International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 11 Issue 04, April-2022

A Review of Recycling Methods for Crystalline Silicon Solar Panels

Abhishek Walunj[1], Nikita Jatar[1], Vishnukant Pandey[1], Aditya Ghongade[1], Prof. Padmini Sawant[2]
1 B.E. final year engineering student, Bharati Vidyapeeth College of Engineering, Navi Mumbai
2 Assistant Professor, Department of Mechanical Engineering, Bharati Vidyapeeth College of Engineering, Navi Mumbai

***Abstract* - Studies have shown that nonrenewable energy sources are rapidly decreasing. To fulfil the demands of today's globe, we will need to find renewable energy sources in the future decades. Solar energy, among the renewable energy sources available today, has contributed 70% of all renewable energy to date. By 2050, solar power is expected to be the world's largest energy source. It is the cleanest source of energy when in use, with a bench life of around 25 years. However, due to its non-degradable and hazardous constituents, it produces E-waste, which pollutes the environment in a variety of ways. In various research publications, the life-cycle of a PV module has been investigated and explored. Furthermore, due to a lack of awareness and use of solar panels today, the end phase of these cells has been neglected, and as a result, people are deficient in the recycling process. The disposal of these PV modules is expected to become a serious challenge in the future decades. As a result, it is necessary to recycle it effectively. We had read various research articles and discovered certain limitations such as toxic emissions, high energy usage, and so on. Depending on the material and kind of dopant utilized, PV modules are classified as monocrystalline, polycrystalline, or thin film. Using a series of chemical and thermal processes, we are attempting to provide the most practicable, cost-effective, and appropriate recycling procedure for c-Si monocrystalline solar cells in this project. Because this project is built on trial and error, this article provides a clear picture of the practical circumstances and flaws we encountered while recycling the solar panel.**

Keywords - PV Modules, Recycling, c-Si, Mono and Polycrystalline, Chemical, Thermal

I. INTRODUCTION

The history of this Solar PV Modules starts from year 1839 by Alexandre-Edmond Becquerel who discovered the photovoltaic effect [1]. Then in 1922, great physicist Albert Einstein gives theory of Planck's constant which helps in following research. In 1946, Russell Shoemaker Ohl patented his P-N Junction barrier research [1]. In 1958, US's Bell Laboratories successfully developed first ever silicon [1-3]. Conversion efficiency of solar cells increased to first 11% in 1958 and then in 1960, 14% [1]. First solar panel was installed on American space satellite Vanguard I having only 6 cells having 100 cm2 to two of transmitters of satellite [1-3]. In 1980's conversion efficiency of silicon cells was increased to 10% [1]. ARCO solar was one of these company who produced about 1MW of electricity with the help of this solar energy using solar panels in year 1980 [1].

After these developments, global Solar PV industry always shows an exponential growth both in production & installation of solar panels as PV modules is one of the greenest and promoted energy-generator. Also cost of solar panel installation played an important role in this. Installation capacity of Solar PV modules from year 2005 to 2020 increases from 50GW to 700 GW which reduces price of from 105.7 USD/Watt in 1970 to 0.2 USD/Watt in 2020 [20]. By the statistic, 106GW of solar PV capacity added in 2018 and the accumulation of PV modules is now increased to 508GW. More solar PV was installed than the net capacity additions of fossil fuels and nuclear power combined. PV modules have an average life of 20-25 years, which means that at 2030 we will have the great amount of PV waste in the future. According to the statistic in IRENA (International Renewable Energy Agency), the waste of solar panels in 2050 will reach 600,000 tons, which means that we should make effort on recycle PV modules right now.

Currently in market, various types of solar panels are available which have different semiconductor material (silicon, cadmium, etc). The range of current technologies in manufacturing photovoltaic modules (or PV modules) is divided into three generations, according to the operation and materials of the photovoltaic cell [12]

1. First generation: Crystalline silicon (c-Si)
    a. Monocrystalline
    b. Polycrystalline
2. Second generation: thin film solar panels
    a. Amorphous silicon (a-Si)
    b. Cadmium telluride (CdTe)
    c. Copper indium gallium Di selenide (CIGS) and copper indium Di selenide (CIS)
3. Third generation:
    a. Concentrated PV cell (CVP and HCVP)
    b. Organic solar cells
    c. Hybrid cells

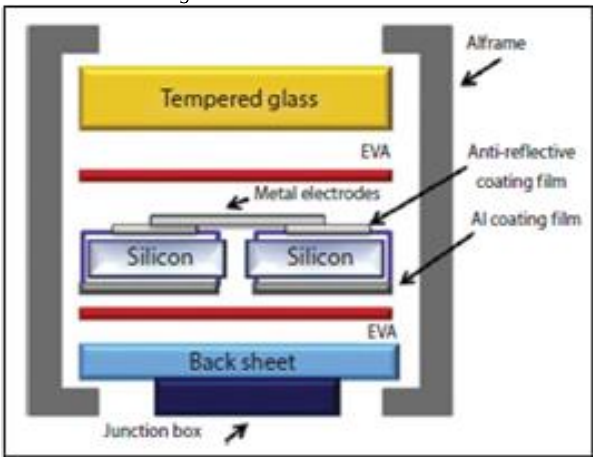
Among this, most commonly used solar panels are crystalline silicon (c-Si) solar cell as they have comparatively cheaper than others. Also, solar panels installed in 1990's and 2000's have come to end of life cycle. So, these solar panels are also easy to access for recycling purpose as they have reached end of life cycle. Hence, we decided to work on recycling of c-Si based solar panels.

II. STRUCTURE OF SOLAR PV MODULES

c-Si (mono or poly-crystalline silicon) solar modules of following main components. [12]

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 11 Issue 04, April-2022

Figure 1: Solar Panel Structure



1. Tempered Glass
2. Aluminium frame
3. Anti-reflective layer
4. Silicon cell wafer
5. Aluminium and Copper or silver wires (wire electrodes)
6. EVA (ethylene vinyl acetate)
7. Electrical Junction box

For recycling of PV modules, first step is to dismantle these modules into several components so that it can be recycled individually [12].

Table 1: Material wise Percentage of Solar Panel

Material	% w/w in a module	Relative economic value	Amount X Value Interesting?
Silicon	2–3	High	Yes
Glass	69–75	Low	Yes
Polymers (EVA, Tedlar/backsheet/ polyvinyl fluoride-PVF)	7	Low	No
Copper	0.6–1	High	Yes
Silver	0.006–0.06	High	Yes
Aluminium	10–20	Medium	Yes

III. LITERATURE REVIEW

Various researches have carried experiments in order to remove silicon and other valuable metals from solar panel. In this process, they have carried out primarily two methods, thermal process (to remove EVA layer and glass) and chemical method (to remove Si and other valuable metals from solar panel).

A. Separation of Glass and EVA layer

Glass used on solar panels are used to provide structural support to solar panel wafers and protect them from any external.

EVA layer, a material that has good radiation transmission and low degradability to sunlight, is an important component of solar modules used as an encapsulating agent since, by applying heat to the assembly, it forms a sealing and insulating film around the solar cells. It can also be reused if recycled properly.

Various researchers have gone through different methods for removing the EVA layer from solar panel. Most common methods are heating of solar panel so that EVA layer will eventually burn and main silicon wafers with electrodes can be received [13-15], while other method uses the organic solvents so that EVA layer will be dissolved in organic solvents [5, 13, 16-19].

B. Applying organic chemical

Takuya Doi, et al, have used organic chemicals like O-dichlorobenzene (O-DCB), trichloroethylene (TCE), benzene, and toluene. These chemicals are able to separate EVA from solar cells in more of less percentage but they require much process capabilities to maintain in certified range like different solvent concentrations, temperatures, ultrasonic powers, and irradiation times. Toluene able to recover EVA but it damages the solar panel cells due to swelling at 70º C and 450 W ultrasonic radiation. TCE and benzene organic chemical reduces the dissolution of EVA as temperature from 55 to 70º C because of pyrolysis and pyrolytic reactions. After cross linking treatment at 155º C, sample of solar module placed in TCE for several days. This causes the swelling of EVA which may damage the solar cell that can be overcome by applying mechanical pressure. O-DCB is also used for separation of EVA from solar cell. Solar module is placed in O-DCB for 120º C for one week and without applying mechanical pressure, solar cell was recovered. But this also requires much parameters to maintain at a time in order to get optimum result in separation of EVA, making overall method difficult to sustain. [4]

Y Kim and J Lee uses ultrasonic waves to reduce the time required for dissolution of EVA in c-Si PV modules from 7-8 days to less than 1 hour. Temperature of organic solvents is controlled by water jacket and thermocouple provide in container. This study shows that of EVA layer dissolution rate can be reduced conveniently [17]. Similar process was adopted by Sukmin Kang, S Yoo, J Lee, et al for separation of tempered glass and EVA layer, process is continued by chemical etching of silicon cells [15].

C. Use of thermal method

Application of thermal method is optimum technique for separating EVA layer have been used by Chitra, et al. This method includes thermal treatment of solar panel at 170º C temperature and application of mechanical force at same time. EVA layer was recovered without any degradation and emission of harmful gases. Solar panel of larger size (98x164cm) is cut in into smaller size (7x8 cm) for easy handling of solar panels during the process. Then the piece of solar panel was thermally treated with thermocouple with displaying unit installed on it to measure its temperature. Initially, back layer (Tedlar) was recovered by mechanical process from solar panel at 130º C. Then remaining solar cell were further heated again up to 170 ± 1 ◦C. Due to this, EVA becomes soft and recovered from solar panel by application of mechanical force from back side of solar panel. During the process, neither yellowing of EVA nor release of residual gas was observed [5].

Variable heating of solar panel is examined by J Shin, N Park, J Park. Solar panel is heated at 480º C with heating rate of 15º C/min [14]. Same procedure was followed by B Jung, D Seo, et al using a gradual heating process. Solar panel exposed to 250º C which removes Al frame as adhesive melts at high temperature. Followed by heating to 480º C which separate different layers of solar panel [18].

D. Chemical method to separate Al, Cu and Ag

In solar panels, metals like aluminium, copper, silver, etc are used to carry current induced in solar cells due to photoelectric effect. These metals like Ag, Cu are expensive making the extraction of metals and reusing them in solar panels or in other electronic components, economically sustainable and viable also than the use of freshly extracted metals. As these metals have different properties and also, they react differently with acids, bases and alkaline, we need unique method in order to extract each of these metals. Most common techniques to extract these metals is chemical method.

1) Extraction of Al and Ag

Wei-Sheng Chen, et al have used nitric acid (0.5-6M concentration) to leach Al and Ag from the PV cells. After acid leaching process, Al-Si alloy still remained on the PV cells. In order to purify the Silicon, Sodium Hydroxide leaching was employed to break the bonding between Si and Al.

$$2\ Al\ (s) + 6\ HNO_3\ (aq) \rightarrow 3\ H_2\ (g) + 2\ Al(NO_3)_3\ (aq)$$

$$Ag\ (s) + 2\ HNO_3\ (aq) \rightarrow H_2O\ (l) + NO2\ (l) + Ag\ NO_3\ (aq)$$

The metals in the leaching solution are separated through selectively solvent extraction and stripping. Aluminium was extracted by Na-Cyanex272 and silver remained in the solution. Using HCl to strip Aluminium from the organic phase. The metals can be separated. The solution with silver was precipitate by sodium chloride into AgCl. This study also carried the parameters of extraction process with pH value 0.5-3 [6].

$$Na+(aq) + H+\ Cyanex272\ \text{-}(aq) \rightarrow Na+(aq)\ Cyanex272\ \text{-}(aq) + H+$$

2) Using Different chemicals like Sulphuric acid, Nitric acid, Potassium hydroxide and other chemicals –

Klugmann-Radziemska, Piotr Ostrowski, et al, also used nitric acid (HNO_3) to remove Ag wire in solar cells. 40% aq HNO_3 at 40° C dissolves Ag coating which can be recovered from waste acid by electrolysis process.

$$Ag\ (s) + 2\ HNO_3\ (aq) \rightarrow H_2O\ (l) + NO_2 + 2\ AgNO_3\ (aq)$$

30% aq solution of Potassium hydroxide (KOH) was used to remove the Al layer from the cell's rear surface; the efficiency of the process was optimum at a temperature of 80° C. This $KAl(OH)_4$ is a salt of Potassium (K) and Aluminium (Al) known as potassium tetra hydroxy aluminate from which Al can separated with the help of hydrochloric acid (HCl). [7]

$$2Al + 2KOH + H_2O \rightarrow 2\ KAl(OH)_4 + 3\ H_2$$

$$4\ HCl + KAl(OH)_4 \rightarrow 4\ H_2O + KCl + AlCl_3$$

F Pagnanelli, E Moscardini, et al for etching process. uses HNO_3 (1 g in 3 ml), HCl (9 ml) and H_2O_2 (0.6 ml) of for 10 min at 220° C and in second step, 20 min at 220° C. This process gives more 24% recovery of glass fractions [19].

E. Chemical etching and mechanical processes –

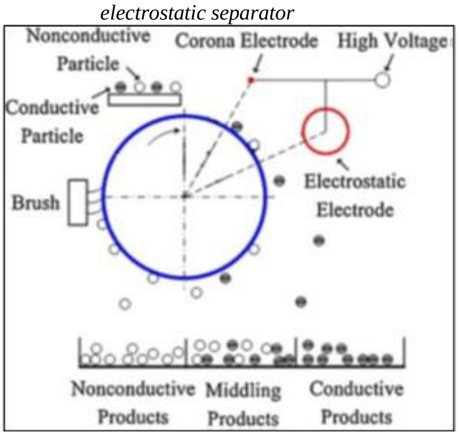
Jongsung Park, Wangou Kim, et al have completed recovery process consisted of three steps [8]:

1. Removal of ag electrodes using 60% nitric acid (hno3) at room temperature for 120 s
2. Mechanical removal at 20 RPM for 20 min using green fine silicon carbide powder, which assists in grinding of Si in the removal of the arc, emitter and P–N junction
3. Simultaneous removal of the grinding damage on the front surface of the cell and the al electrode from the rear side of the cells by using 45% potassium hydroxide (KOH) at 80 °c for 10 min

F. Using electrostatic method of separation –

Pablo Dias, Lucas Schmidt, et al have undergone electrostatic separation process, carried out in a roll-type separator, the metals go through a grounded roller and are subject to an electric charge ionization from an electrode. In these conductive particles discharge as it comes in physical contact with the roller and nonconductive are attracted to the roller due to Coulomb Forces. Thus, particles are separated due to differences in conductivity and electrostatic properties.

Figure 2: Illustrate the electrostatic separation principle in roll type electrostatic separator



The metals we obtained in the container after separation are as follows:

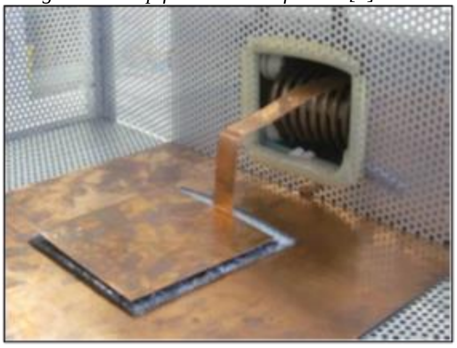
1. The non-conductor(C) fraction contains mostly polymers (white particles).
2. The middling fraction (B) contains mostly silicon (Gray and blackish particles)
3. The conductor fraction(A) mostly contains glass.

Although glass is an electrical insulating material its particles fall into the first pan along with the metals (conductive fraction: A). This happen due to particles being too heavy or due to the influence of metallic particles, which can attach to the glass particles through the encapsulating material [9].

G. Electrothermal heating method to separate the Glass –

Angelo Doni, Fabrizio Dughiero uses electro-thermal heating process is developed for easy removal of glass from C-Si PV module. In this process, 2 non-magnetic flat electrodes are used to produce a uniform transverse radio frequency (RF) electric field between them. The upper one is connected to the RF voltage supply and the lower is grounded. Further The solar panel samples are inserted between the two electrodes and pressure is applied to the upper electrode during the heating process. By keeping the voltage constant, it transmits the optimal RF power to the sample. An air gap will be necessary for test aimed at the development of an in-line system. After the application of 400 W for a total time of 10 minutes, the process has been repeated several times as a result a big portion of glass fragments can manually peeled-off from the PV sample, without using tools but manually rubbing the glass surface with a glove, after 15 minutes of treatment [10].

Figure 3: Setup for Removal of Glass [7]



IV. METHODOLOGY

From various experiments for the separation of EVA layer, method used is the thermal method. Heating the solar panels up to 450-500^{o} C easily removes the EVA layer from solar cell. There is a possibility of formation of some gases like CO_2 (carbon dioxide) and water vapour, but they don't damage to solar cells as well as their proportion is much lesser. But with the help of organic chemicals like carbon tetrachloride, we are able to remove glass as well as EVA layer form solar panel wafer. Also, this do not affect the solar cells.

In order to separate the precious metals like Al, Ag and Cu, most common chemicals like HNO_3, KOH, HCl, Cyanex272 were used. But this all chemicals are acidic in nature which may cause harmful effect on PN junction of silicon cells. So, we have decided to use less harmful acids for the extraction of these precious metals.

We will be using Sodium Hydroxide (NaOH) and water (H_2O) to separate Al from solar cells as Ag is less reactive than Na (sodium) so it cannot react with NaOH (sodium hydroxide) and Si is less reactive than Al so it will not react with NaOH in presence of Al. This gives product as H_2 (hydrogen gas) and NaAl (OH)4 (sodium aluminate)

$$2\ Al + 2\ NaOH + 6\ H_2O \rightarrow 3\ H_2 + 2\ NaAl\ (OH)_4$$

Al needs more reaction to extract in only Al form as it is with Na (sodium). First, we need to take out Na and Al in two compounds and then Al can be separated. For this, H2SO4 (sulphuric acid) can be used which breaks bond between Na and Al in compound NaAl $(OH)_4$. And this reaction gives us Na_2SO_4 (Sodium sulphate) and $Al_2(SO_4)_3$ (Aluminium sulphate) with H_2O

$$4\ H_2SO_4 + 2\ NaAl\ (OH)_4 \rightarrow 8\ H_2O + Na_2SO_4 + Al_2(SO_4)_3$$

At the end, Al can be extracted in pure form from $Al_2(SO_4)_3$ when it reacts with Mg (magnesium) metal to give by product as $MgSO_4$ (magnesium sulphate) and Al.

$$Al_2(SO_4)_3 + 3\ Mg \rightarrow 2\ Al + 3\ MgSO_4$$

Use of one acid for recycling method is inevitable. As Al is separated from solar module, there is no scope of reaction of Al with the acid and as Si is semiconductor, it requires special condition to react with any substances. So, we will we using the sulphuric acid (H_2SO_4) for separation of silver (Ag) which will give following reaction.

$$2\ Ag\ (s) + 2\ H_2SO_4\ (aq) \rightarrow 2\ H_2O\ (l) + SO_2\ (aq) + AgSO_4\ (s)$$

This $AgSO_4$ (silver sulphate) needs to be separated so we can get Ag at the end. Cu (copper) can be used for this purpose as it is more reactive than that of Ag. This gives $CuSO_4$ (copper sulphate) with Ag at the end.

$$AgSO_4\ (s) + Cu\ (s) \rightarrow CuSO_4\ (s) + 2\ Ag\ (s)$$

This is how, we will be left with the silicon (Si) at the end which can be refined as required for manufacturing of solar grade pure silicon. This refining is necessary as there is possibility of some impurities remained during process or may some impurities can be produced due to chemical and thermal methods. These impurities can be removed by conventional refining process for silicon (Si).

V. CONCLUSION

PV module waste will reach millions of tonnes worldwide in the coming decade, creating a need to evaluate all treatment options for end-of-life PV modules. We suggested essential technology improvements to facilitate recycling from an economic and environmental perspective. Among various recycling methods reported in the literature, we mapped out the feasible approaches to dispose end-of-life PV modules. These recycling technologies have progressed steadily. The recovery yields of both conventional and scarce materials have increased in the past 20 years, forming a strong knowledge basis for large-scale application.

VI. REFERENCES

[1] Lorand Szabo, The history of using solar energy, 2017 International Conference on Modern Power Systems (MPS). DOI: https://doi.org/10.1109/MPS.2017.7974451

[2] Kelly Pickerel, The long history of solar PV, Article Link https://www.solarpowerworldonline.com/2018/01/long-history-solar-pv/

[3] The History of Solar Panels, Energy Efficiency and Renewable Energy, US Department of Energy, Article Link https://www1.eere.energy.gov/solar/pdfs/solar_timeline.pdf

[4] Takuya Doi, Izumi Tsuda, et al, "Experimental study on PV module recycling with organic solvent method", Solar Energy Materials & Solar Cells 67 (2001) 397-403, https://doi.org/10.1016/S0927-0248(00)00308-1

[5] Chitra, Dheeraj Sah, et al, "Structural composition and thermal stability of extracted EVA from silicon solar modules waste", Solar Energy Volume 211, 15 November 2020, Pages 74-81, https://doi.org/10.1016/j.solener.2020.09.039

[6] Wei-Sheng Chen, Yen-Jung Chen, et al, "Recovery of valuable metal from Photovoltaic solar cells through extraction", IOP Conf. Series: Materials Science and Engineering720 (2020), doi:10.1088/1757-899X/720/1/012007

[7] Ewa Klugmann-Radziemska, Piotr Ostrowski, et al, "Experimental validation of crystalline silicon solar cells recycling by thermal and chemical methods", Solar Energy Materials & Solar Cells Vol. 94 (2010) 2275–2282, https://doi.org/10.1016/j.solmat.2010.07.025

[8] Jongsung Park, Wangou Kim, et al, "An eco-friendly method for reclaimed silicon wafers from a photovoltaic module: from separation to cell fabrication", Green Chem., 2016,18, 1706-1714, DOI: https://doi.org/10.1039/C5GC01819F

[9] Dias, P., Schmidt, L., Gomes, L.B. et al. Recycling Waste Crystalline Silicon Photovoltaic Modules by Electrostatic Separation. J. Sustain. Metall. 4, 176–186 (2018). https://doi.org/10.1007/s40831-018-0173-5

[10] Angelo Doni, Fabrizio Dughiero, "Electrothermal Heating Process Applied to c-Si PV Recycling", 2012 38th IEEE Photovoltaic Specialists Conference DOI: https://doi.org/10.1109/PVSC.2012.6317715

[11] Dias, P., Dias, P. and Veit, H. (2018). Recycling Crystalline Silicon Photovoltaic Modules. In Emerging Photovoltaic Materials, S.K. Kurinec (Ed.). https://doi.org/10.1002/9781119407690.ch3

[12] Rong Deng, Nathan L. Chang, Zi Ouyang, Chee Mun Chong, A techno-economic review of silicon photovoltaic module recycling, Renewable and Sustainable Energy Reviews 109 (2019) 532–550. https://doi.org/10.1016/j.rser.2019.04.020

[13] Chitra, Dheeraj Sah, Kalpana Lodhi, Chander Kant, Parveen Saini, Sushil Kumar, Structural composition and thermal stability of extracted EVA from silicon solar modules waste, Solar Energy 211 (2020) 74–81. https://doi.org/10.1016/j.solener.2020.09.039

[14] Jeongeun Shina, Jongsung Park, Nochang Park, A method to recycle silicon wafer from end-of-life photovoltaic module and solar panels by using recycled silicon wafers, Solar Energy Materials and Solar Cells Volume 162, April 2017, Pages1-6. http://dx.doi.org/10.1016/j.solmat.2016.12.038

[15] Sukmin Kang, Sungyeol Yoo, Jina Lee, Bonghyun Boo, Hojin Ryu, Experimental investigations for recycling of silicon and glass from waste photovoltaic modules, Renewable Energy 47 (2012) 152-159. https://doi.org/10.1016/j.renene.2012.04.030

[16] Pablo Dias and Hugo Veit, Recycling Crystalline Silicon Photovoltaic Modules, Emerging Photovoltaic Materials, (61–102). https://doi.org/10.1002/9781119407690.ch3

[17] Youngjin Kim, Jaeryeong Lee, Dissolution of ethylene vinyl acetate in crystalline silicon PV modules using ultrasonic irradiation and organic solvent, Solar Energy Materials & Solar Cells 98 (2012) 317–322, https://doi.org/10.1016/j.solmat.2011.11.022

[18] Byungjo Jung, Jong sungPark et al, Sustainable System for Raw-Metal Recovery from Crystalline SiliconSolar Panels: From Noble-Metal Extraction to Lead Removal, CS Sustainable Chem. Eng., DOI: https://doi.org/10.1021/acssuschemeng.6b00894

[19] Francesca Pagnanelli, Emanuela Moscardini et al, Physical and chemical treatment of end-of-life panels: An integrated automatic approach viable for different photovoltaic technologies, Waste Management, Volume 59, January 2017, Pages 422-431. http://dx.doi.org/10.1016/j.wasman.2016.11.011

[20] Evolution of solar PV module cost by data source, 1970-2020. https://www.iea.org/data-and-statistics/charts/evolution-of-solar-pv-module-cost-by-data-source-1970-2020