

A Cradle-to-Deposition Life Cycle Assessment of Emerging Photovoltaic Materials

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ABSTRACT

With the photovoltaic industry receiving a lot of attention due to its potential benefit to alleviate the dependence of fossil fuels. This work analyses the environmental impact of emerging methods for the deposition of leading photovoltaic materials used in thin film technologies.

The impact results are gained from adopting a standardised life cycle assessment (LCA) of which the photovoltaic materials are analysed from their extraction 'cradle' to the point at which they are deposited.

This work focuses on the impact categories such as resource depletion, eco-toxicity and global warming due to literature review highlights that these are the key areas of concern in LCA of photovoltaic materials. The outcome of this analysis allows a clear recommendation to be established as one of the photovoltaic thin films produces a result with significantly lower impact scores in all of the impact categories.

ABBREVIATIONS

CdTe	Cadmium Telluride
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CIGS	$\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$
CZTS	$\text{Cu}_2\text{ZnSnS}_4$
DC	Direct Current
GHG	Greenhouse Gas
ISO	The International Organization of Standardization
LCA	Life cycle Assessment
LCI	Life Cycle Inventory
NPAG	Northumbria Photovoltaics Application group
PV	Photovoltaic
SETAC	Society of Environmental Toxicology and Chemistry
TF	Thin Film
CO ₂ -eq/kWh	Carbon dioxide equivalent (CO ₂ -eq) is a measure describing the climate-forcing strength of a quantity of GHG using the functionally equivalent amount of CO ₂ as the reference. One gram (g) = 10 ⁻³ kilograms (kg, SI) ≈ 0.035 ounces (oz); one kilowatt-hour (kWh) ≈ 3.6 × 10 ⁶ joules (J, SI) ≈ 3.412 × 10 ³ British thermal units (BTU).

Keywords: Life Cycle Assessment; Photovoltaic Materials; LCA; PV materials; CIGS; Toxic Emissions

1. INTRODUCTION

In the wake of an increasing requirement for power created by renewable energy technologies to meet the target of global warming (Yang et al., 2015), the need for alternative energy sources has grown substantially and in turn produced several methods of alternate energy production (Ellabban et al., 2014); most noticeably wind, tidal and solar. Solar energy is the process by which solar radiation converted into electricity by photovoltaic materials (Singh., 2013)). The photovoltaic (PV) materials sector have grown by as much as 85% since 1997 (Haberlin and Eppel., 2012). However as the materials used in solar energy are created using nanotechnology, Candelise et al., (2011) suggest these new materials may have potential risks on the environment. Therefore, Hunt., (2006)., highlights the emphatic need for LCA of these emerging materials using the existing work on ultrafine particles from waste and combustion processes.

Solar energy can be harnessed in several ways but thin film solar modules are now seen as the most viable option for wide scale solar energy (Das et al., 2018). Typically the photovoltaic elements contained in these modules are constructed from one of two materials either cadmium telluride (CdTe) or $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ (CIGS) this due to the materials beginning to realistically produce energy at a cost which is similar to that of the energy already being produced (Wolf et al., 2012).

LCA is an analytical method to determine the environmental impacts of materials or products by looking at a wide array of factors. Using LCA, this work aims to evaluate CIGS and CdTe PV materials to compare with the newly emerged method pioneered by the NPAG of the PV material $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) (Qu et al., 2014).

Advanced nanotechnology can be used to create a wide array of different materials, which have several different purposes. One of these areas attracting a lot of attention is PV paints. PV paints are used to generate electricity as a viable source of green energy (Zhang et al., 2018). Due to the infancy of the area little is known about the long term environmental impacts these PV paints could have; therefore, upon the development of a new PV material CZTS ($\text{Cu}_2\text{ZnSnS}_4$) a cradle to deposition LCA approach is required to determine the potential environmental impacts. These results is compared in a cradle to deposition assessment of two currently active PV materials, CIGS ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$) and CdTe to establish its potential viability.

This work focuses on toxic emissions, resource depletion and any contribution to GHG. All of these areas are of particular concern to any nanomaterial's and due to the scarce nature of some of the materials within the PV films (Celik et al., 2018).

2. LITERATURE REVIEW

Solar energy creates through the process of nuclear fusion, which regards as an ongoing process from the energy output of the sun (Mertens., 2018). This energy then radiates outward and covers the earth. Solar energy is receiving a lot of attention partially due to the significant abundance of the natural power source especially when compared to other types of natural energy (Velloso et al., 2019), this is shown in Table 2. The clear and evident abundance of solar energy highlights its potential ability to

alleviate the over reliance on fossil fuel energy sources and potentially reduce the overall GHG emissions which in turn could reduce the effects of global warming (Salim et al., 2019).

Table 1: Natural Power Source (Wolf., 2012)

<u>Natural Power Source</u>	<u>Power (Terawatts)</u>
Global Power Consumed	14.7
Solar Input onto Land Mass	30500
Wind	840
Ocean Waves	56
Ocean Tides	3.5
Geothermal World Potential	32.2
Global Photosynthesis	91
River Flow Energy	7

Fahrenbruch and Bube, (2012) suggest that when collecting energy there are two positions such as a ground based collection system or space based systems. The latter has an advantage because solar radiation is blocked or deflected by the atmosphere and solar energy is available all the time. However, the initial energy investment are (i) getting a system into place and (ii) the obstacle of transporting the collected energy. Neville then establishes the following table which shows an array of solar energy collection devices from both the natural world and also man made systems.

Table 2: Immediate Source (Fahrenbruch and Bube, 2012).

<u>Immediate Source</u>	<u>Remarks</u>
<u>Biological</u>	
Trees	This energy source does not utilize the energy in sunlight very efficiently
Specialized Plants	
Waste Materials	
<u>Temperature Differences</u>	
Wind	

Waves	Primarily Windmills. However, it has been suggested that the UK could use energy from the ocean waves as its sole source.
<u>Solar-Thermal</u> Heating & Cooling Mechanical	The provision of heat for heating and cooling buildings, process heat and hot water.
<u>Solar-Electric</u> Solar-Thermal Electric Thermoelectricity Photovoltaics	A variety of techniques for converting the energy in sunlight to electrical energy.

One of the most convenient of these methods of transforming solar energy is solar-electric, as it is easy to transport and the energy produced is readily converted into a different form of energy. The excess energy can be stored efficiently onto the plates of capacitors. The work carried out by Nelson., (2003) lead them to the assumption “direct conversion of solar energy to electric power by thin-films (TF) PV devices appears to be the ideal solution”.

PV materials convert solar radiation in a one step process from light to electrical energy by using the photons or “packets of energy” within light to excite electrons to a point which they are released from the material to create a surplus charge and in turn a direct current flow (Nelson., 2003). This current flow can be manipulated into other forms of energy. As such, TF PV devices are seen as the ideal manner solution to harnessing solar energy.

A PV cell consists of a thin film of semi-conducting material typically only a few micrometres thick which is either physically or chemically deposited onto a substrate. These small cells have a typical size of around 100 cm² and produce small currents to amplify the photovoltaic effect to generate a direct current (DC) output voltage. These modules can be implemented in small appliances or together in large modules to generate potentially large quantities of energy.

Just as there are several methods for harnessing solar energy, there is also an array of PV materials. Most notably CdTe (cadmium telluride), CIGS (copper indium gallium selenide) and a-Si all of which are receiving fast growth both in terms of sales and in

terms of research. This is contributing to a decrease in cost of manufacturing as well as increasing efficiencies (Sopori et al., 2012).

In regards to CdTe, Goetzeberger., (1999) sees it relative infancy being “close to an ideal solar cell” with efficiencies of 16% having been achieved and ability to be deposited in an easy manner which attributes the material to potentially being able to be mass produced quickly. However, upon further investigation Goetzeberger (1999) states that this may not be entirely flawless due to its use of cadmium and may produce long scale environmental impacts.

Wolf (2012) states that CdTe and CIGS TF cells are most likely to provide a viable option as both can be produced in economical production lines and have high absorption coefficients. The cells absorption layer can be as low as 3 μ m meaning a very small quantity of the active PV materials need to be generated. The work carried out the Northumbria PVs Application group CZTS can be seen as a viable option to be used in high efficiency TF solar cells (Qu et al., 2014).

Due to the novel nature of the area there is only a limited number of research performed LCA on photovoltaic materials such as CdTe and CIGS (Giacchetta et al., 2013; Xie et al., 2018). In the work published by Fthenkias et al., (2009) establish that there are two methods in the production of CdTe. These are electro deposition and high rate vapour transfer of the two compounds both of these methods are approximately 90% efficient in their use of cadmium and tellurium mass. They illustrate that in the initial production of the cadmium and tellurium is indeed a recycling process. With regards to cadmium it is primarily retrieved as a by-product from the extraction of zinc ores due to zinc is being able to be produced in very large quantities. In the disposal of cadmium it is either buried in cement or disposed of as a hazardous material due to its potentially disastrous effects to eco and human toxicity levels. Tellurium is mainly produced via recovered slimes formed in the electrolytic refining of copper (Fthenakis., 2004)., tellurium production can be incredibly wasteful as high as only 10% of the tellurium in the initial ores being extracted. The majority of the emissions in the creation of tellurium are attributed to copper. Fthenkias and Kim et al., (2014) also state that tellurium is a scarce metal highlighting the need for its resources to be managed carefully.

In the work presented by Kim et al., (2014) the CdTe PV system is shown to have incredibly positive results in terms of a CO₂-eq/kWh which results in a very low impact towards global warming. Kim et al., (2014) state that the initial energy used in the creation of these modules can be paid back within 342 days and the initial CO₂ impact can be paid back after 277 days. The LCA showed that CdTe have a considerably lower environmental impact than a comparative a-Si module. However Raguei et al., (2011)'s work highlight that upon disposal of CdTe PV modules the need for "stringent" controls on cadmium disposal to maintain the low risk of potentially damaging cadmium waste flows.

In the production of CIGS the metals gallium, indium and selenium are of particular concern due to their relative scarcity. Indium and gallium are produced through recovering processes either in the production of other metals particularly copper and zinc or with the two metals being leached into a solution from gaseous streams. The CIGS films toxicity credentials have been questioned in the journal presented by Brun et al., (2016) in which the cadmium, indium and gallium leached into the surrounding freshwater due to acidic rain reacting with the films. This highlights the evident need to pay close attention to the toxicity levels within the potential impact of CIGS films. Due to the novel nature of the production of CZTS there are very limited reliable sources on the LCA of this PV material.

The recent emergence of a potential wide scale use of nanotechnology PV production presents a research gap in the environmental and indeed ethical side of these materials (Kawajiri et al., 2016). As suggested by Rickerby and Morrison (2007) due to the wide potential use of nanotechnology and advanced materials across multiple industries the environmental effect could theoretically be significant as a result the author recommends the use of LCA techniques in the production of new nanotechnology products. In contrast to this, the majority of the population see the more positive ethical implications of PV technologies. This is due to solar energy as a viable and green replacement to the high emitting fossil fuel energy, which has incredibly high ethical concerns into the ability to achieve the 2°C target of global warming. On the basis of the subjects novel nature few LCA reports exist when examining PV materials however the works from Kim et al., (2014); Fthenikas (2004) and Fthenikas et al., (2009) were of particular use highlighting key impact categories of concern in a LCA of PV materials.

3. METHODOLOGY

Adhering to the established LCA ISO 14040 standards and practices. A comparative cradle-to-deposition LCA is developed for comparing the production of three pioneering PV materials namely; CdTe, CIGS and CZTS. This work analyse the new thin films purely on its environmental standpoint which could allow PV films to be produced with lower environmental impacts. Environmental impact results are calculated using the ReCiPe midpoint (E) method. This method is used when a final result is needed and the method such as ReCiPe is strongly recommended by Cheung et al., (2017).

The PV materials selected will follow a standard functional unit in which the area of the films will be 1 m² however the masses will alter due to their differing densities. The environmental impacts of the materials will be assessed with particular attention on resource depletion, human toxicity and eco-toxicity. Global Warming equivalent will also be closely monitored due to the climate change act now establishing legal targets for GHG emissions.

Fig 1 illustrates the underlying principles to an LCA. As is evident all of the standards and different areas of an LCA interact with each other highlighting the importance for each of these to be carried out with integrity so that none of the other areas are affected.

- (i) Goal and Scope Definition
 - Define intended Functional Unit
 - Outline System Boundary
 - Highlight any assumptions used
- (ii) Inventory Analysis
 - Collate data for CdTe, CIGS and CZTS from reputable sources.
 - Feed data into the LCA analytical tool
- (iii) Impact Assessment
 - Analyse results produced from the LCA software focusing particular attention to Toxicity levels, Resource depletion and CO₂-eq/kWh categories.
 - Look at results impact and how each PV material performs in differing categories.

(iv) Interpretation

- Analyse the results in accordance to the intended goal and scope definition.
- Use the results produced to recommend the PV Film with lowest environmental impact.

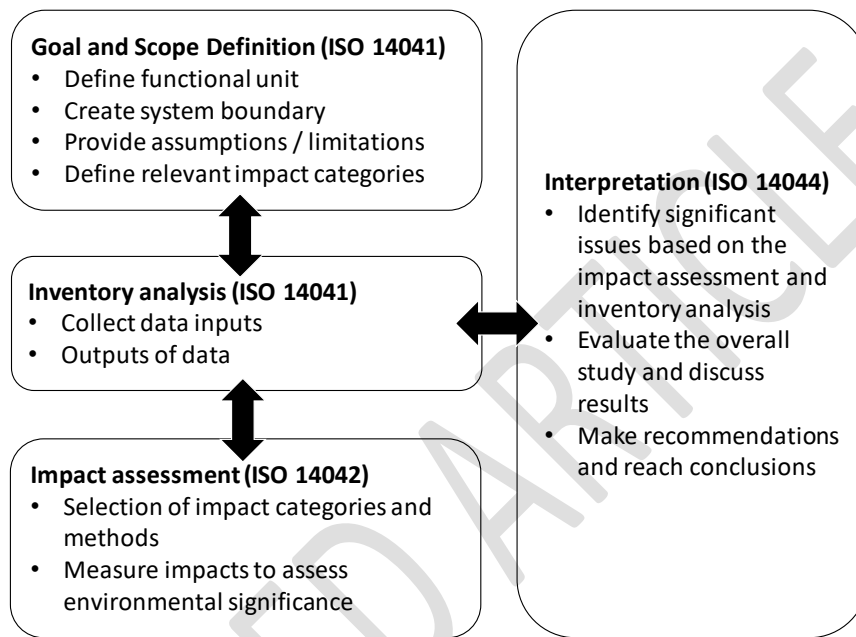


Figure 1 – LCA approach adopted from Klopffer., (2012)

4. CASE STUDIES

In order to generate valid LCA results, reliable data must be collected on CZTS, CdTe and CIGS thin films. These data will be compiled and inputted into a LCA software for a comparative cradle-to-deposition assessment. The three PV materials have been selected due to their potential ability in the future of the PV industry. To ensure that each method analysed is novel, the methods that have been selected will have the potential to affect future synthesis of each type of PV materials. When selecting a method for synthesizing the PV material several factors were taken into account. Firstly, they had to produce high quality films capable of achieving efficiencies of at least 10%. Secondly, the method has to be novel in order to keep the LCA as relevant as possible.

4.1. Data Collection

Throughout the collection of data for the deposition of CZTS thin films the method published by the NPAG was used (Qu et al., 2014).

The data for deposition of CdTe was collected from Schum et al., (2010). This was due to its production of CdTe films which could potentially be used in mass production in an inexpensive route and a more productive method. The data upon the deposition of CIGS was adopted from (Zhou et al., 2013).

4.2. System Boundary

Fig 2 shows the boundary of this investigation in LCA of thin film skin (Kim et al., 2012). The boundary includes water, energy and materials from raw material acquisition to film deposition.

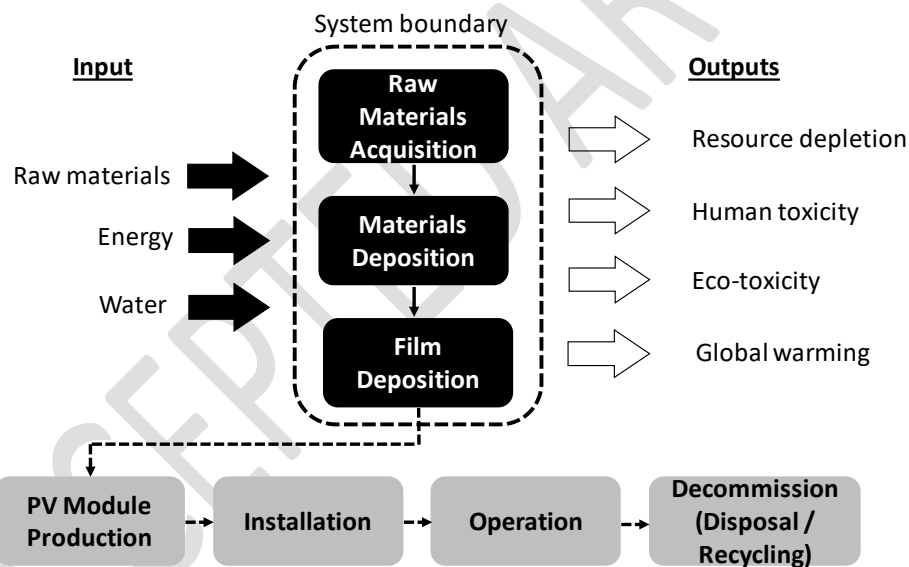


Fig 2 System boundary of LCA PV materials

4.3. Assumptions

The following assumptions have been established for the assessment:

- i. Chemicals are 100% pure.
- ii. Due to the small masses used and the investigation was laboratory based, no transportation values have been used.

- iii. For the addition of heat in the reaction a hot plate has been used and its power consumption increases linearly throughout the heating range (3 W/K of heating with a start power rating of 180 W).
- iv. Vigorous stirring relates to the full watt rating of the motor in the stirring hotplate.
- v. Due to insufficient information available the energy used in creating vacuums have not been accounted for.
- vi. The centrifuges power consumption increases linearly as the rpm increases assuming the max rpm consumes its quoted power rating.
- vii. The use of gases in creating atmospheres is ignored from the LCI.
- viii. As the chamber size in the final step of the deposition of CdTe the ethanol and argon used in flushing the chamber is ignored.
- ix. The spin coater can only coat one film at a time.
- x. The copper, indium and gallium from their acetylacetonate salts used within the CIGS deposition are 25% wasteful and the selenium powder is 66.67% wasteful.
- xi. Within the deposition of CZTS the 25% of the copper inputted is wasted, 47 % of the zinc is wasted, 33.33% of the Tin is wasted and 33% of the sulphur is wasted
- xii. In the deposition of CdTe in accordance to the journal published by Fthenakis [19] the cadmium waste has been set at 10% and from this due to the initial input of molar masses tellurium is assumed to waste 17.5% of the input mass.
- xiii. A functional unit of an area of 1 m² has been decided upon, due to the density differences of CdTe (Schumm et al., 2010), CIGS (Zhou et al., 2013) and CZTS (Qu et al., 2014) results in units of 2477.6 g, 2476.133 g and 2503.04 g respectively.
- xiv. All waste produced has been assumed to be regulated chemical waste.

4.4. The Life Cycle Inventory (LCI) Data Collection of Thin Films Masses

4.4.1 CdTe Data

The molar masses of CdTe are adopted from various sources (Schumm et al., 2010; Sigmaaldrich 2019 a, b) as shown in Table 3:

Table 3 - CdTe

<u>Material</u>	<u>Inputted Value</u>
Cadmium, primary, at plant	370.95 mg
Tellurium, semiconductor - Grade, at plant	459.36 mg
Chemicals Organic, at plant	26970 mg
Ethanol from ethylene, at plant	39.45 mg
Water, Ultrapure, at plant	50 mg
Electricity, high voltage, production GB, at Grid	3924.05 Wh

Please note as illustrated above these mass ratios relate to a production of 0.7129 g. For the production of 1 film a mass of 0.0155 g of cadmium telluride and 1.553 g of washed glass were used (as shown in Appendix A) resulting in a final film weight of 1.5485 g. A thin film of CdTe relates to an area of 625 mm².

4.4.2 CIGS Data

The material for the CIGS film was collated from the method of deposition outlined in Zhou et al., (2013)'s finding. The acetylacetonate salts were inputted into the LCA directory using the method outlined in "4.4.4 Inputted Materials", the values can also be found in Appendix A. The final missing material triethylenteramine was replaced with chemicals organic, at plant" but the mass value of the original triethylenteramine was used.

The mass of CIGS films are adopted from sources of Zhou et al., 2013 and Levi 1984 as shown in Table 4. Please note the values in Table 4 produce 0.14078 g of CIGS. The weight of 1 thin film is 0.55713 g (0.552 g of glass). In this case 1 thin film relates to an area of 225 mm².

Table 4 - CIGS

<u>Material</u>	<u>Inputted Value</u>
Copper (II) Acetylacetonate	130.88 mg
Gallium (III) Acetylacetonate	55.06 mg
Indium (III) Acetylacetonate	144.29 mg
Selenium, at plant	315.84 mg

Chemicals organic, at plant	19640 mg
Electricity, high voltage, production GB, at grid	1909.5 Wh

4.4.3 CZTS Data

The molar masses of CZTS are adopted from various sources (Qu et al., 2014 and Levi 1984) as shown in Table 5. Table 5 illustrates the values used in the LCA software. Please note the values quoted in Table 6 produce a mass of 0.22025 g of CZTS. In order to produce the final film (625 mm²) 1.553 of washed glass is combined with 0.0114 g of CZTS to produce a final film weight of 1.5644 g.

Table 5: Values in LCA

<u>Material</u>	<u>Inputted Value</u>
Copper (II) Acetylacetonate	350 mg
Zinc (II) Acetylacetonate	250 mg
Tin (IV) bis(acetylacetonate)dichloride	290 mg
Sulfur, at Plant	320 mg
Chemicals Organic, at Plant	17532.39 mg
Isopropanol, at plant	51025 mg
Toluene, liquid, at plant	30275 mg
Electricity, high voltage, production GB, at grid	1224.03 Wh

4.4.4 Inputted Materials

The missing acetylacetonate salts from the LCA software were generated through a process outlined by Lappert (1979). Acetylacetone was used in the manufacturing of the acetylacetonate salts; this can be synthesized in the manner outlined by Denoon (2019). Acetylacetone was prepared by mixing 116g of acetone and 510g of acetic anhydride which was then combined with 500g of boron trifluoride. The mixture was then combined with 800g of sodium acetate and 1.6L of water and steam distilled. As no time or temperature is indicated for the steam distilling process, it was assumed that the process took 1h at 120°C. This process also requires the material sodium acetate which is not found within the LCA (Simapro) directory. Sodium acetate can be easily synthesized the reaction of acetic acid and sodium hydroxide. Due to the lack

of information available no energy has been calculated in the creation of sodium acetate and it was assumed to have an 80% yield.

5. Results

The following results were obtained using the Eco-indicator 99 method due to its comprehensive analysis of areas of concern in toxicity and resource depletion. These results were developed upon with the use of the method EDP (2008) V1.03, in order to establish a clear view of the effect these thin-films have on global warming.

Method: Eco-indicator 99 (E) v 2.08: Characterisation

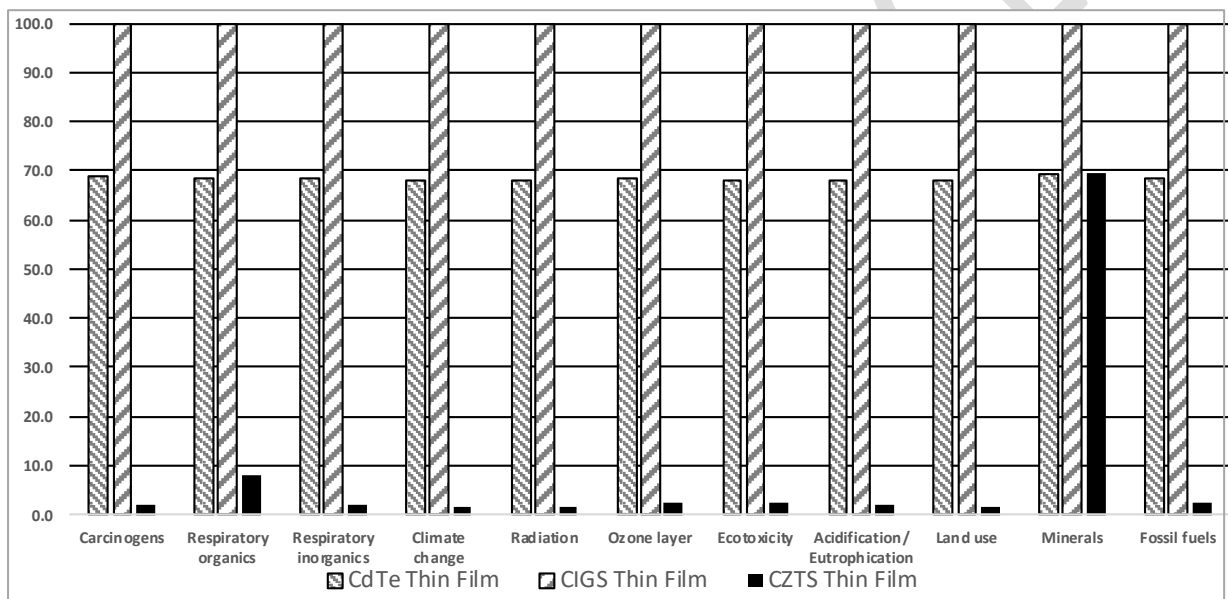


Figure 3 – Characterisation

Table 6 – Characterisation

Impact category	Unit	CdTe Thin Film	CIGS Thin Film	CZTS Thin Film
Carcinogens	DALY	0.000402301	0.000585121	1.15871E-05
Respiratory organics	DALY	5.22708E-07	7.63975E-07	6.27E-08
Respiratory inorganics	DALY	0.001195963	0.001752078	3.50347E-05
Climate change	DALY	0.00062746	0.000919702	1.67403E-05
Radiation	DALY	2.59414E-05	3.80368E-05	5.43436E-07
Ozone layer	DALY	7.20137E-08	1.05406E-07	2.43235E-09
Ecotoxicity	PAF*m2yr	263.520	387.031	9.810

Acidification/ Eutrophication	PDF*m2yr	37.048	54.281	1.046
Land use	PDF*m2yr	18.385	26.937	0.473
Minerals	MJ surplus	7.492	10.797	7.512
Fossil fuels	MJ surplus	2920.678	4278.996	109.359

As can be seen from Figure 3 and Table 6, CIGS consistently achieve the greatest impact and in the opposite manner to CZTS which produces the lowest result except for the field “Mineral Extraction”.

It is worth highlighting that the ratio between the columns relating to CdTe and CIGS produces results that seem in constant proportion to each other with the CdTe falling just below 70% while CIGS always producing a value of 100%.

In Fig 4 and Table 7 the “Damage Assessment” categories which were flagged as areas of concern in the literature review, toxicity values for both human and ecosystem health as well as a view to resource depletion.

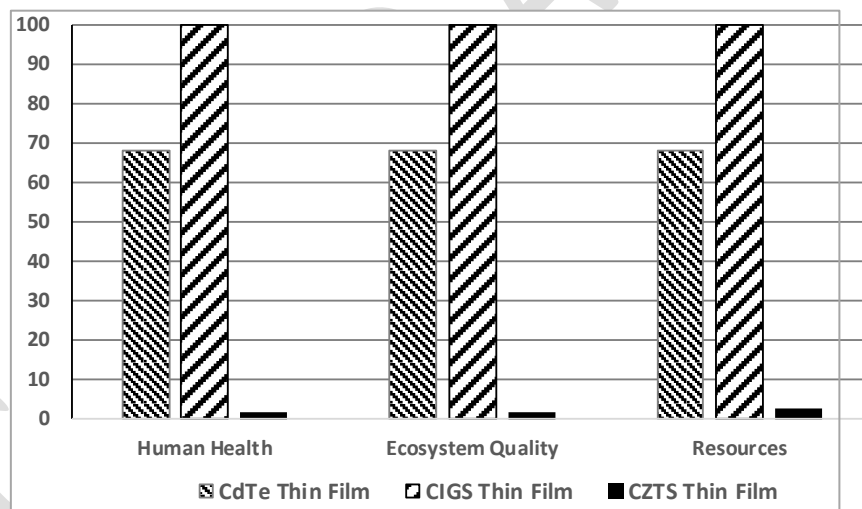


Fig 4 - Damage Assessment (Eco-indicator 99 (E) v 2.08)

Table 7 – Damage Assessment

Damage category	Unit	CdTe Thin Film	CIGS Thin Film	CZTS Thin Film
Human Health	DALY	0.0023	0.0033	0.0001
Ecosystem Quality	PDF*m2yr	81.7852	119.9213	2.5005
Resources	MJ surplus	2928.1692	4289.7926	116.8713

Continuing the trend established in Table 7 and Fig 3 CdTe remains just below the 70% impact rating of CIGS and CZTS shows a vast disparity between the other 2 PV materials.

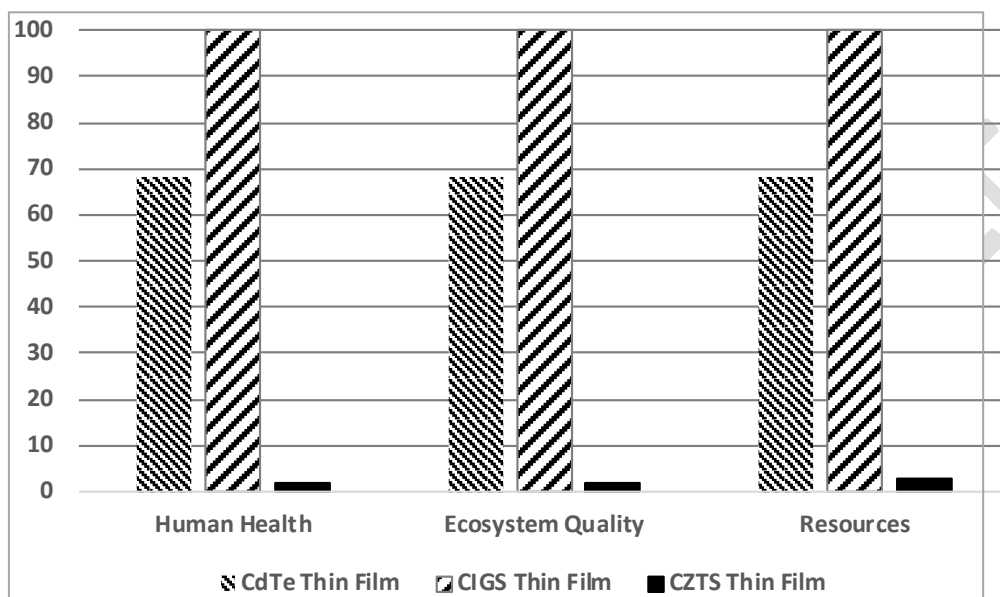


Fig 5 – Normalisation Method: Eco-indicator 99 (E) v 2.08

Table 8 – Normalisation

Damage category	Unit	CdTe Thin Film	CIGS Thin Film	CZTS Thin Film
Human Health	Pt	0.2550	0.3731	0.0072
Ecosystem Quality	Pt	0.0143	0.0210	0.0004
Resources	Pt	0.5236	0.7670	0.0209

When the results were put through a normalisation process, it is evident that following the trend established in the previous results, CZTS still produces vastly lower values than CdTe and CZTS. An important part of this process is to highlight the significant drop in values for the ecosystem quality of which the 0.000437 Pt value produced for CZTS becomes negligible.

The next category is known as “Weighting”, this category weights the important factors to show a truer impact than those produced in the normalisation. These are shown in Fig 6 and Table 9 below.

Table 9 - Weighting

Damage category	Unit	CdTe Thin Film	CIGS Thin Film	CZTS Thin Film
Total	Pt	212.4120	311.0219	7.2507
Human Health	Pt	101.9823	149.2341	2.8966
Ecosystem Quality	Pt	5.7184	8.3849	0.1748
Resources	Pt	104.7113	153.4030	4.1793

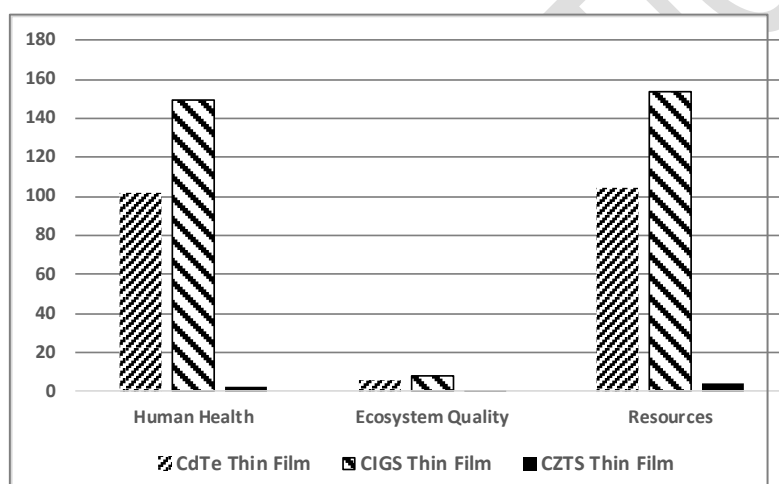


Figure 6 – Weighting

The weighting graph again continues upon previously established trends with CZTS films producing the lowest value consistently. The CIGS film producing consistently the highest values with CdTe producing values just below 70%.

The next results as shown in Fig 7 and Table 10, produce a single score which is designed to contribute the overall impact of each individual thin film.

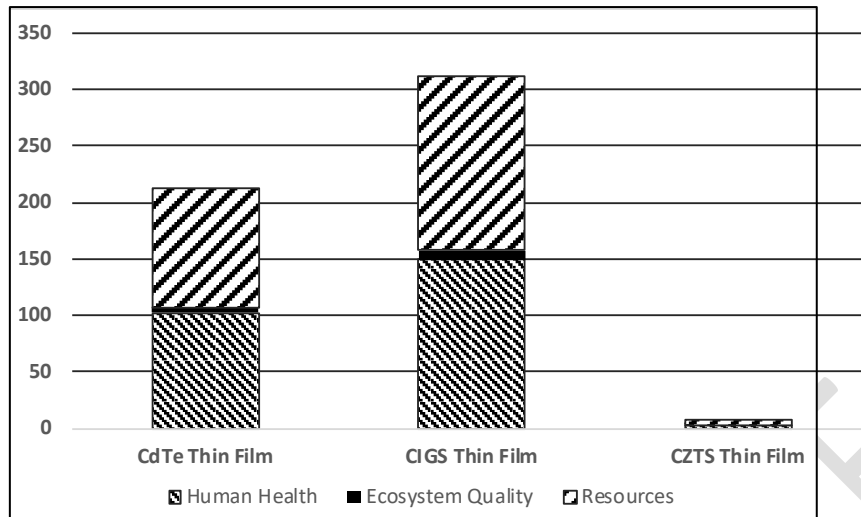


Figure 7 – Single Score

Table 10 – Single Score

Damage category	Unit	CdTe Thin Film	CIGS Thin Film	CZTS Thin Film
Total	Pt	212.4121	311.0220	7.2508
Human Health	Pt	101.9823	149.2341	2.8966
Ecosystem Quality	Pt	5.7184	8.3849	0.1748
Resources	Pt	104.7113	153.4030	4.1793

The final results were collated using EDP (2008) V1.03 in order to produce a clearer view on the PV Films Global Warming impact. This method also continues upon the same trend showing CZTS to be significantly lower. CIGS and CdTe have greater impacts and have a proportional relationship.

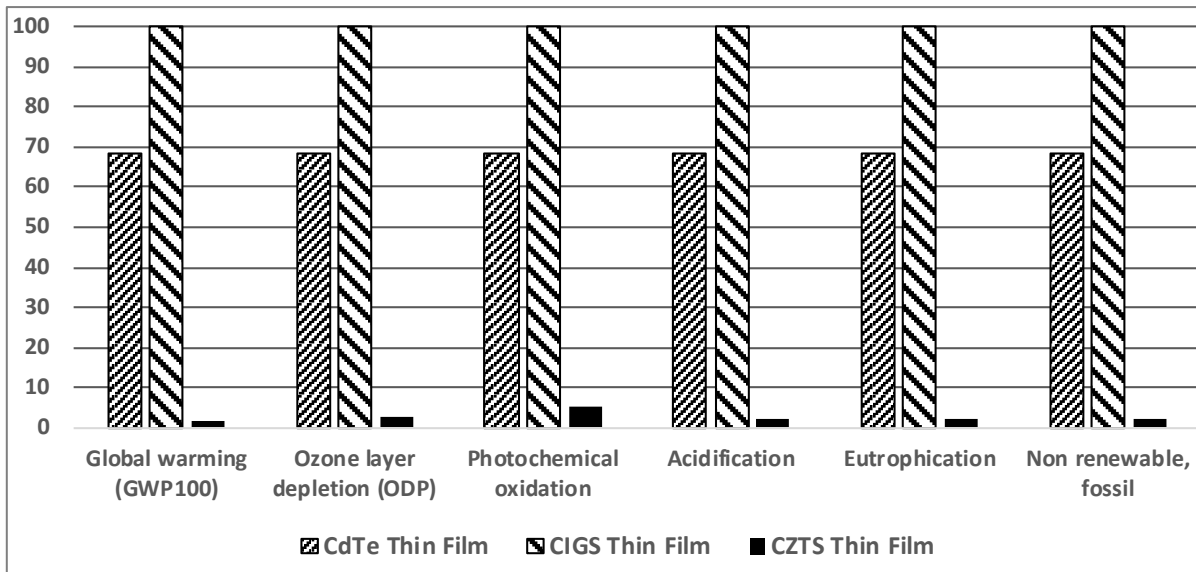


Figure 8 - EDP (2008) V1.03 Characterisation

Table 11 - EDP (2008) V1.03 Characterisation

Impact category	Unit	CdTe Thin Film	CIGS Thin Film	CZTS Thin Film
Global warming (GWP100)	kg CO ₂ eq	2996.8614	4392.6541	80.1171
Ozone layer depletion (ODP)	kg CFC-11 eq	0.000075	0.000110	0.000003
Photochemical oxidation	kg C ₂ H ₄ eq	0.634237	0.927778	0.048350
Acidification	kg SO ₂ eq	8.989699	13.16946	0.263252
Eutrophication	kg PO ₄ --- eq	3.411190	4.992698	0.110400
Non renewable, fossil	MJ eq	52047.2012	76269.5417	1714.3782

6. Discussion

Each of the methods produce coherent results and both methods establishing that CZTS have a significantly lower score in all areas except for 'mineral extraction'. The CdTe film produces results with consistently the second lowest indication, and CIGS persistently produces results with the largest environmental impact.

PV films could consist of different materials and being made in completely different manners, for example cadmium and tellurium are used in CdTe and indium, gallium

and selenium are used in CIGS. The scarcity of these materials and low usage typically are extracted from waste slimes from the production of tin, zinc and copper. This would lead to the emission values for each of these metals exhibiting similar profile due to similarities in the energy need to extract these from the waste slimes in the production of other metals.

One of the areas highlighted from the literature review of particular concern was that of resource depletion. Fig 5 and 6 clearly indicate that CZTS has a significantly lower value to that of CdTe and CIGS films). Thus, CZTS as the material which has the lowest effect in resource depletion.

Another key area of concern is the potential impact upon eco-system toxicity and human health. In Figure 8 the EDP method shows that CZTS has a eutrophication value lower than 5% o produced by CIGS with CdTe produces a value at 67% higher than CIGS. This clearly establishes that the potential leachate materials which were raised as a concern by Brun et al., (2016). Additionally, this trend of results is continued in Fig 6 when viewing the impact values associated with human health and eco toxicity. In Fig 8 it can be seen that the CZTS film has a vast disparity and CdTe has the second least impact, CdTe.

Due to its vastly lower impact in almost all categories the recommendation can be made that with a scope of cradle-to-deposition CZTS has a considerably lower environmental impact than that of CdTe and CIGS. In the key areas of concern in the LCA of PV materials, toxicity, resource depletion and global warming impact factors, CZTS is up to the point of deposition have fractional environmental impacts when compared to the deposition of CdTe and the deposition of CIGS.

7. Conclusions and Recommendation for Future Work

The results produced have allowed the green credentials of emerging PV materials to be analysed and a clear recommendation established which could provide the foundation basis for the future of photovoltaic research to be considerably greener and have a much lower potential environmental impact.

The results produced seemed to be in accordance with the expected profiling which goes some way to validating the results produced. Additionally, as this work is adhered

closely to the previous scholarly concerns in the production of PV materials this work can be seen as a further success due to the tailoring of the LCA method to produce results with further inhibiting conditions.

This work provides a sound basis for further investigation into the environmental impacts of PV materials. One particular area is through widening the boundary to ensure that the product's entire life cycle is included within the LCI. This would allow for a complete analysis of the PV materials end goal and in particular how potentially toxic materials such as cadmium could be dealt with to inhibit the negative environmental impacts they may have. A second method of producing a more thorough LCA is to establish verified material values for the missing material outlined in the processes analysed within this investigation, in particular the acetylacetonate salts.

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CONFLICTS OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this paper.

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