.5 spectrum showing silicon solar cell absorption (gray) and the remainder of the spectrum in red.](image)

A way of increasing the flux of solar energy is to concentrate the sun's radiation by means of various optics. By concentrating light, higher working fluid temperatures for solar thermal collectors can be achieved, as the solar flux (W/cm²) on the receiver increases. In this way thermal energy that is required for various industrial
applications and domestic applications can be generated renewably. The apparent motion of the sun through the sky varies the amount of power striking a stationary receiver and this is dependent on the angle of incidence of light into the aperture of the collector - any radiation that strikes the receiver at an angle that is not normal to the surface incurs losses. Tracking collectors aim to maintain the sun’s angle of incidence to be normal, while stationary non-tracking collectors will incur losses throughout the year but are simpler and more economical to implement. When concentrating solar radiation there is also a trade-off between the angle of incident radiation that can be accepted and the increase in concentration possible. Imaging optics concentrators such as parabolic dishes maintain an image of the sun through the optics, however depending on the design, this is not always necessary and in fact better performance can be obtained with so called non-imaging concentrators that do not need to maintain an image of the sun and therefore have wider acceptance angles, higher concentration ratios and require less precise optics (Winston et al. 2005).

The work done in this thesis investigates two types of non-imaging solar concentrators, the luminescent solar concentrator (LSC) and the compound parabolic solar thermal collector (CPC), in a completely new application of both technologies. Firstly the two technologies were researched and investigated separately and then combined in a hybrid device with the luminescent solar concentrator utilised as a cover for the CPC solar thermal collector. In the hybrid configuration, the LSC cover acts as a beam splitter of solar radiation. The absorption and emission spectra of the fluorescent molecule within the LSC device select a part of the spectrum, where ideally it is totally internally reflected to the solar cells attached to the edges of the LSC. The rest of the solar spectrum is transmitted through the LSC cover to the solar thermal collector. The main aim of this thesis is to present the experimental basis for such a hybrid device.

There are many potential applications for such a technology depending on what the desired outcome is. The CPC solar thermal collector can be designed for domestic applications requiring low temperature heat or for commercial applications where medium temperature heat is required (up to 250°C). The LSC is not yet a high power device as it can generate modest amounts of electricity that could potentially power peripheral devices or sensors. There is of course a trade-off between electricity generated and thermal energy collected and one or the other could be prioritised depending on loads and needs. The potential applications for hybrid photovoltaic and thermal (PV-T) collectors is greatest in urban environments where roof space is often limited (Ramos et al. 2017). By making better use of the solar source PV-T collectors can save on space and improve collection efficiency.
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1.2 Thesis Outline

Chapter 1  Gives the background of the research described in this thesis and presents the aim of the thesis.

Chapter 2  Reviews the design principles and key studies in the literature of the compound parabolic concentrator and the luminescent solar concentrator.

Chapter 3  Presents modeling of incidence angle modifier losses of the compound parabolic concentrator.

Chapter 4  Presents work done on the circular luminescent solar concentrator including use of a liquid waveguide then fabrication of LSCs with the polymer PDMS and an investigation of scattering only LSCs.

Chapter 5  To design the large LSC required for a hybrid collector, Monte Carlo was developed to investigate various geometries.

Chapter 6  Presents the results of the development of a proof of concept small prototype hybrid LSC and CPC.

Chapter 7  Presents the results of a full length hybrid CPC and LSC, with flow experimental results.

Chapter 8  Concludes the thesis and recommends possibilities for future work.
Chapter 2

Review of The Literature

2.1 The Luminescent Solar Concentrator

2.1.1 Introduction

Luminescent solar concentrators consist of a fluorescent material embedded in a waveguide such as PMMA. Photons that fall within the absorption spectrum of the fluorescent material can be absorbed and then isotropically emitted at a longer wavelength. Ideally these re-emitted photons are propagated to the edge of the waveguide via total internal reflection (TIR). Solar cells (or other absorbers) can then be attached to the edges of the device to convert photons to electricity as shown in Figure 2.1. An important benefit of LSCs is that they have the ability to concentrate both diffuse as well as beam radiation (Smestad et al. 1990) and due to their wide acceptance angle they do not require expensive tracking mechanisms. Additionally the fluorescent dye can be chosen to emit photons that the solar cells can convert with higher efficiency. It has also been suggested but not further investigated that LSCs can be used as thermal energy conversion devices (Goetzberger & Greubel 1977).

LSCs were first described in the late 1970s (Goetzberger & Greubel 1977, Weber & Lambe 1976) in an attempt to reduce the amount of expensive PV cells required per unit solar aperture area. With the cost of silicon PV cells dropping drastically in the last years, the aim for reducing cell coverage is less justifiable. Now the goal is to create large scale energy generating construction materials as a means to reduce the carbon footprint of new buildings and the built environment (Debije & Verbunt 2012, Vossen et al. 2015).
CHAPTER 2. REVIEW OF THE LITERATURE

Figure 2.1: Basic LSC operation - An incoming photon is absorbed inside the waveguide, then isotropically emitted where ideally it is totally internally reflected to solar cells coupled to the edges.

LSCs have applications as either direct, low-cost competitors to conventional PV cells or as down-converters to improve silicon solar cell efficiencies. To act as a down converter, the LSC is placed on top of a solar cell and can improve PV cell efficiency by converting high energy photons to longer wavelengths where they are more readily absorbed by solar cells (Ahmed et al. 2016, Richards 2006). Additionally, nano structured gratings can improve solar cell performance by reducing Fresnel reflections and increasing light absorption (Das et al. 2011, Fadakar Masouleh et al. 2016) but are more complex and expensive than LSCs. Due to many loss mechanisms and less than ideal lifetimes of fluorescent materials, it has taken many years for LSC technology to reach commercialisation, with the first device coming on the market only this year, described as the 'Energy Harvesting Window'. This transparent device which is 1 m\textsuperscript{2}, produces 30 W of power at 3 % power conversion efficiency, is most likely based on a scattering layer sandwiched between glass (Alghamedi et al. 2014).

2.1.2 Thermodynamics of Luminescent Solar Concentrators

Luminescent solar concentrators are able to concentrate diffuse light because of the mechanisms involved in capturing the light within the waveguide, namely the down conversion of photons by fluorescent molecules. From the second law of thermodynamics and quantum mechanics (Yablonovitch 1980, Smestad et al. 1990, Winston et al. 2009) derived a limit to the concentration of light possible by LSCs,
the approximation of which is given below in Equation (2.1): \[
CR_{max} \approx \frac{e_3}{e_1} \exp\left(\frac{e_1 - e_2}{kT_0}\right) \tag{2.1}
\]

Where \(e_1\) is the energy of an incoming photon, \(e_2\) is the energy of the emitted photon and the difference between the two is the Stokes shift, \(k\) is Boltzmann’s constant and \(T_0\) is the ambient temperature.

The Stokes shift is defined as the difference in wavelength energy between the absorbed and emitted photon. For characterising the fluorescent material, it is defined as the difference between the wavelengths at the maximum of the absorption spectrum and the maximum of the emission spectrum as shown in Figure 2.2. Indeed the Stokes shift determines the theoretical maximum concentration possible. Substituting organic dye Lumogen Red 300 values into Equation (2.1) gives a \(C_{max} \approx 102\) and for the newer Lumogen Red 305, a \(C_{max} \approx 152\).

While \(C_{max}\) provides the upper limit of concentration of light possible, the actual concentration ratio of an LSC is often described as shown in Equation (2.2): \[
CR = G \eta_{opt} \tag{2.2}
\]

Where \(G\) is the geometric gain of the LSC and \(\eta_{opt}\) is the optical efficiency of the device that currently limits achievable concentration ratios [Giebink, 2012].
To approach the thermodynamic limit various losses will need to be reduced. Work being undertaken in this direction includes the use of photonic structures that act as much as possible, as omni-directional spectral band stop filters to reduce the large escape cone losses (Bronstein et al. 2015, Rau et al. 2005, Xu et al. 2016), the aligning of fluorophores to reduce escape losses (MacQueen et al. 2010) and the development of high Stokes shift materials such as organic dye based (Sanguineti et al. 2013), quantum dot based (Li et al. 2015) and lanthanide and europium based fluorophores (Correia et al. 2014, Reisfeld et al. 1983).

### 2.1.3 Efficiency of a Luminescent Solar Concentrator

The optical efficiency of a luminescent solar concentrator, that is the ratio of photons absorbed at the receiving top face divided by the photons that reach the sides prior to collection with solar cells, $\eta_{opt}$, is commonly described by Equation 2.3 (Debije & Verbunt 2012, Zastrow 1994). A detailed understanding of the different losses is necessary to be able to optimise the design of an LSC.

$$\eta_{opt} = (1 - R) P_{TIR} \eta_{abs} \eta_{PLQY} \eta_{stokes} \eta_{host} \eta_{TIR} \eta_{self} \quad (2.3)$$

$R = \frac{(n-1)^2}{(n+2)^2} = \text{Reflection loss at air/waveguide interface is determined by } n, \text{ the refractive index of the material and is around } 4\% \text{ for PMMA.}$

$P_{TIR} = \sqrt{1 - \frac{1}{n^2}} = \text{Total internal reflection efficiency is the percentage of captured photons that are totally internally reflected. Determined by } n, \text{ the refractive index of the waveguide.}$

$\eta_{abs} = \text{Absorption efficiency of luminescent material with respect to the solar spectrum. This is the percentage of the solar spectrum that the fluorescent material can absorb as shown in Figure 2.3.}$

$\eta_{PLQY} = \text{Photoluminescent quantum yield (PLQY) of the fluorescent material is defined as the probability an absorbed photon will be emitted.}$

$\eta_{stokes} = \text{Every time an absorption and emissions event occurs some energy is lost as heat.}$

$\eta_{host} = \text{Losses caused by scattering or absorption by the host material.}$
$\eta_{TIR} =$ Efficiency of light guiding by total internal reflection. If there are imperfections on the waveguide surface then photons that are undergoing total internal reflection can be lost.

$\eta_{self} =$ Efficiency related to the Stokes shift of the fluorescent species. Emission and absorption spectra overlap contributes to re-absorption losses. This is one of the largest losses in LSCs along with $P_{TIR}$.

The different losses can be broken down into either properties of the waveguide or the fluorescent material as summarised in Table 2.1. Several are related to the refractive index of the waveguide and by increasing the refractive index, losses can be reduced (however Fresnel reflection losses will increase, but not as much). Cheap readily available transparent polymers have a narrow range of refractive indices between 1.3 and 1.7. However there is work being done for example with nano-composites such TiO$_2$ that can achieve refractive indices between 2.4 and 2.7 whilst maintaining transparency (Tao et al. 2011, Maeda et al. 2016). Advanced waveguides can also be chosen that act as antennae to assist with propagating of photons to the edge of the device (Gutierrez et al. 2015).

![Figure 2.3: Lumogen Red 305 dye absorption (red) overlaid with the AM 1.5 solar spectrum (gray). This small percentage of the solar spectrum that can be absorbed is one reason why the LSC power conversion efficiency is low.](image)
CHAPTER 2. REVIEW OF THE LITERATURE

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<th>Property of Fluorescent Material</th>
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<td>$\eta_{\text{host}}$ – Losses due to absorption and scattering in the waveguide can be reduced by choosing good quality waveguides e.g without air bubbles and by choosing waveguides that are transparent in the required region.</td>
<td>$\eta_{\text{abs}}$ – Fraction of solar spectrum absorbed by dye can be increased by using multiple fluorescent species or stacking LSCs. Although the world record LSC is still with a single plate of two dyes, see Table 2.3.</td>
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<td>$\eta_{\text{TIR}}$ – Fraction of light trapped by TIR can be increased by using a higher refractive index waveguide.</td>
<td>$\eta_{\text{PLQY}}$ – Critical property of the fluorescent material, it needs to be as high as possible, for Lumogen Red 305 $\approx 1$.</td>
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<td>$\eta_{\text{TIR}}$ – Surface roughness needs to be minimised to avoid loss of TIR photons. This can be done by polishing the waveguide.</td>
<td>$\eta_{\text{self}}$ – Losses due to re-absorption events affect the size of the device. A larger device with longer photon pathlengths will have higher losses hence it is critical to maximise the Stokes shift.</td>
</tr>
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<td>$\text{R}$ – Reflection of light at surface could be reduced by utilising an anti-reflective coating.</td>
<td>$\eta_{\text{stokes}}$ – Unavoidable heat generation due to down conversion of photons in Stokes shift fluorescence process.</td>
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Table 2.1: Breakdown of LSC losses as either a property of the waveguide or fluorescent material.

Most losses occur due to photons that are re-emitted within the waveguide material at an angle that does not result in total internal reflection. This is exacerbated if there is a large overlap between absorption and emission (low Stokes shift) as each re-absorption event increases the chances of a photon escaping the waveguide due to isotropic emission by the fluorescent molecule.

For a material such as PMMA with a refractive index of approximately 1.5 this results in around 25% of photons lost through the escape cone. However the loss of 25% occurs after each absorption and emission event so losses can be considerably higher particularly for geometrically larger designs (Goldschmidt et al., 2009). Each re-absorption event also has a chance of losing a photon non-radiatively due to a non-unity photoluminescent quantum yield. Hence it is critical to reduce the overlap between absorption and emission, i.e. maximise the Stokes shift. The development of new fluorescent materials is not in the scope of this thesis however selecting appropriate dyes is.
2.1.4 Choosing a Fluorescent Material

Organic Dyes

As the driving force of the luminescent solar concentrator, properties of the fluorescent species need to be carefully considered to minimise losses. An ideal fluorescent species would have the following properties:

- Broad spectral absorption – To capture as much as possible the broad solar source.
- A large Stoke shift – The overlap between absorption and emission spectra of the fluorescent material needs to be minimised to reduce re-absorption losses and increases the maximum theoretical concentration ratio possible.
- A high photoluminescent quantum yield (PLQY) – The efficiency of the fluorescent material in emitting a photon after it has absorbed one should be as high as possible.
- Lifetime of material – For commercial applications the system needs to maintain a certain level of performance over many years.
- Solubility in a host waveguide – The luminescent material must soluble in a host waveguide with desirable optical and economic properties.

Organic dyes have been utilised in LSC research since the technologies inception due their excellent quantum yield, often approaching unity, and large absorption coefficients. Since the 1980s organic dyes have been developed particularly for use as solar energy collectors. The three most commonly used dyes have been the rhodamine, coumarin and perylene classes of molecules (Debije & Verbunt 2012). Research has recently started to converge on perylene dyes and their derivatives due to improved photostability and a very high quantum yield that greatly surpasses that of the coumarins and rhodamines (Griffini et al. 2013, Wilson & Richards 2009).

Current state of the art perylene organic dyes are the Lumogen® series manufactured by BASF. However, a main disadvantage of these and other organic dyes is their limited lifetime under illumination, particularly when compared with the lifetime of solar PV cells (≈ 20 years). When exposed to light for a significant length of time, absorption intensity decreases as fluorescence is quenched. This has been shown by Sark et al. (2008), reproduced in Figure 2.4. The authors undertook an experiment where an LSC plate doped with Lumogen Red 305 was attached to a solar cell and the short circuit current measured at various intervals both under a sulphur lamp (roughly 1/3 sun intensity in the spectral range of the dye) and outdoors. Both the
sample that was kept outdoors and the sample subject to light from the sulphur lamp showed a 20 % decrease in short circuit current after 300 days, a significant amount, whilst the reference plate (stored in the dark), varied little. Interestingly the authors suggest that widely reported differences in degradation rates of organic dyes in polymer matrices are due to factors such as the amounts of monomer, initiator, stabiliser and other additives still present in the waveguide.

Figure 2.4: LSC photo-degradation shown in blue as a decrease of approximately 20 % in short circuit current after 300 days of outdoor testing, testing under a sulfur lamp (red) as well as reference (black). Reproduced from Sark et al. (2008).

Organic dyes have been the material of choice in luminescent solar concentrators for almost 30 years due to their high quantum yield, the ability to combine several dyes for increased spectral absorbance and their ease of incorporation into polymers. Indeed the world record 7.1 % power conversion efficiency LSC used Lumogen dyes. However, their main drawback has been their degradation under illumination, preventing the commercialisation of an organic dye based device but advances in the chemistry of dyes are still occurring and one group has recently discovered a perylene derivative with a high Stoke shift and improved photochemical stability (Sanguineti et al. 2013).

Quantum Dots

Quantum dots (QD) are semi-conducting nanocrystals that exhibit size dependant optical properties due to quantum confinement effects. The most studied QDs come from groups II and IV of the periodic table such as: CdSe, Cds, ZnS and PbS. They can be excited by any photon with energy greater than their bandgap and this bandgap can be tuned by adjusting particle size and concomitantly the wavelength of the emitted light. Quantum dots are now used widely in a variety of solar energy
CHAPTER 2. REVIEW OF THE LITERATURE

harvesting technologies, for example thin film windows and mesoporous TiO\(_2\) based solar cells (Oliva et al. 2003 Samadpour 2017). Recently, they have started to emerge as the fluorophore of choice for LSCs primarily due to their high photostability under illumination (Resch-Genger et al. 2008 Hyldahl et al. 2009), much improved quantum yield and broad excitation spectra. Furthermore the Stokes shift of QDs can be very large as shown in Figure 2.5, reproduced from Krumer et al. (2013), that compares the absorption/emission spectra of various dyes, type I and type II quantum dots. Key studies related to QD LSCs are discussed below and are summarised in Table 2.4 at the end of this section.

Quantum dot based luminescent concentrators were first described theoretically by (Barnham et al. 2000) and then (Chatten 2003) who then further expanded on the theoretical thermodynamic model, following up with the first experimental work with (Chatten et al. 2004). The authors used CdSe/CdS quantum dots embedded in an acrylic waveguide with a quantum yield of 0.5, much less than the 0.95 values of the Lumogen LSCs that were used as references in the study. Organic dye plates and the QD plate were then connected to a PV cell and the short circuit current was measured. The organic dye plates outperformed the quantum dot LSC, however results were of the same order of magnitude. The low quantum yield of the QD has long been a disadvantage for their use in solar concentrators. Reasons suggested for this property include poor passivation (reacts too much with external environment), surface disorder and surface degradation that emerge during different growth stages.

Since their initial investigation for use in solar concentrators, the achievable quantum yield has markedly increased, as methods of fabricating the QD have been improved, and quantum yields of 0.9 can now readily be achieved (Boldt et al. 2013). Recently several studies have shown improved ‘engineered Stokes shift’ QD based LSCs (Krummer et al. 2013 Coropceanu & Bawendi 2014 Meinardi et al. 2014a Bradshaw et al. 2015 Coropceanu et al. 2016) that suppress re-absorption events and losses by fabricating large Stokes shift multi-shell giant quantum dots. However these were still fabricated with CdS/CdSe or similar quantum dots. Although these dots can be fabricated with very high quantum yield and wide absorption band, their emission spectrum lies around 600 nm which is not the optimal band for silicon solar cells and they are fabricated from toxic heavy metal cadmium.

Recent work on copper, indium, selenide and sulfide, CuInSe\(_{x}\)S\(_{2-x}\) quantum dots has shown very promising results and the first to report utilising them for sunlight energy harvesting was (Mcdaniel et al. 2014) then followed by detailed work by (Meinardi et al. 2015) and (Knowles et al. 2015). CuInSe\(_{x}\)S\(_{2-x}\) dots are free from toxic elements such as cadmium and have proven to be better matched to silicon PV cells with
emission tuned to around 1000 nm plus very broad absorption well into the visible region (which is the peak of the solar spectrum). Utilising CuInSe$_x$S$_{2-x}$ quantum dots, Meinardi et al. (2015) reported a quantum yield of 40 % but Knowles et al. (2015) managed to get it up to 86 %. Recently indirect bandgap silicon quantum dots have been shown to be a promising material for flexible LSCs (Meinardi et al. 2017). Silicon is promising, particularly for mass produced commercialised LSCs due to its low-cost, non-toxicity and ultra abundance. The authors reported a quantum yield of 46 % with a device power conversion efficiency of 2.85 %.

The current world record QD LSC is held by (Waldron et al. 2017), based on PbSe dots with a greater than 70 % quantum yield. These lead selenide particles have a good Stokes shift and highlight the importance of a high quantum yield for device performance. The power conversion efficiency (utilising silicon solar PV cells) measured was 4.74 % close to the maximum obtained with organic dyes and silicon PV cells (4.92 %).

Figure 2.5: Comparison of different absorption/emission spectra and Stokes shifts, reproduced from Krumer et al. (2013). Top left figure shows Type I CdSe QD, bottom left shows Type II CdTe/CdSe/ZnS core/multishell QD with excellent Stokes shift, top right shows Rhodamine 6G organic dye, bottom right shows Lumogen Orange.
2.1.5 Waveguide Considerations

A waveguide material is required to host the fluorescent species and operate as medium for the propagation of photons via total internal reflection. For these reasons the optical properties of the waveguide are important to the overall performance of the luminescent solar concentrator. Figure 2.6 shows the refractive index of various polymers and glasses. A good experimental comparison of various polymers was completed by (Zettl et al. 2017). The larger the refractive index, the more photons that can be captured within the waveguide and be totally internally reflected to the edges. However, a higher refractive index material will also have slightly higher Fresnel reflection losses at the air/waveguide boundary.

![Figure 2.6: Refractive index of various materials, reproduced from (Miller 2011). Polycarbonate (PC) has the highest refractive index whilst PDMS has the lowest.](image)

An interesting study was completed by (Kastelijn et al. 2009) that compared five different waveguide materials: PMMA, quartz, B270 glass, polycarbonate I and polycarbonate II. Samples were coated with a layer of Lumogen Red 305 and then illuminated with 300 W. The light emitted from all four edges of the waveguides was captured by an integrating sphere. The authors found that there was not a large difference in performance of PMMA, glass and polycarbonate I (however it is likely that for thicker samples with higher absorption path length the difference would become more pronounced). So when choosing a waveguide other factors such as economics or ease of fabrication could play a more important role.
2.1.6 Improving LSC Performance

Several design considerations need to be made that can significantly improve the performance of a luminescent solar concentrator. The first key point that emerges is the need for a white diffuse reflector beneath the LSC plate. The purpose of this reflector is to scatter photons back into the plate to give them a second chance at absorption. A white diffuse reflector scatters light at random angles and this is necessary so that the photons do not simply return back through the plate by the same path they entered (Slooff et al. 2006, Wang et al. 2011). Secondly the solar cell attached to an LSC needs to be somehow optically coupled to the device and ways of doing this include using a thermal polyurethane film such as Krystal flex or silicone optical coupling gel (Farrell et al. 2010, Mansour et al. 2002).

2.1.7 The Geometry of an LSC

The geometry of the LSC device has generally been that of a square shape with uniform thickness. The geometric concentration ratio is defined as $G$ and is equal to $A_{\text{top}}/A_{\text{sides}}$ where $A_{\text{top}}$ is the large face that receives incoming radiation and $A_{\text{sides}}$ is the area of the edge of the device, as shown in Figure 2.7. The sides have a smaller area than the top leading to a concentration of solar flux (W/m$^2$).

![Figure 2.7: LSC geometric gain defined as the ratio of the top area to the area of the sides.](image)

An increase in geometric gain can be achieved by attaching mirrors to three sides and have light exiting from just one side, however this does not necessarily improve the efficiency of the device. This is due to the relationship between the distance a photon has to travel and chances of incurring losses. If a photon has to be reflected from a various edges before it reaches the collector edge, the efficiency of the device will decrease due to increased probability that the photon will be lost because of an increased chance of re-absorption due to increased path length. A good example of this is given by (Slooff et al. 2008) where on one device they attached a single GaAs solar cell achieving a geometric gain of 10 but a power conversion efficiency of 4.6 %. On a second device they attached four GaAs cells, achieving a geometric gain of 2.5 but a much larger power conversion efficiency of 7.1 %.
Several groups have attempted to increase LSC performance by optimising the geometry of the device. The first such paper by (Goetzberger & Greubel 1977) argued that the optimal shape would be a triangle with only two reflecting sides, thereby minimising losses incurred from additional reflections. This paper provided the theoretical groundwork for investigating this particular geometry but no research has been published pertaining to any experimental results with this configuration.

The next paper to discuss the effects of geometry on efficiency presented a Monte-Carlo simulation that the authors claim confirmed that efficiency is relatively independent of collector geometry (Loh & Scalapino 1986). They confirmed that LSC performance was insensitive to geometry due the equation of efficiency as a function of mean free path being almost identical for various geometries investigated.

Interestingly, (Markman et al. 2012) suggests combining non-imaging optics with the LSC concentrator by simply tapering the edges of the device to form a compound parabolic concentrator shape. In this way using ray-tracing the authors showed that the concentration ratio can be increased by up to 34 % whilst also maintaining > 90 % of the original optical efficiency. This was achieved by changing the shape of the mould of the device. Finally it has been established, using ray-tracing that device geometry does not influence performance a large amount (in two dimensions), in terms of re-absorption probability, although the triangle geometry did perform better overall (Meyer et al. 2009).

A geometry that has been shown to have increased totally internally reflected photons is the bent and cylindrical shape. A theoretical study completed by (McIntosh et al. 2007) showed that when luminescence occurs close to the surface of a cylindrical shaped LSC, the optical concentration can be up to 1.9 higher when compared with a square planar geometry. This was a nice theoretical result but practically difficult to implement due to the requirement of having to place solar cells somewhere on the device. The cylindrical shape, also known as a fiber geometry was investigated theoretically by (Edelenbosch et al. 2013) whose work also showed high concentrations can be achieved with this geometry.

Similarly (Vishwanathan et al. 2015) completed an experimental study and simulations comparing the flat square planar geometry and a bent geometry with an idea that this geometry can be useful for example to wrap around a lighting pole. Using simulations, the authors found the bent shape performed better when comparing conversion efficiencies. It is expected that this shape would perform better than the conventional planar geometry outdoors and in the urban environment due to its reduced sensitivity to angular dependence of incoming light and would work on cloudy as well as sunny days.
2.1.8 Power Conversion and Solar Cell Choice

To convert captured photons to electricity a solar photovoltaic cell, or a combination of solar cell and reflecting mirrors are placed around the edges of the waveguide. The overall device efficiency also known as power conversion efficiency (PCE) of the LSC is given by the product of the optical efficiency and the efficiency of the solar cells attached to the edges, as shown in Equation 2.4.

\[ \eta_{PCE} = \eta_{opt} \cdot \eta_{solarCell} \]  

(2.4)

The highest reported power conversion efficiency of any LSC is 7.1 % (Slooff et al. 2008), achieved with gallium arsenide solar PV cells. Gallium arsenide cells have high efficiencies up to 28 % and a large bandgap of 1.52 eV, however they are very expensive and not practical for real world devices. The highest PCE using silicon PV cells is a certified 4.92 % (Chou et al. 2015), overtaking the previous 4.2 % (Desmet et al. 2012). Silicon solar cells come in various types, such as mono-crystalline and poly-crystalline and have efficiencies up to 24 %. In this thesis two types of silicon solar cells are used the 'SLIVER' solar cell that is bifacial (Blakers et al. 2006), meaning it can be illuminated from both sides and high efficiency Sunpower back contact cell. The spectral response of a silicon PV cell is shown below in Figure 2.8 overlaid with the AM 1.5 spectrum it can be seen how down converting the visible region of the solar spectrum to longer wavelengths has a higher chance of conversion.

![Figure 2.8: AM 1.5 solar spectrum in gray overlaid with the spectral response of a silicon solar PV cell, the spectral response is a ratio of current generated by cell to power input into cell. The peak of the orange curve is where photons are most efficiently converted and this is offset from the peak of the solar spectrum.](image)
Sunpower back contact high efficiency solar cells

Most solar cells have bus bars running along both front and back of the cell to collect electricity. Sunpower have developed unique back contact cells as shown in Figure 2.9a (Mulligan et al. 2004). These back contact cells are particularly well suited to LSC applications as the front face is coupled directly onto the device and no shading occurs (they are readily available for purchasing on Ebay). Sunpower cells are also high efficiency, currently holding the world record for silicon solar photovoltaic modules at 24.1% (Kurtz et al. 2017).

Silicon SLIVER solar cells

Sliver cells are thin, flexible and bifacial mono-crystalline silicon solar cells. The unique technique used to fabricate these cells was developed at Australian National University (ANU) and first reported in (Stocks et al. 2003, Verlinden et al. 2006). It is claimed that SLIVER cells perform better at cell thicknesses less than 3mm because they minimise recombination losses at the edges of the cell. Conventional fabrication of silicon solar cells converts one wafer into a cell by treating the surfaces of the wafer. On the other hand, SLIVER cell fabrication produces hundreds if not thousands of small cells from one wafer. The development of these types of solar cells has led to devices that embed cells onto the front face of the LSC not just the waveguide edges (Yoon et al. 2008, 2011, Lee et al. 2014). Some SLIVER cells are shown in Figure 2.9b, the busbars are added manually after fabrication.

Characterising performance of solar cells

The current voltage or IV curve is used to describe the performance of solar cells and LSCs, an example curve taken from the data sheet of a Sunpower cell is shown in Figure 2.10. Solar cells are made of semi-conducting materials that create a current when illuminated with solar radiation. The current generated is proportional to the intensity of light and the wavelength of light. PV cells behave essentially as a current source parallel with a diode and therefore require a device (source measuring unit) that can both source and sink current to be able to obtain IV measurements. Without illumination the solar cell has the same characteristics as a diode and under illumination and the IV curve shifts as the cell is generating power. The convention is to draw the IV curve in the positive I and V regions.
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(a) SLIVER solar cells with attached busbars.

(b) Sunpower back contact cells

Figure 2.9: Silicon solar PV cells used in this thesis.

Figure 2.10: Sunpower IV characteristics (Taken from datasheet of a cell). The different lines show performance at various levels of illumination, also shown is $I_{sc}$ (short circuit current) the intersection with the current axis, $V_{oc}$ (open circuit voltage) the intersection with the voltage axis and $V_{mp}$ (the voltage at maximum power) on the black curve.
The following factors can be calculated from the forward bias illumination test (IV curve sweep).

- The open circuit voltage ($V_{oc}$)
- The short circuit current which is most often used as a metric for determining solar cell performance ($I_{sc}$)
- The maximum power point and its corresponding voltage and current at maximum power ($P_{max}$, $I_{mp}$, $V_{mp}$)
- The fill factor (FF) is a measure of the quality of the cell, it measures the ‘squareness’ of the IV curve by taking the ratio of $P_{max}$ and $P_t$ as shown in Figure 2.11 and Equation 2.5
- Solar cell efficiency is determined by comparing $P_{in}$ and $P_{max}$ (under one sun conditions) as shown in Equation 2.6

$$FF = \frac{P_{max}}{P_t} = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}}$$ (2.5)

$$\eta_{Solar\ Cell} = \frac{P_{max}}{P_{in}}$$ (2.6)

![IV curve diagram](image)

**Figure 2.11:** An example IV curve is shown in green (taken from Chapter 7). Shown in orange is the rectangle made with $I_{sc}$ and $V_{oc}$ and in blue is the rectangle made by the voltage and current at maximum power. The ratio of these two rectangles is the fill factor.
2.1.9 Current State of the Art

Lumogen Red 305 is a perylene based red organic dye manufactured by BASF, it is used throughout this thesis. Unfortunately there is often confusion with the previous version Lumogen Red 300. The properties of Lumogen Red 305 and Lumogen Red 300 are summarised below in Table 2.2. The molecular weight for Lumogen Red 300 is known and reported however, for the newer Lumogen Red 305 BASF are not releasing the molecular weight and are only providing a range of bulk density values which makes some concentration and absorption coefficient calculations difficult. This leads to studies reporting concentrations of Lumogen Red 305 in LSCs in the unit parts per million (ppm) instead of grams per mol. Where grams per mol have been used there is either an error in the study or Lumogen Red 300 has been used. Table 2.3 summarises key organic dye based LSC literature and notes why they are important. Table 2.4 describe the current quantum dot LSC situation and notes of importance.

<table>
<thead>
<tr>
<th>Name</th>
<th>Bulk density</th>
<th>Molecular weight</th>
<th>$\lambda_{\text{abs, max}}$</th>
<th>$\lambda_{\text{em, max}}$</th>
<th>Stokes shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lumogen Red 300</td>
<td>1.4 g/cm$^3$</td>
<td>1078 g/mol</td>
<td>578 nm</td>
<td>613 nm</td>
<td>35 nm</td>
</tr>
<tr>
<td>(MSDS)</td>
<td></td>
<td>(Tanaka et al. 2006)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lumogen Red 305</td>
<td>2.2-4.5 g/cm$^3$</td>
<td>Unknown</td>
<td>576 nm</td>
<td>614 nm</td>
<td>38 nm</td>
</tr>
<tr>
<td>(MSDS)</td>
<td></td>
<td>(Dienel et al. 2010)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 2.2: Comparison of Lumogen Red 300 and Lumogen Red 305 properties.*
<table>
<thead>
<tr>
<th>Reference</th>
<th>Concentration</th>
<th>PCE</th>
<th>Optical Efficiency</th>
<th>Size</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Mansour et al. 2002)</td>
<td>Various</td>
<td>Not reported</td>
<td>Average 30 %</td>
<td>5 x 4 x 0.3 cm³</td>
<td>Outdoor testing</td>
</tr>
<tr>
<td>(Slooff et al. 2008)</td>
<td>LumRed305 0.01 %wt, and Yellow CRS040</td>
<td>7.1 %</td>
<td>Optical efficiency 24 %</td>
<td>5 x 5 x 0.5 cm³</td>
<td>World record LSC</td>
</tr>
<tr>
<td>(Sark et al. 2008)</td>
<td>LumRed305</td>
<td>2.5 %</td>
<td>Optical efficiency 13 %</td>
<td>Unreported</td>
<td>Good report of photodegradation</td>
</tr>
<tr>
<td>(Goldschmidt et al. 2009)</td>
<td>Unreported conc</td>
<td>6.7 %</td>
<td>Optical efficiency 43 %</td>
<td>2 x 2 x 0.3 cm³</td>
<td>Obtained high optical efficiency with band stop filter</td>
</tr>
<tr>
<td>(Desmet et al. 2012)</td>
<td>LumRed305 115 ppm, and Blue Perylene 75 ppm</td>
<td>4.2 % for stack</td>
<td>Optical efficiency 27.1 %</td>
<td>5 x 5 x 0.5 cm³</td>
<td></td>
</tr>
<tr>
<td>(Liu &amp; Li 2015)</td>
<td>Three dye LSC</td>
<td>1.4 %</td>
<td>EQE up to 30 % Solar cell efficiency 11.7 %</td>
<td>5 x 5 x 0.5 cm³</td>
<td></td>
</tr>
<tr>
<td>(Vishwanathan et al. 2015)</td>
<td>LumRed305 200 ppm</td>
<td>2.9 % straight, 2.4 % bent</td>
<td>Optical efficiency 19 % Solar cell efficiency 15 %</td>
<td>10 x 10 x 0.3 cm³</td>
<td>Compared flat and bent configurations</td>
</tr>
<tr>
<td>(Chou et al. 2015)</td>
<td>Coumarin C440 174.2 mg/L, Disodium fluorescein (DSF) 824.24 mg/L</td>
<td>4.92 % with stack of two</td>
<td>Optical efficiency 31.21 % Solar cell efficiency 15.8 %</td>
<td>5 x 5 x 0.5 cm³</td>
<td>World record silicon based LSC</td>
</tr>
<tr>
<td>(Tummeltshammer et al. 2016)</td>
<td>LumRed305 10 ppm - 150 ppm</td>
<td>Not reported</td>
<td>Investigates wavelength dependent optical efficiency</td>
<td>6 x 6 x 0.5 cm³</td>
<td></td>
</tr>
<tr>
<td>(Krumer et al. 2017)</td>
<td>LumRed305 4 ppm - 153 ppm</td>
<td>2.3 %</td>
<td>15.13 %</td>
<td>3.5 x 10 x 1 cm³</td>
<td>Liquid waveguide</td>
</tr>
</tbody>
</table>

Table 2.3: Key organic dye based studies in the literature
<table>
<thead>
<tr>
<th>Reference</th>
<th>Concentration</th>
<th>QY</th>
<th>Efficiency</th>
<th>Size</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chatten et al. 2004</td>
<td>CdSe/CdS, conc not reported</td>
<td>0.5</td>
<td>PCE 4 % with GaAs cells</td>
<td>4.2 x 1 x 0.5 cm³</td>
<td>First QD LSC experiments</td>
</tr>
<tr>
<td>Wang et al. 2010</td>
<td>CdSe/ZnS and 50 uM PbS</td>
<td>0.12</td>
<td>PCE 3.3 % with cells on all edges</td>
<td>4.5 x 1.2 x 0.4 cm³</td>
<td></td>
</tr>
<tr>
<td>Coropceanu &amp; Bawendi 2014</td>
<td>CdSe/CdS 20 %wt</td>
<td>0.4</td>
<td>Optical efficiency 10.2 %</td>
<td>21.5 x 1.3 x 28 cm³</td>
<td></td>
</tr>
<tr>
<td>Coropceanu &amp; Bawendi 2014</td>
<td>CdSe/CdS 0.5 %wt</td>
<td>0.86</td>
<td>Optical efficiency 48 % at 400 nm</td>
<td>2 x 2 x 0.2 cm³</td>
<td></td>
</tr>
<tr>
<td>Meinardi et al. 2014b</td>
<td>CdSe/CdS 0.05 %wt</td>
<td>.45</td>
<td>Optical efficiency 10.2 %</td>
<td>21.5 x 1.35 x 0.5 cm³</td>
<td></td>
</tr>
<tr>
<td>Meinardi et al. 2015</td>
<td>CuInSe coated with ZnS 0.5 %wt</td>
<td>.4</td>
<td>Optical efficiency 3.27 %</td>
<td>12 x 12 x 0.3 cm³</td>
<td></td>
</tr>
<tr>
<td>Knowles et al. 2015</td>
<td>CuInS₂/CdS 0.5 %wt</td>
<td>.86</td>
<td>Unreported</td>
<td>120 x 1 cm³ liquid waveguide</td>
<td>Well matched to solar spectrum</td>
</tr>
<tr>
<td>Zhou et al. 2016</td>
<td>CuInS₂/CdS 0.5 %wt</td>
<td>.4 - 0.5</td>
<td>Optical efficiency 6.1 %</td>
<td>5 x 1.5 x 0.3 cm³</td>
<td>Near IR QD</td>
</tr>
<tr>
<td>Zhao et al. 2016</td>
<td>CdSe/CdₓPb₁₋ₓS 0.5 %wt</td>
<td>.4</td>
<td>PCE 1.15 %</td>
<td>7 x 1.5 x 0.3 cm³</td>
<td></td>
</tr>
<tr>
<td>Meinardi et al. 2017</td>
<td>Si QD 0.09 %wt</td>
<td>.46</td>
<td>PCE 2.85 %</td>
<td>12 x 12 x 0.26 cm³</td>
<td>First to use silicon QD</td>
</tr>
<tr>
<td>Waldron et al. 2017</td>
<td>PbSe QD 12.7 uM</td>
<td>&gt; 0.7</td>
<td>PCE 4.74 %</td>
<td>2.1 x 2.1 x .49 cm³</td>
<td>Record QD performance</td>
</tr>
</tbody>
</table>

Table 2.4: Key quantum dot based studies in the literature
Conclusion

Luminescent solar concentrators have attracted attention in the literature for their beam splitting properties, the fluorescent materials inside the waveguide select via the absorption spectrum, a portion of the solar spectrum and then emitted photons are guided to solar cells. The waveguide can be highly transparent ensuring a significant part of the solar spectrum can be transmitted. This property makes LSCs suitable for building integrated applications such as windows or facades but it also makes the LSC suitable as a cover for a solar thermal collector, a novel application not previously investigated.

Organic dyes such as Lumogen Red 305 are considered state of the art (the world record LSC power conversion efficiency of 7.1 % uses Lumogen Red 305) and often used as a reference to estimate the performance of LSC devices, even though it is understood that for a commercialised product these dyes are not photostable enough.

Quantum dots have become the fluorescent molecule of choice but have faced their own challenges, some that have eventually been overcome. Low quantum yields have been improved, non-toxic alternatives have been discovered, broader absorption and near IR emission materials have emerged all in the last few years. The properties of quantum dots have been improved but it still remains necessary to develop methods to disperse them homogeneously inside polymers. It appears however, that in the near future we will gain the ability to engineer with precision the optical properties of quantum dots and polymers leading to much improved LSC technology performance.

Due to the narrow band of fluorophore absorption (no material can capture such a broad source as the sun), there is an opportunity to allow lost light to be captured by a non-imaging thermal absorber. In the next section the compound parabolic solar thermal collector literature review is presented.
2.2 Compound Parabolic Concentrator

2.2.1 Introduction

The compound parabolic concentrator was developed by Roland Winston when he was investigating means of efficiently detecting Cherenkov radiation (Hinterberger 1966). Described as an ideal light collector after it was realised that such a design, shown in Figure 2.12, improved collection compared with conventional image-forming systems (Winston & Avenue 1988, Smestad et al. 1990). The discovery of the CPC led to the development of the field of non-imaging optics, whose designs approach and even realise the maximum concentration allowable for a given acceptance angle, due to removing the need for point to point mapping required by conventional optics (Winston 1970, Rabl 1976, Winston & Welford 1978, Dickinson & Cheremisinoff 1980, Winston et al. 2009).

The CPC ideally concentrates all rays that fall within its acceptance half angle, $\theta_A$. The acceptance angle will determine the hours of light that can be collected as CPC designs are almost always non-tracking. The concentration ratio $C$ of a two-dimensional CPC is determined by the ratio of the aperture area to the area of the receiver and gives the amount of increase of solar flux on the receiver. $C$ is inversely related to the acceptance angle and this means we can achieve higher concentration ratios but at the expense of hours of daylight that can be collected. A flat absorber, the initial CPC design, shown in Figure 2.12, has the concentration ratio shown in Equation (2.7), where $d_1$ is the length of the entrance aperture, $d_2$ is the length of the absorber.

$$\text{Concentration Ratio} = \frac{1}{\sin(\theta_A)} = \frac{d_1}{d_2}$$

(2.7)

The CPC can be designed in three-dimensions or trough like in two-dimensions, with arbitrary shaped receivers such as flat, fin, wedge or circular (Rabl et al. 1979). The technology has now been applied to a wide variety of fields, for example: solar water disinfection (Vidal et al. 1999, Nalwanga et al. 2014), solar cooling (Winston, Widyolar & Jiang 2014) and methanol reforming (Gu, Taylor, Morrison & Rosengarten 2014).

The two-dimensional involute shaped CPC also known as a CPC with a cylindrical absorber was first described by (Winston & Hinterberger 1975) and is shown in Figure 2.13. This shape is of particular interest for thermal applications where an evacuated tube can be placed along the focal length of the CPC. A major benefit of
using CPCs for collecting thermal energy is that high temperatures, greater than 300°C can be achieved efficiently without tracking (Li, Su, Pei, Yu, Ji & Riffat 2013, Winston, Jiang & Widyolar 2014), resulting in reduced complexity and lower costs of CPC based designs. The involute shaped CPC design principles will be discussed in more detail later in this Chapter.

Along with thermal applications, CPCs can be utilised for electricity generation either by concentrating light directly onto a solar photovoltaic cell (Winston 1975, Tripanagnostopoulos et al. 2000, Gallagher et al. 2002, Schuetz et al. 2012, Li et al. 2016, Jaaz et al. 2017), or onto a thermoelectric device that uses heat to create electricity at low efficiencies (Mgbemene et al. 2010, Lertsatitthanakorn et al. 2013). These were important applications of CPCs, particularly when photovoltaic cells were expensive and by concentrating light, a smaller area of photovoltaic cells was required, however, there remained the constant problem of the CPC providing non-uniform irradiance onto the cells, something the photovoltaic cells particularly don’t like (Baig et al. 2012). As the CPCs in this thesis will only be used for collecting thermal energy, only thermal related designs will be reviewed.

Figure 2.12: Compound parabolic concentrator designed with a flat absorber ($d_2$), entrance aperture ($d_1$) and acceptance half angle $\theta_A$. 

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2.2.2 Studies in the Literature

By 1979, the key design principles and practical aspects of compound parabolic concentrators had been laid out (Rabl et al. 1979). While the optical efficiency for a given design (discussed later on in this Chapter) is dependent on the properties of the materials chosen, thermal performance depends additionally on the configuration of the reflecting walls and receiver.

When considering different designs for thermal applications, it is possible to find some designs that have neither the collector nor the absorber evacuated (Rabl 1976a, Rabl et al. 1980, Carvalho et al. 1987, Fraidenraich et al. 1999). A detailed numerical and experimental work in this configuration was completed by (González et al. 2011). The authors found good correlation between their experimental and theoretical results however with this configuration the highest temperature achieved with their collector was only 70°C, well below the temperatures achievable by a flat plate collector.

To achieve higher temperatures it is necessary to reduce convective heat loss from the absorber and a common approach to achieve this is by simply placing an evacuated tube along the focal length of the CPC, with this type of configuration often referred to as the external CPC (XCPC) (Oommen & Jayaraman 2001, Winston, Jiang & Widyolar 2014, Liu et al. 2014, Wang, Li & Liu 2015, Winston & Jiang 2015, Acuna et al. 2016). One detailed experimental study of such a setup was completed by (Li, Dai, Li & Wang 2013) who found that 3 x concentration ratio design can obtain a 40 % thermal efficiency at 200°C.

To reduce convective heat loss and remove the need for a gap necessary to accommodate an evacuated tube (at the cost of increased manufacturing complexity), it is possible to encase the combination of absorber and reflecting mirrors inside a vacuum, called the internal CPC or ICPC. The first to place the entire CPC within an evacuated tube was (Buehl & Works 1980) who also performed some of the earliest ray-tracing to investigate absorbance and optical efficiency at different angles of incidence, then followed closely by (O’Gallagher et al. 1982) who fabricated a prototype and showed the thermal efficiency remained at around 40 % from ambient to nearly 300°C. The same authors then undertook an economic analysis of an ICPCs collector finding the ICPC design superior to other designs in the market at that time (Gallagher et al. 1993). Another detailed experimental work utilising ICPCs was completed by (Snail et al. 1984), who constructed a test panel with 45 tubes and obtained a thermal efficiency, with oil as the working fluid, of 46 % at 200°C. A comparison study was completed by (Brunold et al. 1994) who compared three different non-tracking thermal collectors, the evacuated tube, the ICPC and a flat plate collector. The
authors found that for temperatures above 150°C the ICPC collector performed best. A similar comparison was completed by (Carvalho et al. 1995) who compared an un-evacuated CPC set up with a flat plate collector and evacuated tube collector. In this case the CPC was found to outperform the others up to 100°C, suggesting that a CPC collector can be designed to be superior to other collectors across a wide temperature range.

Even higher temperatures have been achieved with non-tracking CPCs. For example (Gu, Taylor & Rosengarten 2014) introduced the idea of utilising CPCs for methanol reforming, a process requiring temperatures in the range of 250°C to 350°C and indeed their proposed design achieved the desired temperatures at efficiencies of between 65 % and 70 %, in this set up a vacuum between the CPC and glass cover reduced convective heat loss.

Another important applications of CPCs is for coupling with solar cooling absorption or adsorption cycles. This combination makes sense as the requirement for air-conditioned cool air often coincides with peak solar output. Indeed Prof. Roland Winston has pursued this as one of the main applications of CPCs deploying such a system in Mongolia (Winston, Widyolar & Jiang 2014), where remarkably the CPCs were able to record a maximum temperature of 310°C when the ambient temperature was -10°C.

Other recent work has demonstrated the suitability of CPCs for solar cooling applications such as: (Winston, Jiang & Widyolar 2014, Winston & Jiang 2015) who demonstrated a working prototype of their 53.5 m² of XCPCs coupled with a 23 kW absorption cooling double effect chiller. The CPC array provided temperatures between 160°C - 200°C with an average daily efficiency of 37 % that ran the chiller successfully. It is evident that the CPC can be used to collect thermal energy for a variety of different temperature ranges and applications, without requiring tracking and can withstand harsh conditions. The rest of this part of the review will discuss various aspects and literature related to designing an involute shaped CPC.
2.2.3 Ideal Involute Design

A two-dimensional CPC can be considered as trough like and this shape is ideal for thermal applications where a cylindrical receiver can be placed along the focal length of the collector. A cross sectional view is shown in Figure 2.13. An involute shape CPC with an entrance aperture \( d_1 \) and receiver radius \( r \) has the geometric concentration ratio as shown in Equation 2.8. \( \theta_A \) is the acceptance half angle and ideally all incident rays at and below this angle will be transmitted to the receiver.

![Figure 2.13: Cross sectional view of 2D CPC with involute shaped absorber.](image)

Concentration Ratio = \( \frac{1}{\sin(\theta_A)} = \frac{d_1}{2\pi r} \)  

Equation 2.8

The parametric equations used to describe the involute CPC are broken down into two sections (Mcintire 1979). The involute section of the profile is described by Equations 2.9 and 2.11.

\[ 0 \leq |\theta_A| \leq \theta_A + \frac{\pi}{2} \]  

Equation 2.9

\[ p(\theta) = r \theta \]  

Equation 2.11
The remainder is the parabolic profile is described by Equations 2.10 and 2.11:

\[ \theta_A + \frac{\pi}{2} \leq |\theta_A| \leq \theta_A + \frac{3\pi}{2} \]  

\[ p(\theta) = \frac{\theta + \theta_A + \frac{\pi}{2} - \cos(\theta - \theta_A)}{1 + \sin(\theta - \theta_A)} \]  

Equation 2.10

The points x,y that plot the involute CPC are shown in Equation 2.11:

\[ x = r \sin(\theta) - p(\theta) \cos(\theta) \]  

\[ y = -r \cos(\theta) - p(\theta) \sin(\theta) \]  

Equation 2.11

Where \( p(\theta) \) is the distance of the line tangent from the absorber to the reflector, \( r \) is the radius of the receiver and \( \theta_A \) is acceptance half angle of the CPC.

2.2.4 Involute Shape With Gap Loss

In the ideal involute case the absorber touches the reflector profile at the cusp, however this is not desirable as the reflecting walls then acts like an efficient cooling fin. Additionally, to include an evacuated tube along the focal length of the CPC there will be a necessary gap between the glass, absorber material and reflecting walls. Incorporating this gap leads to optical losses in the system as light that would have otherwise reached the receiver escapes through the gap. An equation to estimate the gap loss has been suggested by Hsieh (1981), shown in Equation 2.12, where \( l_g \) is the gap clearance and \( r_{ro} \) is the radius of the receivers outer diameter.

\[ p = 1 - \frac{l_g}{2\pi r_{ro}} \]  

Equation 2.12

Attempts to deal with the gap loss included design with a V-groove (Mcintire 1980, Oommen & Jayaraman 2002) or over sizing the absorber (Rabl et al. 1979) however, these were shown to lead to a large loss of flux. Instead a design method was proposed that maintained the ideal flux concentration at the expense of over sizing the reflectors (Winston 1978). Equations to describe the involute CPC with a gap loss can be split into in the same way as the ideal case. This design is based on
designing for a virtual receiver which results in a slightly over sized reflector as shown in Figure 2.14. The following equations were modified from (Kim et al. 2013) and a similar approach but with some slight errors was used by (Oommen & Jayaraman 2001). To the best of our knowledge these correct versions have not been reported.

Figure 2.14: Cross sectional view of 2D CPC with involute shaped receiver showing the gap, $l_g$, necessary to avoid the absorber touching reflector profile.

The involute section is described by Equations 2.13 and 2.15:

$$0 \leq |\theta_A| \leq \theta_A + \frac{\pi}{2}$$

$$\theta_m = \cos^{-1}\left(\frac{r}{r + l_g}\right)$$

$$p(\theta) = (r + l_g)\sin(\theta_m) + r(\theta - \theta_m)$$

Where $r$ equals the radius of the absorber and $l_g$ equals the gap between cusp and receiver. The remainder of the parabolic profile can be described with Equations 2.14 and 2.15:

$$\theta_A + \frac{\pi}{2} \leq |\theta_A| \leq \theta_A + \frac{3\pi}{2}$$

$$p(\theta) = \frac{r(\theta_A + \frac{\pi}{2} + \theta - 2\theta_m + 2\tan(\theta_m) - \cos(\theta - \theta_A))}{1 + \sin(\theta - \theta_A)}$$

The points $x, y$ of the involute CPC with gap clearance are shown in Equation 2.15:

$$x = r\sin(\theta) - p(\theta)\cos(\theta)$$

$$y = -r\cos(\theta) - p(\theta)\sin(\theta)$$
2.2.5 Truncation of CPC Height

Often it is useful to truncate the height of a CPC as the top section of the reflector profile contributes little to the collection of light, so the amount of reflector material can be reduced resulting in some cost savings. Early investigations of the effects of truncation were completed by [Rabl 1976, McIntire 1979, Carvalho et al. 1985] and the analytical expressions for truncation of the involute shaped CPC was derived by [Baum & Gordon 1985]. It was shown by [Muschaweck et al. 2000] that the utilisable energy of a CPC collector is almost independent of the degree of truncation, as the gain in concentration makes up for the decrease in diffuse irradiance captured. Table 2.5 below summarises the degree of truncation in various studies reported in the literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Truncation (h/hmax)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Prapas et al. 1987)</td>
<td>0.3</td>
</tr>
<tr>
<td>(Ronnelid &amp; Karlsson 1997)</td>
<td>0.4</td>
</tr>
<tr>
<td>(Buttinger et al. 2010)</td>
<td>0.4</td>
</tr>
<tr>
<td>(Kim et al. 2013)</td>
<td>0.2</td>
</tr>
<tr>
<td>(Baig et al. 2014)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Table 2.5: Examples of CPC height truncation in the literature.*

2.2.6 Optical efficiency and the Incidence Angle Modifier

The optical performance of thermal collectors is determined by the optical efficiency at normal incidence $\eta_{opt}$ and the incidence angle modifier (IAM) or $K(\theta)$, where $\theta$ is the angle between the collector normal and the incident sun ray vector. The optical efficiency of a CPC without a glass cover is given by Equation 2.16.

$$\eta_{opt} = \rho^{<N>} \tau \alpha$$  \hspace{1cm} (2.16)

N is the number of reflections (a function of the acceptance angle), $\rho$ is the reflectivity of the CPC mirrors and $\tau \alpha$ is the absorption/transmittance product of the receiver at normal incidence. To maximise the optical efficiency it is critical to maximise the reflectivity of the mirrors and the absorbance at the receiver [Rabl & Winston 1976, Rabl et al. 1980, Carvalho et al. 1985].
The incidence angle modifier $K(\theta)$ takes into account the change in optical efficiency as the angle of incidence of light varies due to the sun’s apparent motion through the sky. This includes the angular variation of: absorbance of the absorber, gap losses due to a necessary gap between absorber and glass envelope, the average number of reflections and the angular dependence of glass reflectivity of the evacuated tube (the reflectance of the mirrors is taken to be independent of the angle of incidence of incoming rays, see for example \cite{Ronnelid & Karlsson 1997}).

For translationally symmetric 2D collectors such as CPCs, the incidence angle modifier can be approximated as the product of measurements in two planes, one transversal and one longitudinal and this is known as the biaxial approximation \cite{Mcintire 1982}. However, this approximation has been shown to produce high errors at larger incidence angles \cite{Ronnelid & Karlsson 1997}. Equation\ref{eq:2.17} describes an approximation of the incidence angle modifier for such a CPC, where $\theta_l$ and $\theta_t$ are angles made with the incoming solar vector in two planes of the CPC.

\begin{equation}
K(\theta) \approx K(0, \theta_l) K(\theta_t, 0)
\end{equation}

Furthermore, \cite{Pinazo et al. 1992} derived detailed analytical expressions based on the biaxial approximation and determined times at which acceptance of suns rays begins for any arbitrary orientation based on the longitudinal and transverse projected incidence angles of a 2D CPC.

\cite{Rabl 1981} has estimated the IAM of CPCs as a polynomial equation as a function of the acceptance angle however this polynomial expression was never adopted for use by others and no reports exist of the accuracy of such an equation.

An excellent study of the optical efficiency model of a CPC was completed by \cite{Wang, Zhu, Chen, Zhang, Yang & Liao 2015} based on the above key literature related to IAMs. A graphical result obtained by the authors for the biaxial incidence angle modifier is reproduced in Figure 2.15. This is one of the few analyses of a tracking CPC (TCPC) collector array, that is a CPC collector that is non-stationary and mounted to a mechanical tracker that tracks the sun in one plane. The authors first completed a detailed theoretical model and numerical analysis of the 2.3 x concentration TCPC collector and followed up with experimental work. It can be seen in Figure 2.15 that the transverse component limits the optical efficiency at lower angles of incidence compared with the longitudinal component, by tracking along the transverse direction the authors were able to increase the average optical efficiency from 30 % to 60 % and to improve energy output by 1.3 to 1.9 times compared with the non-tracking mode of operation.
There has been no detailed study on the contribution of individual aspects of the IAM to the total IAM and individual components have been analysed sparingly. One interesting work has compared the change in absorptance with change of angle of incidence of two types of solar thermal absorber materials, commercial nickel pigmented aluminium oxide and sputtered nickel/nickel oxide (Tesfamichael & Wäckelgärd 2000). The solar absorptance was calculated for angles of incidence between $5^\circ$ and $80^\circ$. The main result is reproduced below in Figure 2.16. It shows that for these materials the response is fairly flat up to $40^\circ$ after which it starts to decrease for sputtered nickel/nickel oxide and remains flat until $60^\circ$ for nickel pigmented aluminium oxide. This shows the importance of understanding the angularly dependent absorbance of a selective surface however such data is rarely available.

Figure 2.16: Comparison of change in absorptance with angle of incidence of two common selective surface materials. (Tesfamichael & Wäckelgärd 2000).
2.2.7 Collector performance

Thermal performance  Numerical analysis of thermal processes and performance is necessary for detailed design of CPCs. Excellent thermal analyses of a compound parabolic concentrator with an involute absorber, a cover and an evacuated tube along the focal length of the CPC has been completed by (Hsieh 1981, Tchinda et al. 1998, Kim et al. 2008, Karwa et al. 2015). The following description of how to determine thermal performance is taken from (Klevinskis & Bučinskas 2008). This thesis will not be going into detailed numerical modeling but will determine collector performance from experimental data as discussed below.

Collector efficiency  The energy incident on the receiver and absorbed, $\dot{Q}_i$, is given by Equation 2.18 and is equal to the incident radiation on the aperture $G_{eff}$ multiplied by $\eta_o$, the optical efficiency of the collector and $K(\theta)$, the incidence angle modifier (Duffie & Beckman 2013).

$$\dot{Q}_i = G_{eff} \eta_{opt} K(\theta) \quad (2.18)$$

As the temperature of the working fluid increases due to energy being absorbed, thermal losses start to occur due to the temperature difference with ambient. The rate of heat loss $\dot{Q}_o$ depends on the overall heat transfer coefficient $U_L$ and the mean collector temperature $T_{col}$, as shown in Equation 2.19.

$$\dot{Q}_o = U_L (T_{col} - T_{amb}) \quad (2.19)$$

Thus the rate of useful energy extracted by the collector is equal to the difference between energy absorbed and energy lost as shown in Equation 2.20 and $\dot{Q}_U$ can be obtained experimentally as shown in Equation 2.21.

$$\dot{Q}_U = \dot{Q}_i - \dot{Q}_o = G_{eff} \eta_{opt} K(\theta) - U_L (T_{col} - T_{amb}) \quad (2.20)$$

$$\dot{Q}_U = \dot{m}C_p \Delta T \quad (2.21)$$

Where $\dot{m}$ equals the mass flow rate, $C_p$ is the heat capacity of the fluid and $\Delta T$ is the difference in temperature between the outlet and inlet of the collector.
A way of measuring collector efficiency is to compare the useful energy gained \( \dot{Q}_U \) to the incident solar radiation over some time period as shown in Equation 2.22:

\[
\eta = \frac{\int \dot{Q}_U dt}{A \int I dt},
\]

Conclusion

There is a large potential for solar technologies to meet industrial process heat needs, where medium temperatures are required as well as domestic lower temperature needs. CPCs offer a simple robust solution that has the potential to meet these needs and it has also been shown that CPCs can perform better than other solar collectors over a wide range of temperatures and without tracking. These collectors can reach the maximum allowed concentration for a given acceptance angle and consequently are the best choice for a proof of concept collector that utilises a cover made up of a luminescent solar concentrator.

The best CPC design depends on many factors, desired temperature range, desired hours of operation, geographic location, budget etc. As each design will be very context specific it is hard to say any one design is ideal. The CPC design used in this thesis is discussed in Chapters 6 and Chapters 7 and is built based on the equations and discussions within this Chapter. The Matlab code used to plot and design flat absorber and involute shaped CPCs is available open source on the Matlab Mathworks website under the title 'Generate Compound Parabolic Concentrator with Involute Shape Receiver'.

The compound parabolic concentrator technology has matured as it has proven to be a robust and low complexity option for capturing solar thermal energy. Several applications of CPCs are in the research stage and with the falling cost of PV cells, research and development on some applications has died out almost completely. The work in this thesis moves beyond existing applications to introduce a hybrid LSC and CPC collector, introducing a new state of the art application. The next Chapter discusses some work and results from investigating CPC design with the LightTools ray-tracing program.
Chapter 3

Ray Tracing to Investigate Losses in Involute Compound Parabolic Concentrators

3.1 Introduction

Involute compound parabolic concentrators can be arranged in different configurations resulting in variations in optical, thermal and economic performance. One common and economic configuration is to simply place an evacuated tubes along the focal length of the CPC where a vacuum suppresses convective heat loss from the absorber and this configuration is shown in Figure 3.1a). When investigating the optical efficiency of such collectors it is important to consider the reflection loss introduced by the evacuated tube at both normal and non-normal angles of incidence as light is distributed around the evacuated tube (also referred to as the receiver) by the CPC mirrors. The optical efficiency of a CPC is a function of various material properties, the number of reflections undergone before reaching the receiver and the incidence angle modifier as shown in Equation 3.1. For a CPC the incidence angle modifier cannot be calculated analytically and needs to be investigated with ray-tracing. In this Chapter, due to a lack of clear analysis in the literature, two aspects of the incidence angle modifier are investigated, losses due to a gap between absorber and evacuated tube and the reflection loss that occurs at the evacuated tube/air boundary. Losses are determined as a function of the angle of incidence in both the longitudinal and transversal planes of a CPC. The reflection losses are found to be approximately constant except close to the maximum acceptance angle.
Values of reflectivity used in the literature, of the receiver tube of an involute CPC, are summarised in Table 3.1. With the exception of (Li, Su, Pei, Yu, Ji & Riffat 2013), the values were not based on any experimental or simulation study, and resultantly the assumed values in the literature have a very large variation. The detailed numerical study completed by (Li, Su, Pei, Yu, Ji & Riffat 2013) used software to compute the incidence angle modifier and input into their model a changing reflectance with incidence angle, one of the few groups to do so. As light passing through glass actually encounters two air/glass boundaries, around 8% of light is reflected at normal incidence (Furler 1991), this would be a better approximation than some of the low values used in the literature but nevertheless a detailed study completed in this Chapter provides further insights.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Value</th>
<th>Note</th>
<th>Acceptance Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tchinda et al. (1998)</td>
<td>5 %</td>
<td>Reflection taken as constant</td>
<td>23.65°</td>
</tr>
<tr>
<td>(Oommen &amp; Jayaraman 2002)</td>
<td>3 %</td>
<td>Average value of glass used</td>
<td>23.5°</td>
</tr>
<tr>
<td>(Li, Su, Pei, Yu, Ji &amp; Riffat 2013)</td>
<td>12 - 64 %</td>
<td>Varied with transverse angle</td>
<td>10° and 3°</td>
</tr>
<tr>
<td>(Kim et al. 2013)</td>
<td>8 %</td>
<td>Constant value used</td>
<td>34° and 60°</td>
</tr>
<tr>
<td>(Liu et al. 2014)</td>
<td>10 %</td>
<td>Average value estimated</td>
<td>65°</td>
</tr>
</tbody>
</table>

Table 3.1: Reflectivity values of the receiver used in the literature for numerically simulating CPC performance.

3.2 Modeling Reflection and Gap Loss

The equation used to describe the optical efficiency of an involute shaped CPC without a cover is shown below in Equation 3.1

\[
\eta_{opt} = \rho^{<N>} \tau_\alpha K(\theta)
\]  

(3.1)

Where N, the number of reflections is a function of the acceptance angle, \( \rho \) is the reflectivity of the CPC mirrors and \( \tau_\alpha \) is the absorption/transmittance product of the receiver at normal incidence. The incidence angle modifier \( K(\theta) \) takes into
account the change in optical efficiency as the angle of incidence of light varies due to the sun’s apparent motion through the sky. This includes the angular variation of:

- Average number of reflections undergone by rays off the CPC wall (not investigated here but a good example of behaviour is given in (Buehl & Works 1980)).
- Absorptance of the absorber (discussed in section 2.2.6).
- Gap losses due to a necessary gap between absorber and cusp of the CPC.
- Angular dependence of reflectivity of the evacuated tube.

For translationally symmetric 2D collectors such as CPCs, the incidence angle modifier can be approximated as the product of measurements in two planes, one transversal and one longitudinal as shown in Figure 3.1 b). This is known as the biaxial approximation (Mcintire 1982).

\[
K(\theta) \approx K(0, \theta_l) \ K(\theta_t, 0)
\]  

Figure 3.1: a) Two-dimensional CPC with a cylindrical receiver, b) longitudinal and transverse planes used for simulations. The evacuated tube is placed along the longitudinal length of the CPC.

Equation 3.2 describes the biaxial approximation of the incidence angle modifier, where $\theta_l$ and $\theta_t$ are angles made with the incoming solar vector and the planes shown in Figure 3.1 (b). The product of the incidence angle modifier in each plane approximates the overall IAM.

\[
K(\theta) \approx K(0, \theta_l) \ K(\theta_t, 0)
\]  

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LightTools version 8.0.0 is used to model and analyse gap and reflection loss at the receiver of an involute CPC. A utility function is used to create involute shaped CPCs based on the acceptance angle, radius of absorber and CPC length.

The receiver is designed as shown in Figure 3.2 as an absorber sitting concentrically within a glass tube with a vacuum gap between the two. To isolate the loss due to reflection, the gap between the absorber and glass is essentially zero and the glass thickness is kept to a minimum, reflections will occur at both air/glass and air vacuum interfaces and will be isolated from the gap loss. The outer radius of the glass is 20 mm with a thickness of 0.1 mm, the air gap is 0.1 mm and the radius of the absorber is equal to 19.8 mm. In reality the glass will have a finite thickness that will affect the path length and potentially the angle at which rays strike the second glass/air interface, however we are assuming this will be negligible. This investigation consisted of several CPC design iterations with maximum half acceptance angles of: 20°, 30°, 40°, 50° and 60°. The receiver radius was fixed so consequently the entrance aperture of the CPC was varied.

To analyse the contribution to losses of the gap between outer glass tube and absorber, simulations were compared with isolated reflection loss (negligible gap) and with a 4 mm gap, that is setting the absorber radius to 16 mm. This was completed for one acceptance angle design of 30°. The optical properties of the model are shown in Table 3.2 and examples ray tracing results are shown below in Figure ?? for a) measuring reflection loss only (negligible gap between absorber and tube) and b) the case with a 4 mm gap between absorber and tube.

![Figure 3.2: a) CPC model used in simulations](image)
CHAPTER 3. RAY TRACING TO INVESTIGATE LOSSES IN INVOLUTE COMPOUND PARABOLIC CONCENTRATORS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass outer radius</td>
<td>20 mm</td>
</tr>
<tr>
<td>Glass thickness</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>Absorber radius (to isolate reflection loss)</td>
<td>19.8 mm</td>
</tr>
<tr>
<td>Absorber radius (4 mm gap)</td>
<td>16 mm</td>
</tr>
<tr>
<td>Reflectance of CPC mirror</td>
<td>100 %</td>
</tr>
<tr>
<td>Absorbance at absorber</td>
<td>100 %</td>
</tr>
<tr>
<td>Transmission at evacuated tube boundary</td>
<td>LightTools uses Fresnel equations for unpolarized light to calculate transmittance, reflectance and absorbance based on glass properties (index of refraction, extinction coefficient and thickness).</td>
</tr>
<tr>
<td>Entrance aperture</td>
<td>Varied to investigate different acceptance angles.</td>
</tr>
</tbody>
</table>

Table 3.2: Various properties used in LightTools simulations.

The Fresnel equations for unpolarized light used by LightTools were verified based on equations from [Furler 1991]. A 10cm x 10cm x 1cm block of glass with the same properties as used in the CPC model was created. Single rays were then traced at various angles of incidence and compared to equations in [Furler 1991]. The Fresnel loss calculated theoretically matched closely (to within 0.89%) with values obtained by LightTools. The discrepancies can be explained due to LightTools terminating rays when they fall below a threshold value of 0.01% of the power of the initial ray in addition to rounding errors. Many ray tracing simulations were performed with between 8 and 40 million rays to keep the statistical errors associated with finite bin sizes on the receiver to no more than 1.4 % for transversal simulations and no more than 5 % for longitudinal ones. The sun source was modeled as a planar source with an AM 1.5 spectral distribution (modeling the angular spread of the sun was not required as the acceptance angle of the CPC is much greater than 0.55°). The reflection losses were obtained by incrementally increasing the angle of incidence from normal, in either plane. For longitudinal simulations, the end effects needed to be taken into account so the length of the CPC was set to two meters and perfectly reflecting mirrors were placed at either end.
3.3 Results and Discussion

It can be seen in Figure 3.3 when considering the reflection losses in the transversal plane, that, for all acceptance angle CPCs, the curves have similar shapes and the reflection losses varied a small amount between 11% and 14%. Then as the maximum acceptance angle is approached the reflection losses rapidly increase as the angle of incidence that rays strike the evacuated tube increases. The reflection loss variation with longitudinal incidence angle, shown in Figure 3.4, is more or less independent of the acceptance angle. Shown in Figure 3.5 is a comparison of the transmission of a 30° acceptance angle CPC and simulations performed by Theunissen & Beckman (1985) for an evacuated tube with a cylindrical absorber (without a CPC). It appears that the inclusion of a CPC around the evacuated tube contributes little to losses in this plane at lower angles of incidence. At higher longitudinal angles of incidence the end effects of the CPC (radiation spilling due to inclusion of mirrors at ends) are adding to the optical losses, an effect which will not be present with an infinite CPC. A CPC designed with an acceptance angle of 30° was used to analyse gap loss. Figure 3.6 shows the effects of the addition of a 4 mm gap between absorber and glass tube in the longitudinal plane of the CPC. In this case the gap loss stays almost constant and similar in value to the reflection loss until around 50° where it starts to increase. The effects of adding a gap loss in the transverse plane are shown in Figure 3.7. In this case the gap loss stays almost constant and similar in value and behaviour to the reflection loss until it starts to increase rapidly at around 25°, 5° before the acceptance angle. The combined reflection and gap loss will make up the majority of the incident angle modifier. In each plane they do appear to be high ≈ 25% but the value from each plane will be multiplied together to give the overall IAM.
CHAPTER 3. RAY TRACING TO INVESTIGATE LOSSES IN INVOLUTE COMPOUND PARABOLIC CONCENTRATORS

Figure 3.3: Reflection losses for different acceptance angle CPCs in the transversal plane.

Figure 3.4: Reflection losses for different acceptance angle CPCs in the longitudinal plane.
CHAPTER 3. RAY TRACING TO INVESTIGATE LOSSES IN INVOLUTE COMPOUND PARABOLIC CONCENTRATORS

Figure 3.5: Comparison of transmission through an evacuated tube (Theunissen & Beekman 1985) (red) and CPC with acceptance angle = 30°, with an evacuated tube in the longitudinal plane (blue).

Figure 3.6: Comparison of losses in the longitudinal plane of the CPC. Shown in green is the loss due to including a 4 mm gap between absorber and glass, blue is the reflection loss calculated without a gap and red is the total of both losses.
CHAPTER 3. RAY TRACING TO INVESTIGATE LOSSES IN INVOLUTE COMPOUND PARABOLIC CONCENTRATORS

Figure 3.7: Comparison of losses in the transverse plane of the CPC. Shown in green is the loss due to including a 4 mm gap between absorber and glass, blue is the reflection loss calculated without a gap and red is the total of both losses.

It would be useful to be able to extract an average value of reflection loss however the optical behaviour of a CPC collector is highly dependent on its orientation (E-W versus N-S), location, tilt and azimuth. However it can be seen that in the longitudinal plane, up to an angle of approximately 40°, the reflection loss is approximately constant. Similarly in the transversal plane the reflection loss is approximately constant until close to the acceptance angle and close to the reflectance loss of an evacuated tube without concentration.

To further investigate this reflection loss it is worth considering at what angles of incidence (AOI) rays strike the receiver. In order to calculate this distribution the ray data including the ray power, direction, and location at which the ray strikes was obtained from LightTools. The AOI of each ray was calculated as shown in Equation 3.3.

\[
AOI = \cos^{-1}(\hat{r}, \hat{n})
\]  

(3.3)

The mean AOI striking the receiver was calculated is shown in Equation 3.4.

\[
AOI_{\text{mean}} = \frac{\sum_{i=1}^{m} P_i \cos^{-1}(\hat{r}_i, \hat{n})}{\sum_{i=1}^{m} P_i}
\]  

(3.4)
Where $i$ is the ray number that varies from 1 to $m$, $\hat{r}_i$ is the direction of the $i$th ray, $\hat{n}$ is the normal vector of the cylinder surface at the location the ray strikes and $P_i$ is the power associated with the $i$th ray. The angle of incidence spans from normal to $90^\circ$ and is divided into a series of one degree intervals. Due to the fact that rays can be reflected multiple times individual ray power also varies.

A CPC with acceptance angle of $30^\circ$ was investigated by varying the angle of incidence of light entering the CPC aperture, for three different longitudinal angles ($0^\circ$, $15^\circ$ and $23^\circ$) and the transversal angle was increased from normal, up until the maximum half acceptance angle of the CPC. Figure 3.8 shows the variation of the distribution of AOI on the receiver at longitudinal angle equal to 0. It can be seen that for lower angles of incidence on the aperture, rays strike the receiver with a wide distribution of angles and a peak around $30^\circ$. At $24^\circ$ a sharp cut-off appears as rays start to strike the receiver with a narrow distribution of angles. After $27^\circ$ the rays are increasingly striking at a large angle of incidence until at $29^\circ$ they strike the receiver almost tangentially resulting in large reflection loss.

Figure 3.9 shows the spatial distributions of rays along the tube for the same case as Figure 3.8 (longitudinal angle = 0). It can be seen that for lower angles of incidence into the CPC aperture rays are striking the receiver both directly and after reflecting off the CPC walls. In this way the CPC walls acts to redistribute rays around the receiver, at increasing incidence angles the rays are distributed onto a smaller and smaller area. For high angles of incidence into the aperture it is evident the rays strike the receiver in one location and the AOI distribution has narrowed.

Figure 3.10 shows how little the reflection losses change as the longitudinal angle is increased and Figure 3.11 shows the variation in average AOI on the receiver for the different longitudinal angles. While there is an increase of about $10^\circ$ in the average, this is not large enough to increase the reflection loss significantly especially as it is still in the flat part of the curve. This suggests that if the CPC operates within the range of angles that show constant reflection loss in the transversal and longitudinal plane the total reflection loss will be approximately constant, in these simulations it is around 12-14 % which is certainly significant.
CHAPTER 3. RAY TRACING TO INVESTIGATE LOSSES IN INVOLUTE COMPOUND PARABOLIC CONCENTRATORS

Figure 3.8: Distribution of angles of incidence of light striking the receiver of a CPC with acceptance angle = $30^\circ$ (longitudinal angle = 0). Starting from normal incidence, top left, the angle of light entering the CPC aperture was increased in the transversal plane.

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CHAPTER 3. RAY TRACING TO INVESTIGATE LOSSES IN INVOLUTE COMPOUND PARABOLIC CONCENTRATORS

Figure 3.9: Spatial distribution of angles of incidence of light striking the receiver of a CPC with acceptance angle = 30°. Starting from normal incidence, top left, the angle of light entering the CPC aperture was varied in the transversal plane. The longitudinal angle was set to zero.

Figure 3.10: Reflection loss in transversal plane as longitudinal angle is varied.
3.4 Conclusion

A stationary solar collector rarely sees the sun as directly perpendicular to its aperture. The position of the sun varies with seasons and time of day so it is important to understand how different optical properties of the involute CPC collector, as summarised by the incidence angle modifier, vary with angle of incident of light into the collector.

A two-dimensional CPC can be oriented north-south or east-west and the biaxial approximation helps to understand the performance of the CPC in these two planes. Longitudinally, along the focal length of the CPC the losses are constant until a large angle of incidence is reached. This suggests that orienting a collector E-W would be useful if you would like to capture sunlight for an extended amount of time (ie. greater than 6 hours). The transverse performance is fairly flat until the acceptance angle is approached so orienting a collector north-south, the hours captured are limited by the acceptance angle and consequently the acceptance angle has to be increased (decreasing the concentration ratio) to capture more sunlight hours.

Considering the various aspects of the incidence angle modifier, the reflection loss
from evacuated tubes inside CPCs with different acceptance angles was investigated in this Chapter, as a function of incidence angle in the longitudinal and transversal planes. It was found that longitudinally the shape of the CPC did not contribute to reflection loss (it was very similar to an evacuated tube on its own) and in the transversal plane the reflection loss was approximately constant until the acceptance angle was approached.

In the transverse plane when considering the combined gap and reflection loss, it can be seen the performance starts to rapidly degrade 5 degrees before the acceptance angle. So when we think of having designed a collector with an acceptance angle of 30 degrees the incidence angle modifier helps us to understand that this does not mean a significant amount of light will captured at or near the 30 degree limit.

Not explored in this Chapter but also a key part of the incidence angle modifier, the variation of absorbance of the selective surface absorber material is important to consider. As shown in Figure 2.16 the solar absorptance can have a fairly flat response with incidence angle, up to 50° or so. Ideally a selective surface would be chosen where the response stays flat until the acceptance angle of the CPC is reached.

On analysing the spatial and angular distributions of incident rays on the evacuated tube, it became evident that while the CPC acts to spread out the angles of incidence of light striking the evacuated tube, the mean angle of incidence at any longitudinal angle does not vary significantly until the acceptance angle is approached. As the mean angle of incidence does not vary greatly, neither does the reflection loss. One way of reducing this loss is with the use of an anti-reflective coating. New improvements in anti-reflective coatings have shown promising results in reducing reflection losses over broadband AM 1.5 spectrum. Such anti-reflective coatings are a promising option to reduce reflection losses from glass tubes inside CPC receivers.

The work done in this Chapter has led to a better understanding of the incidence angle modifier of a two-dimensional CPC and a better understanding of the importance of various optical properties and receiver configurations. The next Chapter moves on to work done on the luminescent solar concentrator component of the hybrid PV-T collector that this thesis aims to demonstrate.
Chapter 4

Circular Luminescent Solar Concentrators

4.1 Introduction

Luminescent solar concentrators offer the ability to architecturally integrate solar energy harvesting devices into the urban environment. This Chapter explores and introduces a new circular shape of luminescent solar concentrator, made possible by utilising flexible, bifacial mono-crystalline silicon “SLIVER” solar cells (Franklin et al. 2007). This work came about while investigating LSCs for a hybrid collector, it explores the use of very bright quantum dots as a fluorescent material and the use of SLIVER silicon solar cells, the flexible nature of these cells leads to the ability to fabricate non-conventional LSC shapes.

Novel circular LSCs were fabricated and characterised in both solid and liquid waveguides. A liquid collector is useful for investigating LSC performance for several reasons: the performance of the solar cells around the edges of the concentrator is fixed and constant, removing variability in performance when comparing different fluorophores and concentrations. Additionally, for performance measurements, the concentration of the solutions can be easily varied. Solid waveguides were made with the flexible polymer, polydimethyilsloxane (PDMS) and characterised with lifetime imaging microscopy to probe fluorophore distribution in LSCs. Furthermore, non-fluorescent nanoparticles as light scatterers were investigated in liquid waveguides and revealed that a significant amount of light can be totally internally reflected to the edges of an LSC via light scattering alone leading to the concept of “frosted glass” LSCs, useful when a large amount of light transparency is not required.
4.2 Liquid Circular LSC

To investigate the performance of circular shaped LSCs, a liquid collector was fabricated as shown in Figure 4.1. A liquid collector is used for several reasons: the performance of the solar cells around the edges of the concentrator is fixed and constant removing the variability of cell performance when comparing different fluorophores and concentrations. Additionally for spectroscopic and performance measurements, the concentration of the solutions can be easily changed.

The diameter of the liquid concentrator is equal to 5.5 cm and three silicon SLIVER solar cells (connected in parallel) were attached to the outside using Avery SPF1000 surface protection film (polyurethane film), to optically couple the cells to the edge of the LSC. The polyurethane film was gently heated on a hot plate and then placed around the circle mould. This film was sticky and it was consequently possible to easily stick the SLIVER cells onto the film. 3M copper conductive tape was cut into 3mm thin strips and placed above and below the cell. High conductivity silver ink was then used to contact the copper bus bars to the solar cell. The conductivity of this ink is highest when treated for a time at 60°C however, it was not possible to do this with the circle mould as it would melt the polyurethane film. This most likely resulted in a less than optimal SLIVER cell performance but nevertheless useful for investigation purposes. When conducting experiments a pipette was used to measure out the same amount of liquid to just cover up to the top contact. As these cells are bifacial, black tape was wrapped around the outside of the mould to illuminate the cells on one side only (not shown in 4.1).

Figure 4.1: Liquid circle LSC concentrator with three SLIVER cells mounted to the outside, connected electrically in parallel and optically coupled with polyurethane film.
4.3 Fluorophore Characterisation

4.3.1 Characterisation in solvent

Various fluorophores were investigated with the liquid collector: CdSe/CdS quantum dots, were chosen for their high quantum yield, while CdSe/CdS quantum rods were utilised because of their potential as polarised emitters. Finally, Lumogen Red 305 perylene organic dye was included as a reference.

Nanoparticles were fabricated by our collaborators from Melbourne University, using methods as described in Appendix A1. The liquid concentrator was also used to investigate whether a pure scattering regime (with and without fluorescent particles) would lead to significant waveguiding behaviour. Silica particles were used as a non-fluorescent reference material, to quantify the role of light scattering. TEM images were obtained of the dots, rods and silica particles as shown in Figure 4.4.

The average size of the CdSe dots was found to be 7.6 +/- 0.5 nm, the CdSe quantum rods was 27.6 +/- 9.7 nm and the average size of the silica particles was 65 nm. Absorbance, fluorescence spectra were obtained with a Fluorolog and an Agilent UV-VIS 8453 spectrophotometer. The fluorophores were dissolved in toluene and measurements were taken in a 1 cm path length cuvette. Results are shown in Figures 4.5, 4.6, 4.7. Comparing the fluorophores several things can be noticed:

- Figure 4.2 shows the fluorescence decay lifetimes of the fluorophores and the difference between the Lumogen Red 305 organic dye and the nanoparticles clan clearly be seen. The dye has a much shorter lifetime.

- It can be seen in Figure 4.3 a), the quantum rods have higher absorbance in the UV compared with both the dots and Lumogen Red dye.

- Figure 4.3 b) shows the Lumogen dye has the highest Stokes shift and the QD have the greatest overlap between absorption and emission spectra.

- The Lumogen dye has a wide emission band 4.5 b) that is also the most red shifted.

- Excitation spectra are shown in Figures 4.5 4.6 4.7 d). This works backwards from an emission at 620 nm to see which wavelengths of photons would lead to emission. It is different to absorbance as an absorbed photon does not necessarily lead to emission.
• Figures 4.5 c), 4.6 c) and 4.7 c) show absorbance and fluorescence as a function of concentration. Ideally we would like maximum absorbance and maximum fluorescence emission occurring at a similar concentration but that does not occur in each case the maxima of the two are clearly separated and maximum fluorescence occurs at lower concentrations than maximum absorbance.

Figure 4.2: Fluorescence decay of Lumogen 305, quantum dots and rods. The fluorophores are excited by a 305 nm beam and each line represents the fluorescence intensity decay measured. As expected the dye has a much shorter lifetime than the quantum dots and rods.

Figure 4.3: Absorption/emission spectra of fluorophores (left) and offset (right).
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Figure 4.4: TEM images of nanoparticles used: a) CdSe/CdS quantum rods b) CdSe/CdS quantum dots and c) non-fluorescing silica particles.

Figure 4.5: a) Absorbance and b) Fluorescence spectra of Lumogen 305 dye in toluene at concentrations of 0.0005, 0.001, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25 and 0.5 %wt. The emission peak of the dye blue shifts from 613 to 604 with a decrease in concentration. c) Absorbance and fluorescence maxima plotted versus the concentration of fluorophore in toluene. d) Excitation spectrum of Lumogen 305 in chloroform.
Figure 4.6: a) Absorption and b) Fluorescence spectra of CdSe/CdS quantum dots in toluene at concentrations of 0.0005, 0.001, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25 and 0.5 % wt. c) Absorbance and fluorescence maxima plotted versus the concentration of fluorophore in toluene. d) Excitation spectrum of quantum dots in chloroform.
Figure 4.7: a) Absorption and b) Fluorescence spectra of CdSe/CdS quantum dots in toluene at concentrations of 0.0005, 0.001, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25 and 0.5 % wt. c) Absorbance and fluorescence maxima plotted versus the concentration of fluorophore in toluene. d) Excitation spectrum of quantum dots in chloroform.
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4.3.2 Characterisation in PDMS

Solid waveguiding LSCs were fabricated as described in the Experimental Procedures Section 4.5. PDMS is a flexible polymer highly transparent in the visible region and simple to work with for investigating the circular shape. An attempt was initially made to fabricate with a ligand exchange to increase the dispersability of QD at high loadings by modifying the surface ligands of the QD with PDMS-SH however, the resultant QD-PDMS became too polar and did not mix with the bulk PDMS.

Figure 4.8 shows the absorbance of various concentrations of CdSe/CdS quantum dots in PDMS and it is noticeable that aggregation and scattering of light starts to occur at concentrations above 0.01 %, due to the absorbance profile losing the typical peaks of QD absorption measure in hexane.

Figure 4.9 shows absorbance measured at various concentrations of Lumogen 305 dye dispersed in PDMS. It can be seen the dye is dispersed well in the PDMS and there is no noticeable scattering by comparing with the Figure 4.5 a) of dye in solution. The integrity of the shape is maintained. PDMS discs with various dye concentrations, illuminated under UV radiation are shown in Figure 4.10.

![Absorbance of various samples of QDs dispersed in PDMS at several concentrations compared with QDs in hexane (black line).](image-url)
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Figure 4.9: Absorbance of Lumogen dye 305 in PDMS at different concentrations.

Figure 4.10: Discs of PDMS with varying Lumogen Red 305 dye concentrations under UV illumination. From left to right the concentrations are: 0.0005 %wt, 0.005 %wt, 0.01 %wt, 0.05 %wt.
4.3.3 Fluorescence lifetime imaging of PDMS samples

Fluorescence lifetime imaging microscopy (FLIM) produces images where the colour scale represents the fluorescence lifetime rather than the intensity of the fluorophores’ emission, and can be used to investigate how well the fluorophores disperse in the polymer. A typical set up is shown in Figure 4.11 reproduced from (Suhling et al. 2015). FLIM gives insight into fluorescence behaviour spatially, this gives much more insight than average fluorescence lifetime measurements and furthermore this technique has not previously been used to investigate LSC characteristics. The FLIM images (Figure 4.12 and Figure 4.13) provide maps of the average fluorescence lifetime over the scanned region of the sample, and the inset figures show the normalised histograms of the average fluorescence lifetime of all the pixels in the image. Ideal decay behaviour is described by a single lifetime constant \( \tau \) and is valid if the emission emanates from only one fluorescing species in a homogeneous environment. However, in practice many processes such as molecular aggregation, species heterogeneity and concentration quenching may occur and a single fluorescence lifetime is often insufficient to describe the emission temporal behaviour. The FLIM images of the Lumogen red dye samples in Figure 4.12 show that the dye is remarkably well dispersed in the PDMS. The average fluorescence lifetime distribution across each image is shown in the inset and is quite narrow, indicating a uniform environment around the dye molecules. The decay is close to mono-exponential, and a small shift to shorter lifetimes as the dye concentration is increased. Conversely, the FLIM images and their average lifetime distributions of the QD based LSCs shown in 4.13 reveal significant heterogeneity of the QDs in these LSCs. The fluorescence decay behaviour was not mono-exponential and the broadness and position of the lifetime distributions changed significantly with QD concentration.

![Figure 4.11: FLIM setup incorporating time correlated single photon scanning (TCSPS) using a pulsed laser that scans the sample (Suhling et al. 2013).](image)

Figure 4.11: FLIM setup incorporating time correlated single photon scanning (TCSPS) using a pulsed laser that scans the sample (Suhling et al. 2013).
Figure 4.12: FLIM images of Lumogen Red 305 dye dispersed in PDMS at different concentrations. Clockwise from top left: 0.0005 %wt, 0.001 %wt, 0.01 %wt and 0.005 %wt. Inset: Average fluorescence lifetime distributions of the dye at different concentrations.
Figure 4.13: FLIM images of CdSe/CdS quantum dots dispersed in PDMS at different concentrations. Clockwise from top left: 0.0001 %wt, 0.005 %wt, 0.02 %wt and 0.01 %wt, showing non-uniform dispersion in the polymer. Inset: Average fluorescence lifetime distributions of the QDs at different concentrations.
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4.4 SLIVER Solar Cell Characterisation

In this work for both the liquid and solid circle LSCs silicon SLIVER solar cells were used. These flexible bifacial cells were obtained from the Australian National University where they were originally invented and fabricated. The cells do not come with conducting bus bars, they need to be added manually then connected to the micrometer sized n and p contacts on either side of the cells. Wire then needs to be soldered onto the busbars for measuring current and voltage.

![Image of SLIVER cells showing busbars and silver ink epoxy contacts added manually.]

Current voltage (IV) curves are used to describe solar cell performance. These can be measured using a solar simulator, and source measuring unit (SMU) which is a device that can both sink and source voltage and current as shown in Figure 4.15.

The following factors were found to effect SLIVER cell performance:

- Busbar material – In Figure 4.14 the material used for the busbar is tin plated copper. Another busbar material investigated was 3M conductive copper tape. This conductive tape has the advantage that it can be stuck onto LSCs and is flat and can be cut to a desired shape. The disadvantage of using conductive tape was that it increased series resistance and decreased performance of LSCs.

- Type of silver ink used for contacts – Highly conductive silver epoxy ink needs to be used to connect the cells to the busbars. The highest conductivity is also the most expensive.

- Quality of SLIVER cell – Different batches of cells performed differently.

- Test cable - Old leads were very lossy and new ones improved performance.
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Following on from initial SLIVER cell characterisation experiments a methodology was set up that produced the most consistent results. Shown below is the performance of four different SLIVER solar cells. An attempt was made to manufacture them identically with the aim of testing reproducibility. The experiment of the four cells was repeated on a different date.

<table>
<thead>
<tr>
<th>Reference</th>
<th>SLIVER cell 1</th>
<th>SLIVER cell 2</th>
<th>SLIVER cell 3</th>
<th>SLIVER cell 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isc/cm² (test1)</td>
<td>28.4mA</td>
<td>28.8mA</td>
<td>29.6mA</td>
<td>28.4mA</td>
</tr>
<tr>
<td>Isc/cm² (repeat)</td>
<td>29.1mA</td>
<td>27.7mA</td>
<td>28.8mA</td>
<td>broke</td>
</tr>
<tr>
<td>PCE (mean)</td>
<td>13.2 %</td>
<td>12.7 %</td>
<td>13.1 %</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Summary of SLIVER cell characterisation experiments - four different SLIVER cells were fabricated then the IV measurement was repeated twice. The power conversion efficiency (PCE) is shown in the last row.

As shown in Table 4.1, it was found that the SLIVER cell could be reproduced consistently to within 3 %, with a power conversion efficiency of approximately 13 % with tin plated copper conducting bus bars and highly conductive silver ink used to make contacts. It was important to cure the cells on a hot plate on at least 60°C to increase the electrical conductivity compared to room temperature curing.

4.5 Experimental Procedures

Current voltage (IV) curves are used to describe solar cell performance. These can be measured using a solar simulator, and source measuring unit (SMU) which is a device that can both sink and source voltage and current as shown in Figure 4.15. The device under test is placed in the solar simulator which is calibrated to provide one sun illumination and the IV sweep is captured on a computer via the SMU. From the IV curve, short circuit current, open circuit voltage, fill factor and power conversion efficiency values can be determined which describe the performance of the cell. IV measurements of the liquid and solid PDMS concentrators were carried out using a 1 kW Oriel solar simulator, outputting 1000 W/m², with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. The light intensity was calibrated using a reference silicon solar cell (Measurements Inc.) certified by the National Renewable Energy Laboratory, CO, USA.
Testing of the liquid concentrator took some effort as we had to eliminate stray light sources from entering the collector by testing it with a solvent only, to obtain a baseline. A black cloth was found to be reflecting a significant number of photons into the concentrator and furthermore we found the stand the experiment was situated on was reflecting photons into the collector significantly enough to detect current. After all stray photons, had been prevented from entering the collector we commenced with the experiment. The short circuit current was used as a measure of performance for it is less sensitive to variations in temperature that would affect measurements of voltage and hence power. Current-voltage measurements were taken with either a highly diffuse white reflector placed underneath the concentrator or a highly absorbing selective surface, TiNOX, which absorbs over 95% of the solar spectrum and minimises stray diffuse light reflecting back into the collector.

Various fluorophores were then investigated with the liquid collector: CdSe/CdS quantum, CdSe/CdS quantum rods and Lumogen Red 305 perylene organic dye was included as a reference. Nanoparticles were fabricated using methods as described in Appendix A1. The liquid concentrator was also used to investigate whether a pure scattering regime would lead to significant waveguiding behaviour. Silica particles were used as a non-fluorescent reference material, to attempt to quantify the role of light scattering.

Figure 4.15: IV measurement set up consisting of a AAA rated Photo Emission Tech solar simulator, a source measuring unit is used for IV curve sweeping measurements.
Various solid waveguiding LSCs were then fabricated in the flexible polymer polydimethysiloxane (PDMS) with: (i) a Lumogen Red 305 circular LSC with a concentration of dye of 0.05 % wt, (ii) a CdSe/CdS QD circular LSC with a concentration of 0.02 % wt and (iii) a CdSe/CdS quantum rod circular LSC with a concentration of 0.02 %wt.

To prepare the samples, a solution of quantum dots in dichloromethane (DCM) of known concentration (%wt) was prepared. Then the PDMS 182 pre-polymer and curing agent was thoroughly premixed in a tray and approximately 10 g per sample was mixed at a ratio of 10 % curing agent to pre-polymer. The required volume of quantum dots in DCM was mixed thoroughly with the PDMS in a beaker and the solution was then poured into a mould under reduced pressure overnight to evaporate DCM at room temperature. The solvent must not be allowed to boil (pressure was kept above 250 mbar). Finally, the sample was cured overnight on a hotplate at 30°C. Circular PDMS discs were fabricated with a thickness of 0.5 cm and a diameter of 5.5 cm giving a theoretical concentration ratio of 2.75. SLIVER cells were then attached to the edges of the samples with UV curing glue and silicone optical coupling gel. Copper conductive tape was used to add busbars to the SLIVER cells and silver ink was used to connect the cells to the bus bars.

4.6 Results and Discussion

4.6.1 Fluorescent liquid concentrator

The liquid circle concentrator was used take IV measurements with different fluorophores at different concentrations. Figure 4.16 shows the short circuit current, taken from IV characteristics, plotted as a function of % weight concentration of the fluorophore with either (a) highly absorbing surface TiNOX or (b) a white diffuse reflector placed beneath the liquid concentrator. The concentration of fluorophore was varied between 0.001 %wt up to 0.5 %wt and an IV curve was measured at each point. As expected adding a white diffuse reflector beneath the concentrator increased the performance of the device by giving photons that were transmitted a second pass chance to get reabsorbed. Lumogen Red 305 dye was found to give the best performance with a maximum occurring at around 0.05 %wt concentration.

A reason for this better performance can be seen in Figure 4.3 b), which shows the absorbance and emission spectra of the different fluorophores investigated. Lumogen Red 305 has a higher Stokes shift which results in lower reabsorption losses and better overall solar energy conversion. Note that the Lumogen Red 305 has a photoluminescent quantum yield of 99.6 %, only slightly higher than that of the
quantum dots (96.4 %) but almost twice as high as that of the CdSe/CdS quantum rods (51.9 %), as shown in Table 4.2 (quantum yield measurements obtained using reference dye method (Würth et al. 2013). Although Lumogen Red 305 performs well, it is not practical for real-world LSCs due to its poor photostability under solar illumination (Sark et al. 2008).

The quantum dots and quantum rods exhibited similar performance, with a maximum short circuit photocurrent being generated at nanocrystal concentrations around 0.1 %wt with both a white and black absorbing layer beneath the concentrator. Interestingly the CdSe/CdS rods performed almost as well as the QDs, despite their lower quantum yield. This is due to the rods having a higher absorption in the ultra-violet region.

Figure 4.16: Short circuit current plotted against concentration for the three fluorophores investigated in the liquid collector with a) Black absorber TiNOX placed beneath the LSC, b) White diffuse reflector placed beneath the collector.

4.6.2 PDMS circular luminescent solar concentrators

Following on from the circle liquid LSC investigation, several samples were fabricated in the polymer PDMS. The PDMS circle LSCs were then tested under the solar simulator in the same set up as described for the liquid collector. For the Lumogen Red 305 based circular LSC, a concentration of 0.05 %wt was used to obtain IV characteristics. For both the CdSe/CdS quantum dot and CdSe/CdS rods LSCs, a concentration of 0.02 %wt was used as there was difficulty obtaining a clear sample at higher concentrations due to agglomeration of quantum dots. The performance of
the PDMS circle LSCs is summarised in Table 4.2 and Figure 4.17. It is clear that a significant amount of light is lost through the bottom surface because addition of the white reflector almost doubles the performance of both the QD and dye LSCs. Thus, back reflectors are critical. These perform better than the liquid collector mainly due to the thick glass walls the light has to travel through around the liquid mould.

![Figure 4.17](image)

*Figure 4.17: a) IV curve collected from a Lumogen Red 305 circular LSC
b) IV curve of a 0.02 %wt concentration CdSe/CdS quantum dot circular LSCs
C) IV curve of a 0.02 %wt concentration CdSe/CdS quantum rod circular LSCs.*
The Lumogen dye has a higher short circuit current compared to the quantum dot and quantum rod doped LSCs. We wanted to investigate whether the very high quantum yield of the dots could counter the re-absorption losses that occur due to the low Stokes shift in semiconductor nanocrystals used. However, it is apparent from the results in Figure 4.17 that this did not occur. As photons are re-emitted in the LSC they still have a high chance of leaving through the escape cone so it is still critical to the performance of LSCs to have as high Stokes shift as possible, as a priority when designing LSCs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quantum Yield (± 5%)</th>
<th>Isc(mA) White Ref</th>
<th>Isc(mA) Black Abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/CdS dots</td>
<td>96.4</td>
<td>47.6</td>
<td>19.5</td>
</tr>
<tr>
<td>CdSe/CdS rods</td>
<td>51.9</td>
<td>25.9</td>
<td>11.1</td>
</tr>
<tr>
<td>Lumogen Red 305</td>
<td>96.4</td>
<td>83.2</td>
<td>58.0</td>
</tr>
</tbody>
</table>

Table 4.2: Quantum yield measurements obtained using a reference dye method (Würth et al. 2013) and short circuit current values of PDMS based LSCs that incorporate either a white diffuse reflector or a black absorbing TiNOX.

### 4.7 Scattering Liquid Concentrator

Nanocrystals such as CdSe have a high refractive index and it is possible that elastic light scattering of incident radiation also contributes to the photocurrent. To assess the effect of scattering, we performed a liquid LSC experiment using non-absorbing silica nanoparticles 100 nm in size, the preparation of silica particles is described in Appendix A1. Current voltage measurements of the silica particle based scattering liquid concentrator were made on the absorbing black material to reduce the amount of diffuse light entering the collector. The concentration of silica in toluene was increased up to 20 % wt and we found considerable improvement in the short circuit current performance of the LSC.

Figure 4.18 a) presents the short circuit photocurrent as a function of the silica concentration. It is evident that light scattering inside the liquid concentrator is leading to a significant photocurrent. Figure 4.18 b) shows the effect of increasing scattering particle concentration while maintaining a constant concentration of QD (0.02 %wt). In this case, there was not a significant increase in the performance of the liquid LSC with increasing concentration of silica nanoparticles because the peak
photocurrent in the presence of QDs occurs at 0.02 %wt. Hence the silica particles could not be used to enhance the performance of the LSC. Based on these results we can say that scattering leads to significant waveguiding of photons but further work needs to be done to understand if and under what conditions this could be combined with fluorescence based waveguiding to improve LSC performance over fluorescence only based waveguiding.

Figure 4.18: a) The short circuit photocurrent as a function of the silica nanoparticle concentration (in the presence of a black absorber). b) The short circuit photocurrent as a function of the silica nanoparticle concentration in the presence of 0.02 %wt. CdSe/CdS core-shell nanocrystals (in the presence of either a white or black absorber)
4.8 Conclusion

A circular liquid LSC was fabricated to investigate the efficiency of different fluorophores at different concentrations. The device utilised flexible bifacial silicon SLIVER cells enabling circular LSCs to be constructed. One of the disadvantages of SLIVER cells is that, it is unavoidable to have contacts above and below the cell. As the LSC power conversion efficiency is ratio of power out and power input to the top face, the requirement of the SLIVER contacts mean that some efficiency is lost due to not being able to collect all the light. That being said, it is anticipated that the contacts will reflect some light back into the LSC giving photons another chance at conversion.

When comparing the performance of CdSe/CdS quantum dots and CdSe/CdS quantum rods with the reference dye, it can be seen that the both rods and quantum dots did not perform as well as the reference Lumogen Red dye as the high quantum yield of the QDs was insufficient to compensate for the low Stokes shift and consequent reabsorption losses. It can be concluded that fluorophores with higher Stokes shift are necessary to maximise LSC performance.

The circular liquid concentrator is used to show significant light guiding behaviour by dispersion of non-fluorescent scattering particles, although light guiding was not significantly improved with the combination of scattering particles and fluorescent particles. These results pave the way for “frosted glass” concentrators.

Circular LSCs were then fabricated in the polymer PDMS and their photovoltaic response was characterised. Lumogen Dye is easier to disperse in the PDMS and consequently has better performance. Finally, fluorescence imaging microscopy is used to show how well fluorophores are dispersed in the polymer PDMS. This technique gives invaluable information on spatial distribution of fluorophore in polymer blends, showing that it is much more difficult to uniformly disperse QD in PDMS.

The next Chapter will move onto presenting work done on simulating LSC performance. This work was necessary for choosing a design for the large LSC cover to go on the hybrid collector. The simulations and code in Chapter 5 were completed after the work in this Chapter 4 was published.
Chapter 5

Monte Carlo LSC Model

5.1 Introduction

After investigating various means of fabricating luminescent solar concentrators, as shown in Chapter 4, it was realised larger sizes, greater than 10cm x 10cm, required for a hybrid collector would be difficult to fabricate in the lab. Some research groups working in this field have industry collaborators to assist with fabricating large sheets of LSCs with specific fluorescent materials and concentrations (Kerrouche et al. 2014). Other studies have used commercially available Plexiglass (PMMA) sheets doped with Lumogen Red 305 (Debije 2015, Rajkumar et al. 2015). The work done in the following chapters utilises LSCs made from large sheet of fluorescent Plexiglass manufactured by Evonik, imported from Germany. As the large sheet needed to be cut into smaller modules, it remained to be decided with what geometries to make the modules. This led to the development of Monte Carlo ray-tracing code, programmed in Matlab and described in this chapter. This code is shared on the Matlab Mathworks open source sharing platform with the title ‘Monte Carlo Raytracing of a Luminescent Solar Concentrator’ and the package is made up of several functions some of which are referred to throughout this Chapter.

The Monte Carlo technique is a statistical approach to modeling propagation of photons through a system. Random numbers, cumulative distribution functions (CDFs) and probability density functions (PDFs) are used to sample from functions or spectra such as the solar AM 1.5. In this way the random number determines the fate of the photon and complex radiation transfer equations can be avoided.
The Monte Carlo technique was first used for LSC modeling by (Carrascosa & Unamuno 1983) and first with quantum dots by (Gallagher et al. 2004). The work in this Chapter is based on previous work by (Prahl et al. 1989) (Sahin et al. 2011). While, Sahin et al were following the work of Prahl too, they made errors in the equations relating to quantum dot emission. In LSCs, emission is always isotropic and therefore the anisotropy equations are not needed as discussed later on in this Chapter.

5.2 Sampling from Air Mass 1.5

If ξ is a random number drawn from the uniform distribution [0,1] then a CDF can be set equal to ξ and re-arranged for the variable that needs to be randomly selected. In this way the area under the CDF will be equal to the area under the random number selected from the uniform distribution and the randomly chosen variable when sampled enough times will be able to re-create the original probability density function that was sampled from.

For simulating the solar source photons are sampled from the standard AM 1.5 spectrum obtained from NREL (NREL 2010). This solar spectrum (shown in Figure 1.1) has the units of flux (W/m².cm) along the y axis and wavelength (nm) along the x axis. In order to sample the AM 1.5 spectrum, a tabulated discrete form is used to generate the cumulative distribution function. The CDF is computed using numerical integration by the trapezoidal rule as shown in Equation 5.1. Then it is normalised and stored for each wavelength as shown in Equation 5.2. The resulting AM 1.5 CDF is shown in Figure 5.1.

Given an array of wavelengths \( \lambda(i) \) and corresponding flux values \( F(i) \) where \( i = 1, 2, 3...N \)

\[
\int F(\lambda) \, d\lambda \approx \sum_{i=1}^{N-1} \frac{1}{2} (F_{i+1} + F_i)(\lambda_{i+1} - \lambda_i) \quad (5.1)
\]

\[
C(\lambda) = \frac{\int_{\lambda_{min}}^{\lambda} F(\lambda') \, d\lambda'}{\int_{\lambda_{min}}^{\lambda_{max}} F(\lambda') \, d\lambda'} \quad (5.2)
\]
Monte Carlo sampling from the AM 1.5 CDF is shown in Equation \[5.3\] A random number \(\xi\) is set to equal the CDF and since this is a discrete function often \(C(\lambda)\) lies between two discrete points. Equation \[5.4\] interpolates the discrete CDF between its closest defined points \(i\) and \(i+1\) to obtain an interpolated \(\lambda\) and finally a randomly chosen value of flux, \(F\).

\[
\xi = \int_{\lambda_{min}}^{\lambda} F(\lambda')d\lambda' = C(\lambda) \tag{5.3}
\]

\[
\lambda = \lambda(i) + \left[\lambda(i + 1) - \lambda(i)\right] \frac{\xi - C(i)}{C(i + 1) - C(i)} \tag{5.4}
\]

\[
F = F(i) + \left[F(i + 1) - F(i)\right] \frac{\lambda - \lambda(i)}{\lambda_{i+1} - \lambda_i}
\]

In this way the function SamplingFromAM1.5(N).m, in the package developed, takes solar flux values in the file S.csv, the corresponding wavelengths are in lambdaS.csv and creates a cumulative distribution function of the solar spectrum, a random number is then used to sample from this spectrum.

5.3 Main File (MC_LSC.m)

The main file MC_LSC.m contains the declarations of the global variables used throughout the program. Including the LSC geometry (units in cm). As shown in

Figure 5.1: CDF of the solar spectrum generated by the function SamplingFromAM1.5(N).m
Figure 5.2. P2 is considered the origin and P1 goes in the negative z direction so the LSC height in the z direction is described by a negative number. The concentration of the fluorophore needs to be input in PPM and the extinction coefficient should be correspondingly calculated using the same concentration units.

The main file requires a CDF of the emission spectrum of the fluorophore. A function called createCDF_Emission_Spectrum.m takes as input a csv file with wavelengths in the first column and emission counts in the second column (does not need to be normalised). Using trapezoidal integration in the same way as for sampling the solar spectrum, a CDF is created and saved in the folder. The spectral extinction coefficient of the fluorophore also needs to be loaded as a csv file in units to match the definition of concentration input.

To begin the simulations SamplingFromAM1_5.m is called N times and the randomly selected photons are placed into an array. The xyz coordinates of the initial photon striking the air/top face boundary are determined by the function initial_xyzphotons struck().m. Incident photons strike the receiving face of the LSC at a normal angle. The coordinates the LSC strikes are randomly selected after breaking down the receiving face into a grid N/LSC width and N/LSC length where N is the number of photons to be simulated [Shin Woei 2014]. The function removeReflected.m is then called to remove a weight from the array of photons striking the LSC as a percentage determined by the refractive index of the waveguide. The photons that are left are then passed into the function first_absorption().m.
5.4 Absorption

Absorbance can be defined in terms of Naperian (base e) or decadic (base 10) Beer-Lambert law. The following section will follow the decadic definition of absorbance as the spectrophotometer used in obtaining the extinction coefficients of the dyes and quantum dots used throughout this thesis is based on log_{10}, as shown in Equation 5.5. Fractional absorbance is itself a cumulative distribution function as it gives the probability a photon will be absorbed at or below a distance z (Wilton 2012):

\[ A = 1 - 10^{\frac{\epsilon(\lambda) C z}{\tau}} \]  

(5.5)

Where \( \epsilon(\lambda) \) is the decadic wavelength dependent extinction coefficient, if measured with a spectrophotometer, C is the concentration of the fluorophore that should match the extinction coefficient units and z is the path length (often in cm). Therefore a PDF can be obtained by taking the derivative of the absorbance as shown in Equation 5.6.

\[ \frac{dA}{dz} = \epsilon(\lambda) C \frac{1}{10^{\frac{\epsilon(\lambda) C z}{\tau}}} \]  

(5.6)

Now we go back through obtaining the CDF again from the PDF in Equation 5.6 to derive an expression for using a random number to generate a path length a photon undergoes until it is absorbed.

Let: \( \tau = \epsilon(\lambda) C \)

\[ \xi = \int_{0}^{z} \tau 10^{-\tau z} \]

\[ \xi = [-10^{-\tau z}] + 1 \]

\[ 1 - \xi = 10^{-\tau z} \]  

(5.7)

\[ \log_{10}(1 - \xi) = -\tau z \]

\[ z = \frac{-\log_{10}(1 - \xi)}{\tau} \]

Since \( \xi \) in the range of \([0,1]\), can write the randomly generated path length as:

\[ z = \frac{-\log_{10}(\xi)}{\epsilon(\lambda) C} \]  

(5.8)
Equation 5.8 is the equation that describes the propagation of photons inside the LSC. Random number $\xi$ is used to determine a step size based on the extinction coefficient and concentration of the fluorescent material inside the LSC. After a photon has propagated it has a chance of interacting with the boundaries of the LSC or being absorbed again.

5.5 Moving a Photon

The step size, described as $z$ or $S$, is then used to move the photon after absorption. Firstly after each absorption, a random number is used to compare against the quantum yield. If a photon is absorbed, a random number $\xi$ is drawn from a uniform distribution to determine if it is emitted based on the QY of the fluorophore. If $\xi < QY$ then a photon is emitted by the fluorophore. If a photon is not emitted, a counter is updated and a loop is broken by setting the output of move_pho.m function equal to a logical 0. The function photon_emitted.m is then used to randomly sample a photon from the emission spectrum based on a CDF of that emission profile. The extinction coefficient at this wavelength is then used along with the isotropic emission angles to move by a step size $S$.

A photon is described by 5 variables: three spatial coordinates for position and two directional angles for direction of travel. Often it is more convenient to describe them in terms of 3 Cartesian coordinates and three direction cosines. The direction cosine is specified by taking the cosine of angle the photon makes with each axis. $u_x$, $u_y$ and $u_z$ (Prahl et al. 1989, Sahin et al. 2011). With a photon located at $x,y,z$, travelling distance $S$ the new coordinates are updated as follows:

Firstly, the angles of emission are determined using random number $\xi$.

The azimuthal angle is sampled as:

$$\phi = 2\pi \xi \text{ where } \phi \in [0, \pi]$$

The zenith angle $\theta$ is sampled as:

$$\cos(\theta) = 2\xi - 1 \text{ where } \theta \in [0, 2\pi]$$
The new x,y,z coordinates are then determined:

\[
x' = x + \mu_x \Delta S
\]

\[
y' = y + \mu_y \Delta S
\]

\[
z' = z + \mu_z \Delta S
\]

(5.9)

Where \( \mu_x, \mu_y, \mu_z \) are direction cosines determined from the spherical emission angles \( \phi \) and \( \theta \) and calculated as shown in Equation 5.10 (These equations are different when there is scattering involved, this is only for isotropic emission, a mistake made by \cite{Sahin2011}).

\[
\mu_x = \sin(\theta)\cos(\phi)
\]

\[
\mu_y = \sin(\theta)\sin(\phi)
\]

\[
\mu_z = \cos(\theta)
\]

(5.10)

After the photon has been moved, the function isInsideLSC.m is used to determine if the photon is in the LSC by drawing a convex hull around the point and the LSC and comparing to just a convex hull around the LSC. If the photon is still in the LSC it is moved again. If it is not then the function surface_interaction.m is called.

## 5.6 Surface Interaction

Surface interactions are at the heart of the program. The algorithm for determining the outcome of a surface interaction first checks which face, as described in Figure 5.3 is being interacted with and then checks if the photon is reflected or transmitted by calling is_TIR.m function. The state of the boolean variable PH_ACTION is then set depending on if the photon is in the LSC after reflection or if it strikes another boundary. If after reflection the photon remains in the LSC, the new coordinates are updated as according to Equation 5.15 and then the photon is moved again, repeating until it is transmitted through one of the faces.
CHAPTER 5. MONTE CARLO LSC MODEL

Figure 5.3: How each face of the LSC is defined: f1, f2...f6. Taken from Matlab code.

The following are short descriptions of important functions referred to in this Chapter.

**Which_Surface.m**  First, the face the photon interacted with is determined by the function whichSurface().m which returns the face number. Which_surface first checks if the photon has intersected a plane. Then performs a second check by determining if the intersection of the photon and plane lie within the LSC boundaries.

**Is_TIR.m**  Once the face is known the photon is reflected at the air/LSC boundary or transmitted. After striking a face of the LSC, surface interaction calls the function is_TIR to determine if the photon is totally internal reflected or transmitted through the surface. First the critical angle of total internal reflection is taken based on the parameters input in to the main program:

\[
\theta_{\text{crit}} = \sin^{-1}\left(\frac{n_{\text{air}}}{n_{\text{LSC}}}\right)
\]
Then the angle that the photon striking the surface makes with the normal can be easily taken from the direction cosine. For example for faces on the x plane, the direction cosine $\mu_x$ gives the cosine of the angle and the normal of the surface on the x plane so if $|\mu_x| > \theta_{\text{crit}}$ then the photon is internally reflected, otherwise it is transmitted and a photon counter is incremented for that face.

**Reflecting photon at a boundary** To find the final position of a totally internally reflected photon after reflection, we need to find the x,y,z coordinates of the intersection of the line connecting the start and the final position (Equations 5.13). The line is then reflected at the intersection point. To determine the intersection, first need the plane equations for each face of the LSC. The equation of each face can be determined given the normal of that plane and a point on the plane $p_0$:

**Face 1:**

$\hat{n} = (0, 1, 0) = (a, b, c)$

$p_0 = (\text{lsc width}, 0, 0)$

$a(x - x_0) + b(y - y_0) + c(z - z_0) = 0$

$1(y - 0) = 0$

$y = 0$  \hspace{1cm} (5.11)

The equation for **Face 1** plane is $y=0$. Using the same method equations were obtained for:

**Face 2:** $x = lsc_{\text{width}}$

**Face 3:** $y = lsc_{\text{length}}$

**Face 4:** $x = 0$  \hspace{1cm} (5.12)

**Face 5:** $z = 0$

**Face 6:** $z = lsc_{\text{height}}$

**Parametric equation joining lines** Once the plane equations are known, need a parametric form of the vector joining two points P0 – the origin of the photon in the LSC and P1 the final location of the photon after being moved. The parametric
form of vector joining $P_0$ and $P_1$:

$$r(t) = P_0 + t \overrightarrow{P_0P_1}$$

where $P_0 = (x_0, y_0, z_0)$ and $P_1 = (x_{pos}, y_{pos}, z_{pos})$

Finding the point of intersection for example for Face1:

Face 1 plane Equation is $y = 0$ and parametric equation can be expanded as:

$$x = x_0 + t \overrightarrow{P_0P_1}(1)$$

$$y = y_0 + t \overrightarrow{P_0P_1}(2) = 0 (plane\ equation)$$

$$z = z_0 + t \overrightarrow{P_0P_1}(3)$$

(5.13)

t can be solved for by setting the parametric Equation 5.13 equal to the plane Equation 5.11

$$t = \frac{y - y_0}{\overrightarrow{P_0P_1}(2)}$$

(5.14)

The solution to Equation 5.14 can then be substituted in to the remaining Equations of 5.13 to find the remaining coordinates of the point of intersection with the plane.

For Face 1 after reflection, the new points would be: $P_{new} = [x_{pos}, -y_{pos}, z_{pos}]$.

$$P_{new} = [x_{pos}, -y_{pos}, z_{pos}]$$

(5.15)
CHAPTER 5. MONTE CARLO LSC MODEL

Figure 5.4: Monte Carlo simulations program flow.

5.7 Comparison with Literature

The output of the program is a count of number of photons that exited each face of the LSC. The optical efficiency ($\eta_o$) is then determined from the ratio of photons leaving the side faces divided by photons entering the LSC top receiving face. Table 5.1 compares the model with good experimental work done by Tummeltshammer et al. (2016) for two different concentrations. At both concentrations the model compares well with experiment. For the lower concentration of 10 ppm there is slightly higher
discrepancy that could be due to effects such as waveguide scattering/absorption playing a more prominent part in the experimental work but that effect is neglected in the Monte Carlo simulations. Furthermore, the fractional absorption of Lumogen Red 305 at a particular concentration was compared by integrating the actual AM 1.5 spectrum and dye absorption spectrum, in Excel. The results agreed to within 0.5 %.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Concentration</th>
<th>(\eta_0)</th>
<th>(\eta_0) this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tummeltshammer et al. (2016)</td>
<td>10 ppm</td>
<td>59.2</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>150 ppm</td>
<td>49</td>
<td>52.5</td>
</tr>
</tbody>
</table>

*Table 5.1: Comparison of optical efficiency with published work*

### 5.8 Investigating LSC Geometry

The Monte Carlo code described in this Chapter was developed to assist with selecting a geometry for later work. An Evonik fluorescent for fabricating LSCs was purchased and imported from Germany. The properties of the sheet are summarised in Table 5.2. This sheet is used for the hybrid prototype in Chapter 6 and also for the full length collector in Chapter 7.

The size of the LSC modules to be used in Chapter 7 was determined by using the Monte Carlo code to investigate various geometries as summarised in Table 5.3. The width of the modules is fixed at 12.5 cm (the aperture of the CPC), the length was then varied in the simulations. We do not know the exact concentration of dye in the sheet but from the literature can estimate it to be around 200 ppm (Desmet et al. 2012, Kerrouche et al. 2014) and for comparison various concentrations were investigated. The geometric concentration ratio for all geometries is 1.67, as one length is kept constant. The final design for Chapter 7, taking into account a desire not to have too many modules was to have 4 modules of 12 cm x 25 cm with an optical efficiency of between 2.2 % and 2.7 %. To collect generate more electricity, initially it was planned to have solar cells around all edges of the module however, it was eventually decided to put solar cells along the length of the modules and not in between modules as it was realised that they would heat up significantly. and wiring would be much more complicated. Consequently the size of the modules matters less.
CHAPTER 5. MONTE CARLO LSC MODEL

<table>
<thead>
<tr>
<th>Sheet Specifications</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>4 m x 3 m</td>
</tr>
<tr>
<td>AM 1.5 Transmission</td>
<td>Advertised as 85%, measured 91.4%</td>
</tr>
<tr>
<td>Thickness</td>
<td>3 mm</td>
</tr>
<tr>
<td>Fluorescent material</td>
<td>Assumed to be Lumogen Red 305</td>
</tr>
<tr>
<td>Concentration</td>
<td>Unknown</td>
</tr>
<tr>
<td>LSC waveguide</td>
<td>Perspex (PMMA)</td>
</tr>
</tbody>
</table>

Table 5.2: Evonik Fluorescent sheet PLEXIGLASS Red 3C50 GT properties.

5.9 Conclusion

This Chapter has presented the development of Monte Carlo ray-tracing code, for simulating planar LSCs at normal angles of incidence. The code has been shared open source and can be found on the Matlab Mathworks open source sharing platform with the title 'Monte Carlo Raytracing of a Luminescent Solar Concentrator'. The results were compared with literature and found to match well. The code was then used to estimate optical performance of large area LSCs. The following chapters in this thesis present work done demonstrating the hybrid CPC and LSC collector.
<table>
<thead>
<tr>
<th>LSC Conc</th>
<th>Length cm</th>
<th>Optical Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 ppm</td>
<td>100</td>
<td>2.03</td>
</tr>
<tr>
<td>250 ppm</td>
<td>50</td>
<td>2.2</td>
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<tr>
<td>250 ppm</td>
<td>25</td>
<td>2.6</td>
</tr>
<tr>
<td>250 ppm</td>
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</tr>
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</tr>
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</tr>
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</tr>
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<td>100</td>
<td>1.78</td>
</tr>
<tr>
<td>100 ppm</td>
<td>50</td>
<td>1.91</td>
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<tr>
<td>100 ppm</td>
<td>25</td>
<td>2.18</td>
</tr>
<tr>
<td>100 ppm</td>
<td>12.5</td>
<td>2.53</td>
</tr>
</tbody>
</table>

Table 5.3: Investigation of different size LSC modules for full length collector. The width of all sizes is 12 cm and the thickness 0.3 cm, the length was then varied. The optical efficiency is the percentage of incident photons that are transmitted through all four edges. Number of photons propagated for each case was 1 million.
Chapter 6

Hybrid CPC and LSC Prototype

6.1 Introduction

In this Chapter, an experimental basis for a novel hybrid solar photovoltaic and thermal collector is presented. This is the first such example of combining the two technologies. The hybrid collector is based on two non-imaging concentrators; the luminescent solar concentrator (LSC) and the compound parabolic concentrator (CPC). The beam splitting LSC is used as a cover for the thermal collector, necessary as in the field to protect reflective mirrors from soiling and gathering dust. At the same time, the LSC guides a narrow band of incoming photons, shifted to more efficient wavelengths, to its edges where solar cells are attached. In this configuration the thermal absorber is decoupled from the LSC allowing the cells to operate at a cooler temperature. Furthermore LSCs are one of the few solar concentrators that can collect diffuse radiation.

This Chapter presents a proof-of-concept device consisting of an involute shaped compound parabolic concentrator and an evacuated tube placed along the focal length, but only a part of the tube is used. The CPC is 3D printed, suitable for a proof of concept however, this technique is not economically viable for larger collectors. Two different LSC covers are compared with different transmission characteristics. The performance of the hybrid collector is characterised indoors under one sun condition. Current-voltage curves are used to characterise electrical performance of the LSCs and the no-flow stagnation test is to characterise the performance of the CPC. By comparing the performance of the hybrid prototype in different configurations this work essentially demonstrates the experimental basis for a new hybrid PV and thermal collector.
6.2 CPC Specifications

As a proof of concept, a small prototype CPC and LSC hybrid was developed based on the concept schematic shown in Figure 6.1. The involute compound parabolic shape was designed to be combined with a cylindrical receiver made up of an absorber within an evacuated tube and a 3 mm clearance gap between absorber and glass envelope. The evacuated tube was manufactured in China and obtained from Greenland Systems solar company - it has been difficult obtaining detailed information about the nature of the selective surface absorber, furthermore some evacuated tubes arrived from the manufacturer with no vacuum at all.

The CPC has an aperture area of 15 cm and an absorber of radius 0.87 cm, giving a concentration ratio on the absorber of 2.74. Using Equations 2.15, an extruded profile of length 10 cm was generated. Then using CAD software, a profile was created as shown in Figure 6.2, the height was truncated by 70% to save on material costs. This was then 3D printed with the polymer ABS, polished until smooth and coated with highly reflective sputtered aluminium. The properties of the CPC are summarised below in Table 6.1 and the properties of the evacuated tube receiver are summarised in Table 6.2.

![Figure 6.1: Schematic of a hybrid involute shaped CPC with an LSC cover.](image)
CHAPTER 6. HYBRID CPC AND LSC PROTOTYPE

Figure 6.2: CAD image used to 3D print the CPC prototype used in this Chapter.

<table>
<thead>
<tr>
<th>CPC Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius absorber</td>
<td>8.7 mm</td>
</tr>
<tr>
<td>Gap between absorber and glass</td>
<td>3 mm</td>
</tr>
<tr>
<td>Aperture</td>
<td>15 cm</td>
</tr>
<tr>
<td>Concentration ratio</td>
<td>2.74</td>
</tr>
<tr>
<td>Acceptance half angle</td>
<td>21.4°</td>
</tr>
<tr>
<td>Mirror reflectance</td>
<td>AM 1.5 weighted average of 91 %</td>
</tr>
<tr>
<td>Truncation</td>
<td>70 %</td>
</tr>
<tr>
<td>Cost to 3D manufacture</td>
<td>$200 (material cost only)</td>
</tr>
</tbody>
</table>

Table 6.1: Prototype CPC specifications.

<table>
<thead>
<tr>
<th>Evacuated Tube Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius absorber</td>
<td>8.7 mm</td>
</tr>
<tr>
<td>AM 1.5 Absorption ($\alpha$)</td>
<td>Unknown</td>
</tr>
<tr>
<td>Selective surface</td>
<td>Unknown</td>
</tr>
<tr>
<td>Glass thickness</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Glass type</td>
<td>Borosilicate</td>
</tr>
<tr>
<td>Glass AM 1.5 Transmission ($\tau$)</td>
<td>92 %</td>
</tr>
</tbody>
</table>

Table 6.2: Evacuated tube specifications.
6.3 LSC Specifications

6.3.1 Sunpower cell characterisation

Sunpower back contact cells arrive as large squares and are cut to desired size with a silicon dicing saw. The thickness of fluorescent sheets used is 3 mm so all PV cells had a 3 mm width as shown in Figure 6.3. Two lengths were used, 5 cm and 9.5 cm. Bare cell testing of the 9.5 cm length was found to have an average efficiency of 9.5 % and the 5 cm length was found to have an efficiency of 15 %. A possible explanation for the discrepancy of the performance is that the thinly cut cells could have micro fractures effecting performance and recombination losses could be occurring at the edges before electron/hole pairs get a chance to be converted to electricity (so called edge recombination losses). The LSCs described below had 9.5 cm cells placed along the 10 cm edge of the LSC and along the 15 cm length both 9.5 cm an 5 cm cells were attached. Each cell had individual wiring that was connected together in parallel externally. Shown in Figure 6.3 is a magnified view of the microwire required to connect the cell to a bus bar where a larger wire can be soldered. These microwires are very difficult to solder and reduce the robustness of the device. Epoxy resin is added over the top in attempt to protect the wires on the LSC device.

![Magnified view of wires of Sunpower back contact PV cell set up for bare cell testing.](image)

6.3.2 LSC design

For the prototype cover, two LSCs were fabricated from commercially available fluorescent sheets as shown in Figure 6.9 (left). A pink sheet, commercially fabricated by Evonik and a red sheet named Mars Red 4156 purchased on the online trading...
The properties of the LSCs are summarised in Table 6.3. Several attempts were made to discover the specific fluorescent material used in the red sheet, particularly since this red sheet performed very well. A mass spectrum was obtained as shown in Appendix A2 and the atomic mass of the dye must be either 376 or 375 (dye-H+) or 353 (dye-Na+) Daltons, despite having this information, the dye could not be identified.

The absorption and emission spectra of both red and pink LSCs are shown in Figure 6.4 and Figure 6.5. It can be seen from spectra of the two sheets that the red absorbs much more of the visible spectrum than the pink, with a small overlap between emission and absorption. The pink sheet however has a large separation between absorption and emission, a high Stokes shift, good for LSC performance. Figure 6.6 shows the pink and red sheet absorption overlaid with the AM 1.5 solar spectrum. Here it’s very obvious just how transparent the pink sheet is to the solar spectrum. The AM 1.5 averaged absorption was calculated for the pink sheet to be 8.6 % and red sheet to be 32.8 %. The high transparency of the pink sheet is useful for collecting most of the energy as heat in the solar thermal collector.

<table>
<thead>
<tr>
<th>LSC Specifications</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>10 cm x 15 cm x 0.3 cm (both)</td>
</tr>
<tr>
<td>Geometric concentration</td>
<td>15 (both)</td>
</tr>
<tr>
<td>Optical coupling</td>
<td>Silicone Elastosil Solar 2202</td>
</tr>
<tr>
<td>Red LSC fluorescent material</td>
<td>Unknown</td>
</tr>
<tr>
<td>Pink LSC fluorescent material</td>
<td>Lumogen Red</td>
</tr>
<tr>
<td>LSC waveguide</td>
<td>Perspex (both)</td>
</tr>
<tr>
<td>Solar Cell</td>
<td>Sunpower cell cut to 3 mm thickness and coupled on each edge, then all outputs connected in parallel</td>
</tr>
</tbody>
</table>

Table 6.3: LSC prototype cover specifications.
CHAPTER 6. HYBRID CPC AND LSC PROTOTYPE

Figure 6.4: Absorption/emission spectra of the Evonik pink fluorescent sheet.

Figure 6.5: Absorption/emission spectra of the red fluorescent sheet.

Figure 6.6: Absorption spectra of the red and pink sheets overlaid with the AM 1.5 solar spectrum.
6.4 Experimental Setup

Indoor performance testing of the hybrid collector was undertaken with a triple-A rated Photo Emission Tech Inc. solar simulator, in an experimental set up as shown in Figure 6.7. The solar simulator was calibrated with a (calibrated) pyranometer to provide 1000 W/m$^2$ onto the aperture of the CPC.

To measure electrical performance of the LSC cover, IV curves were taken with the same set up as described in Figure 4.15. The experiment compared both pink and red LSC covers. IV curves were measured under three different conditions shown below with their corresponding labels on the resulting IV curves:

- LSC only (without the CPC) placed onto an absorbing material (TiNOX). This is necessary to stop reflected photons passing back into the LSC.
- LSC coupled with the CPC collector at the start of illumination (cold).
- LSC coupled with the CPC collector and after three hours of illumination (after 3 hours).

Thermal performance is characterised by measuring the stagnation temperature of various configurations of the device. Performance testing of solar collectors describes stagnation temperature as maximum achievable collector temperature, this occurs at zero flow conditions where the heat input is equal to the heat loss. The collector is left illuminated until this maximum temperature is reached, providing a useful comparison of the different configurations. Because heat input is equal to heat loss a simple equation could be used to estimate the heat loss coefficient. However, this requires knowledge of detailed characteristics of the absorber, something the manufacturer of the evacuated tube did not want to disclose.

The thermal receiver used in the experiment is shown in Figure 6.8, the 10 cm required was left bare while the remainder of the tube was wrapped in foil and the ends were insulated. The tube is comprised of a selective surface absorber in an evacuated tube. To measure the stagnation temperature three k-type thermocouples were placed inside the tube - one at the far end, one in the middle in the active area and one at the near end of the entrance. The values reported are from the middle thermocouple, placed in the active area.

A national instruments data logger was used to measure the temperature and the hybrid configuration was left to stagnate under the solar simulator for up to 3 or more hours, there were at least 5 measurements made of each configuration. The hybrid prototype under test conditions can be seen in Figure 6.9 (right).
CHAPTER 6. HYBRID CPC AND LSC PROTOTYPE

Figure 6.7: Experimental setup for indoor testing of the hybrid CPC and LSC.

Figure 6.8: Thermal receiver used for prototype LSC and CPC. 10 cm of receiver was left bare and the rest covered with aluminium foil.

Figure 6.9: Pink and red LSCs covers (left) and the hybrid device under solar simulator (right).
6.5 Results

The stagnation temperature results for different configurations are shown in Figure 6.10. The stagnation temperatures of the different configurations (ambient subtracted) are: 208°C for the CPC without an LSC cover, 192°C for the CPC with the pink LSC cover, 150°C for the CPC with the red LSC cover and 77°C for the tube on its own under one sun illumination (this value is comparable to the full length tube stagnation test). This value is representative of the poor quality of these tubes received from the manufacturer, an evacuated tube with a proper vacuum and a good selective surface should be able to stagnate at over 200°C [Pailthorpe et al. (1987)]. Nevertheless it is suitable for comparing different configurations.

The red LSC performed better electrically than the pink one, as expected, with a corresponding trade-off in thermal energy absorbed at the receiver. This arrangement is more suitable if increased electrical output is desired. The pink LSC allows a much higher stagnation temperature, which would maximise thermal power but produce less electrical output. The overall power conversion efficiency (with respect to the AM 1.5 solar spectrum) is low as expected, the pink LSCs with their low solar absorption generate a very modest amount of power and the red LSCs perform well. Without an LSC, the CPC increased the stagnation temperature of the tube from 77°C (with no concentration) to 208°C, a result indicative of the excellent performance of these types of solar concentrators. Attaching the pink LSC lowered the stagnation temperature to 191°C and the less transparent red LSC lowered the stagnation temperature to 150°C but increased electrical output by a bit over three times. Adding the pink LSC corresponds to a decrease in stagnation temperature of only 8.2% and the red LSC reduces the stagnation temperature by 27.9%. Thus the prototype collector has successfully demonstrated the ability to reach high stagnation temperatures even with an LSC cover.

Pink and red LSC IV curves were measured twice during the stagnation temperature experiment, at the beginning of the experiment and after three hours. The performance of both LSCs decreased after three hours, the pink LSC short circuit current reduced by 40% and the red LSC short circuit current reduced by 16% (results are summarised in Table 6.4). This is an interesting result considering LSCs are claimed to decouple PV cells from the heat generating area, since it’s the LSC that receives light and heats up and is thought not to transmit much heat to the solar cells around the edge. It remains unclear however if it is the solar cell around the edge of the device that is heating up, if the performance of the polymer itself is degrading or even if the behaviour of the fluorescent material changes with temperature.
the temperature of a polymer such as PMMA is increased, its refractive index changes due to a change in its thermo-optic coefficient, an increase in temperature causes a decrease in refractive index which would lead to a decrease in waveguiding performance of the LSC \cite{Zhang16}. This behaviour is little reported in LSC literature. An analysis of thermal performance of LSCs was completed by \cite{Rajkumar15}, who studied the temperature of LSCs under illumination. The authors found the surface of the LSC reached a temperature of 50°C after one hour and the edge mounted solar cells remained 10°C cooler. In reality all these effects come into play as well as ambient temperature and presence of heat transfer due to conduction (it is not windy inside the lab). Measurements were also taken by placing the LSC only, on a highly absorbent “black” material TiNOX that does not reflect any photons back into the LSC. The IV curves are summarised in Figure 6.11 and Figure 6.12. It can be seen that simply placing the LSC on the CPC improves performance, that is the performance of the LSCs improves compared with simply measuring on the black absorber, shown as an increase in short circuit current. The reason for this is that some isotropically emitted photons from within the LSC are emitted into the CPC at angles that do not result in them being transmitted to the receiver and hence reflect back into the LSC. This is an interesting result showing LSCs perform better in this new application than on their own. When comparing the open circuit voltages, in both Figures 6.11 and 6.12 it can be seen that the open circuit voltage decreases after 3 hours in the solar simulator, expected semi-conductor behaviour. Voc also decreases when the LSCs are measured with TiNOX, this could be due to the LSC heating up as the TiNOX absorbs most of the light heats up.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/chapter6/figure6_10.png}
\caption{Stagnation temperature results of various configurations of the hybrid collector.}
\end{figure}
Figure 6.11: Pink LSC IV curves of various configurations.

Figure 6.12: Red LSC IV curves of various configurations.
### CHAPTER 6. HYBRID CPC AND LSC PROTOTYPE

#### Configuration Short circuit current LSC PCE at maximum power point Stagnation temperature (Tabs - Tamb) °C

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Short circuit current</th>
<th>PCE at maximum power point</th>
<th>Stagnation temperature (Tabs - Tamb) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red LSC on CPC after 3 hours</td>
<td>485 mA</td>
<td>0.98 %</td>
<td>150°C</td>
</tr>
<tr>
<td>Red LSC on CPC</td>
<td>578 mA</td>
<td>1.30 %</td>
<td></td>
</tr>
<tr>
<td>Red LSC on TiNOX</td>
<td>473 mA</td>
<td>0.99 %</td>
<td></td>
</tr>
<tr>
<td>Pink LSC on CPC after 3 hours</td>
<td>111 mA</td>
<td>0.20 %</td>
<td>191°C</td>
</tr>
<tr>
<td>Pink LSC on CPC</td>
<td>185 mA</td>
<td>0.43 %</td>
<td></td>
</tr>
<tr>
<td>Pink LSC on TiNOX</td>
<td>68 mA</td>
<td>0.14 %</td>
<td>191°C</td>
</tr>
<tr>
<td>CPC with no LSC</td>
<td></td>
<td></td>
<td>208°C</td>
</tr>
<tr>
<td>Tube alone</td>
<td></td>
<td></td>
<td>77°C</td>
</tr>
</tbody>
</table>

*Table 6.4: Summary of performance of LSC and CPC hybrid collector showing short circuit current, power conversion efficiency (PCE) and stagnation temperature results.*

### 6.6 Conclusion

The experimental basis for a new type of hybrid photovoltaic and thermal concentrator based on two non-imaging technologies, the CPC and the LSC has been successfully demonstrated. As a solar thermal collector requires a cover to protect it from the environment, this work demonstrates a new type that generates electricity with LSCs. There exists much scope on optimizing such a system depending on what the desired fluid temperature is or desired power output for a given load (for example powering a motor or sensors). Additionally, performance of LSCs will continue to improve with new material breakthroughs. It was interesting to see how the LSC performance increased upon combination with the CPC. The LSC emits some photons into the CPC at angles that do not get reflected to the receiver, these photons are then reflected back into the LSC getting a chance to be absorbed again, indicative of a good coupling of the two technologies.
Chapter 7

Full Length Hybrid CPC and LSC Collector

7.1 Introduction

In the previous Chapter a small prototype hybrid CPC and LSC was shown to reach high stagnation temperatures even with the LSC cover. In this Chapter the previous work is extended further to a full length, 1 meter long CPC. This full length collector was connected to a solar test rig on the roof of building 57 at RMIT University in Melbourne at GPS coordinates 37°48'20"S, 144°57'56"E. The collector was mounted in the east-west direction and connected to a fluid delivery system. The CPC was covered with LSCs and flow experiments were performed to determine the instantaneous thermal efficiency whilst IV curves determined electrical output. This work demonstrates the benefits of using this system as a decoupled photovoltaic and thermal collector capable of delivering medium temperature heat and electricity.

Figure 7.1: Hybrid CPC and LSC solar collector mounted on the test rig.
7.2 LSC Configuration

7.2.1 LSC design

A large sheet of Evonik PLEXIGLASS Red 3C50 GT was cut into four modules to cover the 1 m length CPC collector. The Monte Carlo code developed in Chapter 5 was used to determine the size of modules to be 25 cm x 12 cm, as shown in Section 5.8. The thickness of the sheet was 3 mm and the edges were all polished until they became optically smooth using sandpaper and polishing oil. Solar cells were placed along the top edge and bottom edge as shown in Figure 7.2 but not sandwiched in between modules as they would heat up too much and it would be difficult to seal the collector.

<table>
<thead>
<tr>
<th>LSC Specifications</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>12 cm x 25 cm x 0.3 cm</td>
</tr>
<tr>
<td>No. modules</td>
<td>4</td>
</tr>
<tr>
<td>Optical coupling</td>
<td>Silicone Elastosil Solar 2202</td>
</tr>
<tr>
<td>Fluorescent material</td>
<td>Lumogen Red</td>
</tr>
<tr>
<td>Concentration</td>
<td>Unknown</td>
</tr>
<tr>
<td>LSC waveguide</td>
<td>Perspex</td>
</tr>
<tr>
<td>Solar cell</td>
<td>Sunpower cell cut to 3mm thickness</td>
</tr>
</tbody>
</table>

*Table 7.1: LSC module specifications for full length collector.*

*Figure 7.2: A close up view of the CPC and LSC collector describing the top edge and bottom edge electrical outputs.*
CHAPTER 7. FULL LENGTH HYBRID CPC AND LSC COLLECTOR

7.2.2 Sunpower cell characterisation

As introduced in section 6.3.1, the Sunpower PV cells need to be diced to a desired geometry and soldered with micro wires. The front active face of the cells are then coupled with the LSC edges with silicone gel that is left to set overnight, while the back contacts and wires face away from the device. For the larger LSCs in this Chapter sizes of 11.5 cm and 11 cm were cut, one of each to be accommodated onto each module length of 25 cm. To obtain bare cell efficiencies four samples of each size were soldered and mounted as shown in Figure 7.3. For the 11 cm cells after fabrication only two were working and measured efficiencies of 9.6 % and 14.1 %. A large variability in power conversion. For the 11.5 cm cells, three were working and measured efficiencies of 12.5 % and 12.1 % 15.9 %. These results highlight the variability and sensitivity of these cells to fabrication by human hand. The micro wires are delicate and the diced edges appear crudely cut at times. The sliver cells used in Chapter 4 had similar issues. For this reason the optical efficiency of LSCs has not been estimated as it would require a performance measurement with and without solar cells. The large variability in performance renders such a measurement meaningless.

![Figure 7.3: 11 cm (left) and 11.5 cm (right) length Sunpower cells used to test bare cell efficiency.](image)
7.3 CPC configuration

A one metre length CPC was fabricated in the workshop at RMIT University, from jelutong, a type of wood. The specifications of the full length CPC are slightly different to Chapter 6. The properties of the receiver remain the same but the aperture is reduced to 11 cm. The CPC was sanded and then coated with high gloss polyurethane ready for the reflective foil to be laid down. The reflective film, purchased online was found to have a solar weighted reflectivity of 90%.

The receiver consisted of an evacuated tube with a selective surface absorber purchased from Greenland Systems, with the same specifications as the tube used in Chapter 6. Unfortunately the supplier refused to provide samples of the selective surface on a flat piece of metal for characterisation.

<table>
<thead>
<tr>
<th>CPC Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius absorber</td>
<td>8.7 mm</td>
</tr>
<tr>
<td>Gap between absorber and glass</td>
<td>3 mm</td>
</tr>
<tr>
<td>Aperture</td>
<td>11 cm</td>
</tr>
<tr>
<td>Concentration ratio</td>
<td>2.01</td>
</tr>
<tr>
<td>Half acceptance angle</td>
<td>$29.8^\circ$</td>
</tr>
<tr>
<td>Mirror reflectance</td>
<td>AM 1.5 weighted average of 90 %</td>
</tr>
<tr>
<td>Truncation</td>
<td>70 %</td>
</tr>
</tbody>
</table>

*Table 7.2: Full Length CPC specifications.*

<table>
<thead>
<tr>
<th>Receiver Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius absorber</td>
<td>8.7 mm</td>
</tr>
<tr>
<td>Radius of outer glass</td>
<td>11.7 mm</td>
</tr>
<tr>
<td>Outer glass thickness</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Material</td>
<td>High borosilicate glass</td>
</tr>
<tr>
<td>Glass transmission</td>
<td>$&gt; 90 %$</td>
</tr>
<tr>
<td>Selective coating</td>
<td>Unknown</td>
</tr>
<tr>
<td>Length including bellows</td>
<td>1.2 m</td>
</tr>
</tbody>
</table>

*Table 7.3: Evacuated tube specifications.*
CHAPTER 7. FULL LENGTH HYBRID CPC AND LSC COLLECTOR

7.4 Experimental Setup

The CPC and LSC hybrid collector was mounted east-west orientation onto a test rig that also performs two dimensional solar tracking. Tracking was used to keep the collector normal to the sun for performance measurements, to minimise as much as possible non-normal incidence angle effects. This is a standard method for testing solar collectors as found in the AS/NZS 2535.1:1999 standards.

The collector is connected to the fluid delivery system via T junctions that were placed at the inlet and outlet of the collector. The closed loop fluid delivery system is composed of a heater and cooling fan that can control the input temperature of the collector via a PID controller and thermocouple at the heater outlet. The SCADA screen to control the rig is shown in Figure 7.4.

The front view of the solar test rig is shown in Figure 7.5. In this Figure can be seen the two pyranometers on top of the rig used to measure global and diffuse radiation incident on the collector. The inlet and outlet of the fluid delivery system are also shown. Figure 7.6 shows a side view of the collector mounted on the tracker, set up for IV curve measurements. The fluid delivery system is not shown in these Figures. To determine the thermal instantaneous efficiency several measurements need to be made as described next.

Figure 7.4: SCADA screen shot of test rig and fluid delivery system.
CHAPTER 7. FULL LENGTH HYBRID CPC AND LSC COLLECTOR

Temperature measurements

Three temperature measurements are required: the fluid temperature at the collector inlet, $T_{in}$ ($^\circ C$), the fluid temperature at the collector outlet $T_o$ ($^\circ C$) and the ambient temperature, $T_{amb}$ ($^\circ C$). These temperature measurements as well as flow rate and other measurements are measured in steady state or quasi-steady-state. That is when the variables have stabilised enough to be considered essentially constant. To measure inlet and outlet temperature, two pt100 4 wire RTD thermocouple probes were placed at T junctions. The RTDs were calibrated with a high precision reference and measurements were stable to two decimal points. All plumbing exposed to air was covered in insulated wool and thick Al tape. Another RTD was used to measure ambient temperature.

Measurement of collector fluid mass flowrate

The mass flow rate in the fluid delivery system is controlled with a variable speed pump and measured with a micro Coriolis effect flow meter. The heat transfer fluid used in this experiment is Therminol 66, a widely used high performance fluid for solar thermal collectors, for use with temperatures up to 345$^\circ$C. Using the data sheet of Therminol 66, a target mass flow rate was calculated with the aim of minimising the flow rate (maximising $\Delta T$) whilst maintaining the fluid in the turbulent regime as described in Appendix A4.

Radiation incident on collector

To calculate efficiency, the radiation incident on the collector needs to be measured. Two pyranometers that are mounted on the tracker measure global and diffuse irradiance (W/m$^2$). As the LSC and CPC hybrid can collect diffuse radiation the global incident radiation measurement ($G$) is used when calculating instantaneous thermal efficiency. The solar energy intercepted by the collector is equal to $A_g G$, the product of the aperture area of the collector $A_g$ and global incident radiation.

IV curve measurements

The IV curve measurement set up is shown in Figure 7.6. A laptop and Ketithley source measuring unit were brought to the roof and connected to the LSC for measurement. Several measurements were taken, initially and after several hours of
tracking. At least four measurements were taken at a time. The top and bottom outputs of the LSC were connected either in parallel or series for comparison.

Figure 7.5: Front view of the solar test rig showing the CPC and LSC hybrid collector mounted onto the 2D tracker as well as pyranometers measuring radiation.

Figure 7.6: Side view of the collector mounted onto the tracker, in this case set up for IV measurements of the LSCs.
7.5 Results

Thermal performance

The thermal performance of the collector was determined by obtaining values of instantaneous efficiency for combination of measured incident radiation, inlet/outlet temperatures and flow rate in a steady or quasi steady state. The useful power extracted $\dot{Q}$ is determined by Equation 7.1

$$\dot{Q} = \dot{m} C_p \Delta T$$  \hspace{1cm} (7.1)

Where $C_p$, the specific heat capacity at the mean fluid temperature is taken from the data sheet of Therminol 66, the mass flow rate $\dot{m}$ and $\Delta T$ are measured as described in Section 7.4. From this, the steady state thermal efficiency of the collector can be calculated by the following equation:

$$\eta = \frac{\dot{m} C_p \Delta T}{G_{eff} A}$$  \hspace{1cm} (7.2)

Where: $G_{eff}$ is the global solar irradiance measured by the pyranometer and $A$ is the area of the collector, in this case 0.12 m$^2$. The measurements were made after waiting for the inlet temperature and mass flow rate to stabilise, then the values were recorded for at least 10 minutes at a rate of one measurement per second. Then the inlet temperature was increased again and the process repeated. The efficiency was calculated for each sample and then averaged.

To maximise $\Delta T$, the temperature increase in the collector it was necessary to aim for as low mass flow rate as possible whilst maintaining a turbulent regime (Table 7.4 summarises the $\Delta$Ts measured in the experiment).

The thermal efficiency as a function of fluid inlet temperature is shown in Figure 7.7. An uncertainty analysis was undertaken as shown in Appendix A5. The reason for the large error bars is due to the small $\Delta T$ being measured. While each RTD that measures inlet and outlet has an uncertainty of $+/−0.082 \, ^\circ\text{C}$ when uncertainties are propagated due to taking a difference between the two measurements the uncertainty of $\Delta T$ becomes $+/−0.117 \, ^\circ\text{C}$ and results in the large error bars despite the results showing as expected behaviour. In future work, a different heat transfer fluid which allows operating at lower flow rates or a longer receiver may be considered to increase the temperature at the outlet and minimise uncertainties in the measurements.
CHAPTER 7. FULL LENGTH HYBRID CPC AND LSC COLLECTOR

Figure 7.7: Instantaneous thermal efficiency plotted as a function of fluid inlet temperature the CPC with and without an LSC cover.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Δ T bare CPC</th>
<th>Δ T LSC + CPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>110</td>
<td>0.23</td>
<td>0.21</td>
</tr>
<tr>
<td>130</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>150</td>
<td>0.19</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 7.4: Average delta T at various inlet temperatures measured in the experiment.

LSC performance results

The LSC cover was made up of four LSC modules with properties described in Table 7.1. The modules all have Sunpower solar cells along the two long edges. All the cells along the top of the LSC and all the cells along the bottom of the LSC are connected in parallel as shown in Figure 7.2, these form two outputs at the top and the bottom of the collector. IV curves were measured with these outputs connected in series or parallel and representative curves are used below.

Figure 7.8 shows the IV curve when the outputs are connected together in series. The power-voltage curves comparing series and parallel connections are shown in Figure
The series connected output has a maximum power of 0.220 W and performs better than the parallel connected output achieving only 0.167 W. With a power input on to the LSC area of 120 W gives an overall LSC cover efficiency of 0.183 %. This is an efficiency based on the AM 1.5 solar spectrum.

As described at the end of Chapter 5 in Table 5.3, the optical efficiency of each module is low (and unknown as the dye concentration is unknown). To calculate the expected power conversion efficiency, the optical efficiency is then multiplied by the solar cell efficiency (approximately 15 %) so this value of LSC efficiency is in the expected range. It is worth remembering the pink LSC itself only absorbs 8.5 % of the solar spectrum then various other losses reduce this.

IV measurements were repeated after 3 hours in the sun, there was found to be negligible change in the IV performance indicating that the cells were not heating up significantly. This is different to the results in Chapter 6 could possibly be explained by the low ambient temperatures recorded during the experiment of 12°C and windy conditions on the roof where the experiment took place.

Figure 7.8: IV curves of top and bottom outputs connected in series.
7.6 Conclusion

In this Chapter the feasibility of using a luminescent solar concentrator as a cover for a full one meter length CPC solar thermal collector was demonstrated. Four LSC modules were fabricated with high efficiency Sunpower silicon solar cells and placed along the two sides of the LSC modules.

The hybrid collector was mounted to a two-dimensional solar test rig that also comprises a fluid delivery system. In this way thermal efficiency values were obtained of the collector with and without the LSC cover.

It was found that there was only around a 3 % difference in thermal efficiency for inlet temperatures of 110\(^o\)C and 130\(^o\)C that increased to over 5 % for 150\(^o\)C. For an inlet temperature of 90\(^o\)C the flow was not yet turbulent and the values were very similar. However, after completing uncertainty analysis, due to the small temperature difference being measured, large uncertainties were introduced into the calculation rendering it difficult to tell the difference between a CPC on its own and a CPC with an LSC cover.

IV curves were used to characterise the LSCs and measurements were taken after first mounting on the collector and also after tracking the sun for several hours. It was assumed that the LSCs would heat up and their performance would decrease however there was no noticeable change in their performance, most likely due to cool
ambient air (between 10 - 12 °C) preventing them from heating up.

IV measurements compared connecting outputs together in series or parallel. It was found connecting them in series reduced losses in the contacts compared to parallel. In the best performing series configuration the LSC has an overall power conversion efficiency of 0.183 % generating only a modest amount of power while most is converted to thermal. There is a lot of scope as LSC technology performance improves for these types of collectors to further improve electrical performance.
Chapter 8

Conclusion

This thesis presents the work done over three and a half years at RMIT University. The main aim of this work was to investigate if the two non-imaging technologies, the luminescent solar concentrator and the compound parabolic collector could be combined in a novel hybrid configuration to generate both electricity and medium temperature heat.

The two components were studied separately, it was shown in the literature review that the compound parabolic concentrator performs better than other solar thermal collectors at a wide range of temperatures and was a good choice for a photovoltaic and thermal collector. It was realised that losses in the receiver of an involute compound parabolic concentrator were not being consistently evaluated in the literature and ray-tracing was used to better describe those losses.

The luminescent solar concentrator was investigated with collaborators from The University of Melbourne. By using flexible silicon SLIVER solar cells, circular shaped LSCs were investigated with very bright, high quantum yield quantum dots. Both liquid and solid waveguides were investigated and it was realised that at higher concentrations the Stokes-shift of the fluorescent material used needs to be significantly improved to improve device efficiency and work needs to be done on modifying surface properties of quantum dots to be able to embed them successfully in polymers at high concentrations.

Using liquid waveguides, scattering only regimes were investigated for light guiding in luminescent solar concentrators and it was found that a significant amount of light can be guided to the edges based on scattering alone, essentially coming up with the basis of a frosted glass style LSC.
CHAPTER 8. CONCLUSION

Utilising commercially available large area fluorescent sheets, it was demonstrated experimentally that a photovoltaic-thermal collector can work well when an LSC is used as a cover for a CPC. First a small 10 cm x 15 cm prototype was stagnated in indoor test conditions and found to reach temperatures of up to 208°C without an LSC and 191°C with an LSC with a high transmission, in this configuration not much thermal energy is sacrificed for a modest gain in electricity generation.

Finally a solar test rig was used to demonstrate a full length CPC and LSC hybrid collector. Four LSC modules were fabricated and connected first in parallel then it was found less losses occurred (noticed by a much better fill factor) when the two sides of cells were connected in series, producing over 220 mW. IV measurements were taken again after several hours on the rig and it was found the performance of the LSCs did not decrease but this was most likely due to the experiment being run during cold days when ambient temperature was around 10-12°C. The thermal efficiency was measured for a variety of inlet temperatures and varied between 55% and 40% but with a high uncertainty. It was demonstrated that an LSC works well as a cover for a solar thermal receiver, although only generating modest amounts of power. The near future holds exciting possibilities of precisely engineering optical properties of LSCs, perhaps one day we will be able to fabricate LSCs bottom up, molecule by molecule similar to 3D printing and once materials breakthroughs occur and LSCs can be engineering with tightly controlled optical properties, this type of PV-T collector will be able to perform even better.

Suggestions for future work

- As a high refractive index of the waveguide is key to trapping a large amount of photons, it is surprising how little work has been done focusing on improving waveguide materials. There exists scope to investigate materials such as high refractive index nano-composite waveguides, for example made with TiO₂.

- Nano rods emit photons preferentially in one plane, work needs to be done on aligning nano-rods in a polymer so photons can be emitted in the direction of solar cells in the waveguide.

- Quantum dots cannot be embedded nicely in polymers at high concentrations, there needs to be detailed work done on the surface chemistry required to disperse nano-particles in polymers nicely.

- The complexity of the Monte-Carlo developed in this thesis can be increased to add effects of scattering, variation in angles of incidence and ability to simulate thin films.
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Appendix A

A.1 Fabrication of quantum dots, quantum rods and silca nanoparticles

Preparation of stock solutions
Cd-phosphonate was formed by reacting 0.06 g CdO with 0.28 g octadecylphosphonic acid (ODPA) in 3 g TOPO. All reagents were weighed into a 3-neck round-bottom flask equipped with a glass magnetic stirrer and degassed at 100°C for 1 hr under vacuum (~1 mbar pressure). The flask was then flushed with nitrogen and heated in TOPO at 350°C until the solution became clear, indicating the formation of Cd-ODPA. Once the solution was clear, 1.8 mL TOP was added via syringe. Water formed during the reaction was removed by degassing the solution at 150°C for 1 hr under vacuum. TOP-Se (1.5 M) was made by dissolving 2.37 g Se in 20 mL TOP at room temperature in a nitrogen glovebox. Cadmium oleate (0.168 mol L⁻¹) was prepared in a nitrogen glovebox by mixing anhydrous cadmium acetate (0.50 g, 2.17 mmol), oleic acid (1.225 g, 4.34 mmol) and ODE (10.14 mL) in a glass bottle. The mixture was heated to 300°C until the solution became clear then allowed to cool to room temperature. When the solution reached 150°C during cooling, oleylamine (1.43 mL, 4.34 mmol) was added to prevent solidification of the cadmium oleate at room temperature.

CdSe core synthesis
CdSe cores of various diameters were synthesised by injecting TOP-Se into a heated solution of cadmium phosphonate in TOPO as reported by (Carbone et al., 2007). The as-prepared Cd-ODPA precursor in TOPO was heated to 370°C in a three-neck
APPENDIX A.

flask. Once the solution reached 370°C, 0.5 mL of 1.5 M TOP-Se (0.75 mmol Se) was swiftly injected into the flask. The solution changed colour from clear to yellow to red as quantum dots nucleated and grew. To prevent further growth once the desired size was reached, the reaction was quenched by removing the heat source. Once cooled to 100°C, 5 mL of toluene was injected to prevent solidification of the TOPO. The cores were washed three times by precipitation with methanol and re-dispersion in chloroform. The precipitate was isolated from the supernatant by centrifugation (3,300 RCF, 4 minutes) and discarded. After the final wash the cores were dissolved in hexanes and passed through a 0.2 micron PTFE filter.

Growth of CdS shells

The epitaxial growth of CdS onto CdSe cores was performed according to the method published by Boldt et al. (2013). Briefly, ODE (3 ml), oleylamine (3 ml) and 100 nmol of CdSe cores in hexane were loaded into a three-neck flask and degassed under vacuum at 50°C for 45 minutes followed by 15 minutes at 120°C. The temperature was raised to 310°C under a nitrogen atmosphere at a heating rate of 12°C /min. Starting at 230°C solutions of cadmium oleate and octane thiol were injected from separate syringes with a syringe pump, each diluted with ODE to give a final volume of 3 mL per 2 monolayers of shell to be added. The precursor amounts were calculated from the core particle sizes and desired shell thickness using the expected change in shell volume per monolayer, as described (van Embden et al., 2009). A 1.2-fold excess of thiol (to Cd) was used, and the injection rate was adjusted to add the equivalent of two monolayers of CdS per hour. After the addition of precursors was completed the temperature was lowered to 200°C and 1 ml of oleic acid was added drop-wise. The reaction mixture was annealed for 1 hour at this temperature then washed three times via precipitation with acetone, centrifugation (3,300 RCF, 4 minutes), and re-suspension in hexanes. Growth of CdSe/CdS dot-in-rods The epitaxial growth of CdS rods around CdSe cores was performed according to the method published by Carbone et al. (2007). Briefly, 3 g TOPO, 0.290 g of ODPA, 0.080 g of hexylphosphonic acid, and 0.086 g of CdO were added to a three-neck flask and heated under vacuum at 150°C for 1 hour. The resulting solution was heated to 350°C under nitrogen until clear after which 1.5 g of TOP was injected. When the temperature recovered to 350°C, a solution of CdSe cores in TOP and (80 µmol of QDs dissolved in 1.5 g TOP + 0.120 g ) was injected and allowed to grow for 6 minutes before cooling and washing three times with toluene and methanol.

Silica particle preparation Silica particles dispersible in toluene were prepared by surface modification of commercial silica particles (Ludox HS-40) with octadecyltrimethoxysilane. 3 ml of silica particles, originally dispersed in water, were precipitated by 1 ml
of ethanol and centrifuging at 3,000 RCF for 10 minutes. The precipitate was resuspended in 25 ml of ethanol, then added of 0.05 ml of octadecyltrimethoxysilane and 5 ml of an ammonia solution.
A.2 Mass spectroscopy of red fluorescent sheet

Figure A.1: Mass spectrometer data - A fragment of about 1 g of the sample was dissolved in 10 ml of chloroform, then diluted with methanol 20 times. 100 uL of that solution were analysed using an Exactive Plus Orbitrap Mass Spectrometer (Thermo Scientific).
A.3 Geometric concentration ratio calculations for chapter five

![Diagram showing LSC dimensions with fixed width of 12.5 cm and varied length.]

**Figure A.2: LSC dimensions, width is fixed at 12.5 cm and length is varied**

<table>
<thead>
<tr>
<th>Thickness (cm)</th>
<th>Width (cm)</th>
<th>Length (cm)</th>
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<th>Asides</th>
<th>CR/module</th>
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<td>100</td>
<td>1250</td>
<td>750</td>
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</tr>
<tr>
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<td>375</td>
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<td></td>
<td>1.67</td>
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</table>
A.4 Reynolds number calculation for flow experiment

When conducting collector thermal efficiency experiments, the flow in the absorber is required to be turbulent to enhance heat transfer (Re > 3000). The Reynolds number equation for a flow through a pipe is used to characterise the flow.

\[ Re = \frac{\rho v D_h}{\mu} = \frac{v D_h}{\nu} = \frac{Q D_h}{\nu A} \]  

(A.1)

Where \( Q_d \) is the hydraulic diameter of the pipe (m), \( Q \) is the volumetric flow rate (m\(^3\)/s), \( A \) is the pipe cross-sectional area (m\(^2\)), \( v \) is the mean fluid velocity, \( \nu \) is the kinematic velocity = \( \frac{\mu}{\rho} \) (m\(^2\)/s), \( \mu \) is the dynamic viscosity of the fluid (Pa.s = N.s/m\(^2\) = kg/m.s) and \( \rho \) is the density of the fluid (kg/m\(^3\)).

Our high temperature rig measures mass flow rate, the volumetric flow rate is shown in Equation A.2 (Density data obtained from Therminol 66 data sheet).

\[ \dot{Q} = \frac{\dot{m}}{\rho} = kg \frac{1}{s} m^3 \frac{1}{kg} = \frac{m^3}{s} \]  

(A.2)

\[ \dot{v} = \frac{\dot{m}}{\rho A} = kg \frac{1}{s} m^3 \frac{1}{kg} \frac{1}{m^2} = \frac{m}{s} \]  

(A.3)

Utilising these equations it was decided to keep the mass flow rate at .15 kg/m\(^3\) then the Reynolds number is above 3000 for temperatures above 100\(^\circ\)C.
A.5 Uncertainty analysis

To calculate instantaneous thermal efficiency of the hybrid collector, measurements of the above mentioned variables need to be calculated to obtain the desired result. Experimental measurements will inherently contain errors that differ from the true value, uncertainty analysis attempts to quantify the range in which the error lies. The uncertainty $U_r$ of the result $r$ is calculated as the root sum square of two components: the bias (systematic) error and the precision (random) error, as shown below in Equation (A.4).

$$U_r = B_r^2 + P_r^2$$  \hspace{1cm} (A.4)

An error is a precision error if it contributes to scatter of data, otherwise it is a bias error. The systematic nature of bias errors means the same error will be measured no matter how many times the measurement is repeated. The precision error is calculated based on how many times the measurement is repeated.

**Bias Error**  
Bias errors can be inferred for example from data sheets and often can be reduced by proper calibration. Sometimes they can be correlated for example when sensors have been calibrated on the same instrument. When several uncorrelated bias sources, $k$ exist for an $i_{th}$ measured variable, the estimate is measured as the root sum square of the sources as shown in Equation (A.5).

Uncertainty of the standard - calibration Steady state - no heating up differences

$$B_i^2 = \sum_{n=1}^{k} b_k^2$$  \hspace{1cm} (A.5)

**Precision Error for a single measurement**  
Precision errors can be analysed using statics and repeating a measurement will reduce the precision error. The precision error can be estimated as shown in Equation (A.6).

$$P_r = t S_r$$  \hspace{1cm} (A.6)

Where $S_r$ is the standard deviation of the sample of N readings and $t$ is the statistical coverage factor. Essentially a scaling number that represents how close the spread of data is to a normal distribution. For the calculations in this Chapter a value of $t = 2$ suffices. This value gives a confidence of 95%.
Calculated Value  Sometimes it is necessary to calculate the uncertainty of a value based on several measured variables. If the uncertainties of the direct measurements are known, the total uncertainty is calculated using the common formulas for propagating uncertainties as shown in Appendix.

Temperature

The pt 100 RTDs used to measure temperature inlet and outlet are calibrated with a high accuracy reference RTD with uncertainty of +/- 0.03°C. They are calibrated with the same DAQ system used for testing the solar collector so bias errors to do with the DAQ are accounted for in the calibration. The RTDs are connected in a 4-wire configuration to reduce lead resistance losses.

The bias error for input and output RTDs is shown below:

\[ B_{\text{input,RTD}} = \sqrt{0.03^2 + 0.017^2} = +/ - 0.035 \, ^\circ\text{C} \]  \hspace{1cm} (A.7)

\[ B_{\text{output,RTD}} = \sqrt{0.03^2 + 0.0072^2} = +/ - 0.031 \, ^\circ\text{C} \]  \hspace{1cm} (A.8)

The maximum precision error for each RTD is shown below (multiplied by 2 due to the coverage factor):

\[ P_{\text{input,RTD}} = 2 \times 0.037 = +/ - 0.074 \, ^\circ\text{C} \]  \hspace{1cm} (A.9)

\[ P_{\text{output,RTD}} = 2 \times 0.038 = +/ - 0.076 \, ^\circ\text{C} \]  \hspace{1cm} (A.10)

Therefore the overall uncertainty is:

\[ U_{\text{input,RTD}} = \sqrt{0.074^2 + 0.035^2} = +/ - 0.082 \, ^\circ\text{C} \]  \hspace{1cm} (A.11)

\[ U_{\text{output,RTD}} = \sqrt{0.076^2 + 0.031^2} = +/ - 0.082 \, ^\circ\text{C} \]  \hspace{1cm} (A.12)

The uncertainty of the ambient temperature RTD was calculated by a previous research group member as shown below:

\[ U_{\text{ambient,RTD}} = +/ - 0.125 \, ^\circ\text{C} \]  \hspace{1cm} (A.13)
APPENDIX A.

Mass flow rate

The data sheet of the flow meter showed a 0.2 % bias error. The random error of the flow meter, calculated by a previous research group member, was 0.000362 kg/s. The desired flow rate for the thermal efficiency experiment was 0.16 kg/s.

\[ B_{m} = \sqrt{(.002 \times .16)^2 + .000362^2} = +/- 0.00048 \text{ kg/s} \quad \text{(A.14)} \]

The largest standard deviation associated with flow rate measurements was 0.00398.

\[ U_{m} = \sqrt{(0.00048)^2 + .00398^2} = +/- 0.0004 \text{ kg/s} \quad \text{(A.15)} \]

Pyranometer

The pyranometers used in experiments are class A Middleton EQ08. In the data sheet the following uncertainties are reported:

- \( B_{\text{zero offset}} < 3 \text{ W/m}^2 \)
- \( B_{\text{non-stability}} < -0.5 \% \)
- \( B_{\text{non-linearity}} < +/- 0.5 \% \)
- \( B_{\text{directional response}} < 15 \text{ W} \% \)
- \( B_{\text{spectral selectivity}} < +/- 3 \% \)
- \( B_{\text{temperature response}} < 2 \% \)
- \( B_{\text{tilt response}} < +/- 0.25 \% \)
- \( B_{\text{calibration}} = 46 \text{ W/m}^2 \)

Therefore at 1000 W/m\(^2\):

\[ U_{\text{pyro}} = \sqrt{3^2 + 5^2 + 5^2 + 15^2 + 3^2 + 20^2 + 2.5^2 + 46^2} \\
= +/- 53.1 \text{ W/m}^2 \\
= +/- 5.31 \% \quad \text{(A.16)} \]

Propagation of uncertainty

To calculate the instantaneous thermal efficiency the following equations must be solved.

\[ \eta = \frac{\dot{m}C_p(t_{out} - t_{in})}{G_{eff} A} \quad \text{(A.17)} \]

First the propagation of uncertainties must be calculated.
**APPENDIX A.**

**Propagation for addition or subtraction**  For calculating the uncertainty of a value $Q$ that is either a result of addition or subtraction of some variables $x,y$. Then the sum of root of the squares is used:

$$U_Q = \sqrt{(U_x)^2 + (U_y)^2} \quad (A.18)$$

Therefore the uncertainty of $t_{out} - t_{in}$:

$$U_{t_{o} - t_{i}} = \sqrt{(0.082)^2 + (0.082)^2} = +/ - 0.117 \, ^\circ\text{C} \quad (A.19)$$

**Propagation for division or multiplication**  The method for calculating the propagation of uncertainty due to division or multiplication is shown below:

$$Q = \frac{a b ..}{x y ..} \quad (A.20)$$

$$\frac{U_q}{|Q|} = \sqrt{\left(\frac{U_a}{a}\right)^2 + \left(\frac{U_b}{b}\right)^2 + \left(\frac{U_x}{x}\right)^2 + \left(\frac{U_y}{y}\right)^2}$$