**Article**

**Recycling c-Si PV Modules: A Review, a Proposed Energy Model and a Manufacturing Comparison †**

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**Abstract:** As human activities are increasingly exploiting our planet’s scarce resources, managing them has become of primary importance. Specifically, this study examines the management of photovoltaic (PV) waste that is produced when PV modules reach end-of-life (EoL). PV modules contain precious and valuable materials, as well as toxic materials that may be harmful to human health and the environment if not disposed of properly. First, this study aims to review and analyze the current literature in order to gain a deeper understanding of the recycling of PV modules, particularly c-Si modules, which represent the largest market share. In the second part, an analysis is conducted of the energy consumption of these recycling processes using a proposed model based on the full recovery end-of-life photovoltaic (FRELP) process. PV modules manufactured from raw materials and PV modules manufactured from recycled materials are also compared in this section. In addition, improvements are suggested with respect to the design of PV modules (eco-design). According to this study, c-Si PV modules can be recycled with an energy consumption as low as 130 ÷ 300 kWh/ton of treated PV waste, estimating an overall recycling yield of about 84%.

**Keywords:** energy model; FRELP; life-cycle; photovoltaic (PV); PV waste; raw materials; recycled materials; recycling; silicon

1. Introduction

Globally, installed PV capacity reached 942 GW at the end of 2021, and this figure has been increasing exponentially in the years since the early 2000s [1]. The PV technology currently dominating the market is based on solar cells made of c-Si, with a market share of more than 90% [2]. Many PV modules installed in previous decades are nearing their EoL due to their lifespan of 25–30 years. According to [3], PV waste will reach 78 million tons by 2050, resulting in a huge flow in the coming years. Consequently, the management of this waste will soon have to be addressed. Furthermore, PV modules contain precious and valuable materials (such as silicon, silver, aluminum, etc.), as well as toxic materials (such as cadmium, lead, etc.) which can harm human health and the environment when improperly disposed of [4]. In this study, the focus is on c-Si PV modules. There is no consideration in this study for balance of system (BoS), which includes other components such as inverters, racking systems, and batteries. A circular economy can be developed through the 3Rs strategy: (reduce, reuse, and recycle) to address the huge amount of PV waste emerging worldwide [5]. Reducing means using fewer materials and eventually making PV modules less harmful. By reusing, old modules are repaired and put back on the market. In contrast, recycling, being the least favorable (due to the higher effort needed), is the only process able to recover materials at the EoL, giving them a new life. Today, only 10% of the total PV waste worldwide is recycled [6]. Landfilling, incineration, illegal sales, storage, and land filling are some possible disposal options. This study focuses on recycling.
At present, only the European Union (EU) has developed specific regulations and policies to deal with the EoL management of PV modules. The extended producer responsibility (EPR) implemented by the European Waste Electrical and Electronic Equipment (WEEE) directive 2012/19/EU requires producers and importers in each country of the EU to organize the collection, transportation, treatment, recycling, and financing of these operations for their PV modules [7]. PV waste production is expected to increase significantly over the next several decades, with China leading, followed by the USA, Japan, and India [3]. There are two types of recycling: bulk recycling (recovery of high-mass fractions of materials such as glass, aluminum, and copper) or high-value recycling (recovery of both bulk materials in semiconductors and trace metals) [8]. The study’s objective focuses on the second approach. It is crucial to decide whether to recover the whole silicon wafer for use in PV modules or to recover it as a powder that can be used in other ways. According to the current trends, recovering Si powder may be more advantageous, as intact wafers may not find a market in the future [9].

According to [3], three main panel failure phases for PV modules can be identified: infant failures (0–4 years from installation), midlife failure (5–11 years), and wear-out failures (12–30 years, where 30 years is considered to be the lifetime of a PV panel). For these phases, the main causes of failure and degradation mechanisms are: (i) Infant: light-induced degradation, poor planning, incompetent mounting work, and bad support constructions. Other failures concern the electrical system (junction boxes, cabling, grounding, etc.). (ii) Midlife: degradation of anti-reflective coating of the glass, discoloration of EVA, delamination, and cracked cell isolation. Additionally, due to loads (wind and snow), contact failure in junction box, glass breakage, loose frames, cell interconnection breakages, and diode effects. (iii) Wear-out: the same causes as midlife failure with the addition of the corrosion of cells and interconnectors.

Generally, recycling consists of three phases: component separation, material recovery, and material purification [6,9–11]. There are two main environmental impacts associated with recycling processes: harmful emissions from incineration and pyrolysis processes and the use of toxic chemical solutions that need special treatment. Furthermore, recycling is usually not economically advantageous, even though it is technically feasible. Most often, the cost of equipment, labor, and logistics required to recycle PV modules is greater than the revenue generated by the sales of materials. The low amount of PV waste also makes economies of scale impossible.

This paper is based on an extension of the conference paper “Recycling of c-Si PV Modules: an Energy Analysis and Further Improvements” [12]. For this paper, the literature was expanded and reviewed in more detail. Consequently, data were updated regarding the energy analysis and the recycling shares. Finally, a PV manufacturing comparison model was developed for this study to conceptually schematize how PV modules manufactured using raw materials would compare with those manufactured using recycled materials. Therefore, the materials needed were determined for both scenarios.

In this study, two approaches were used to determine the energy consumption of recycling c-Si PV modules. One approach involved reviewing the literature and considering how much energy recycling processes consume. The other approach involved redesigning and updating a recycling process based on an existing one, the full recovery end-of-life photovoltaic (FRELP) process. As a result, some energy consumption data were estimated. The final step consisted of comparing the two approaches in order to determine intersections and final results. Then, some comparisons were made between the production of PV modules using raw materials and those using recycled materials. The objective of this analysis was to estimate recycling processes’ energy consumption and to compare it with production of new PV modules. According to the literature, improvements were subsequently suggested based on scientific evidence. Eco-design was also considered, and some potential features have been proposed.

This paper is organized as follows: Section 2 presents the literature review related to the treatment of PV waste, considering only recycling. Section 3 presents the
proposed model, the specific system, and the PV manufacturing comparison model, whereas Section 4 presents the results of the proposed and comparison models. Section 5 presents the improvements that could make recycling easier and more sustainable from technical, economic, and environmental perspectives. Finally, Section 6 reports the final conclusions.

2. Literature Review

According to the literature, recycling is technically feasible and is most commonly accomplished through three approaches: mechanical, thermal, and chemical [13]. It is possible to recycle glass to produce the same product in many cases, and the glass can usually be separated intact [14]. In most cases, plastics are burned to produce thermal energy and electricity [15]. Si can be recovered as wafers or powder, but the focus today is on recovering it as a powder with high purity to increase its economic value [9]. It is also possible to recover precious metals, such as silver (Ag), with high yields [16]. A number of factors affect the profitability of recycling, including the low value of materials contained in PV modules, the cost of labor, technology, and collection [17]. A high amount of PV waste can make many recycling processes economically viable [18]. The rising prices of materials could also make recycling economically feasible [4]. EPR was found to be an effective mechanism for increasing PV module recycling [19].

It is possible to reduce the environmental impacts associated with PV module life cycles through recycling. The authors of [20–22] found that the impacts are primarily related to transportation and electricity consumption. Recycling can provide environmental benefits and should, in principle, be pursued because recovering materials requires less energy than processing the same raw materials [23]. The lower energy consumption of recycled materials translates into a shorter energy payback time (EPBT) for modules made of recycled materials [24]. In addition, recycled wafers are not inferior to new ones in terms of quality [25]. Life cycle assessments (LCAs) do not usually consider the BoS, despite its large impact on the environment [22]. Databases and life cycle inventories (LCIs) used in current studies are not complete and not very up to date [26,27]. According to [28], PV panels become less recyclable as their complexity increases. Eco-design approaches aim at substituting the encapsulating material, whose removal represents one of the most important steps in recycling [9].

In the next section, several recycling processes for c-Si PV modules are considered and described. Mechanical, thermal, and chemical approaches or a mix of those approaches are used in these processes.

2.1. Mechanical Approach

In this section, recycling processes using mainly a mechanical approach are considered. In [29], it was shown how c-Si PV modules were separated after mechanical milling using an electrostatic separator. During electrostatic separation, substances with different electrical conductivities are sorted based on their electric conductivity. The electrostatic separation process is considered to be an efficient, low-cost mechanical process that requires less energy than thermal processes and produces no waste products, unlike hydrometallurgical processes. Although electrostatic separation has the potential to assist in the recycling of PV modules by segregating various materials, it has not been extensively studied. A voltage of 24 kV or higher and a rotation speed of 30 rpm or higher yielded the best results. The modules were c-Si PV with the composition of 72% glass (front glass), 15% of Al (frame), 7% EVA and Tedlar (encapsulant and back sheet) and 2.5% Si, 0.8% Cu, 0.03% Ag, 0.1% Sn and 0.1% Pb (solar cell). The rates of the material recovered were 95% of the glass, 95% of the Cu and 95% of the Ag. Despite the energy consumption of this method, up to 85% of the recycled cells can be reused, reducing the energy consumption to produce new PV modules by up to 70%. In general, electrostatic separation can help recycle PV waste, but it cannot concentrate the polymers present in PV panels and the parameters for an optimal separation are still unknown.
In [30], a grinding process was investigated for the liberation of glass from sealed particles of glass and resin obtained by shredding c-Si PV modules. A carbon content of less than 1% made the resulting glass particles suitable for glass fiber manufacturing. An eccentric stirring mill was used in this study. Using selective grinding, liberation of the fraction of glass between 2 and 13 mm was attempted. By grinding particles smaller than 5.6 mm at 2500 rpm for five minutes, 97% of the glass in a PV module can be recovered with less than 1% carbon (C) contamination. Selective grinding is therefore effective for removing resin from glass during its initial phase.

In [31], the modules were c-Si PV with composition of 68% glass (front glass), 20% of Al (frame), 1% copper (Cu), plastics, and adhesives (junction box and cables), 5.5% EVA (encapsulant), 1% PVF (back sheet) and 3.5% Si, 0.8% aluminum (Al) and Cu and 0.2% Ag, tin (Sn), and lead (Pb) (solar cell). In this work, modules were pre-treated and panels were sheared (separating cables, connectors, and aluminum frames, as well as reducing their sizes and introducing them into the system). A variety of mechanical separation techniques were used, including glass separation (grinding and mechanical separation of fragments), Si separation (grinding and shredding of the small fraction and mechanical treatments for separating materials), and separation of Cu and polymeric fractions (supplementary sieving of the plastic–copper compound). This approach consumed 0.79 kWh during pre-treatment, 0.51 kWh during glass separation, 0.46 kWh during Si separation, and 0.16 kWh during Cu and polymeric fraction separation for every 20 kg of EoL PV modules.

2.2. Thermal Approach

In this section, recycling processes using mainly a thermal approach are considered.

In [32], the modules used were polyc-Si (polycrystalline) PV fabricated on 1986 with composition of 74.16% glass (front glass), 10.3% of Al (frame), 1.16% plastics, and adhesives (junction box and cables), 6.53% EVA (encapsulant), 3.6% Tedlar (back sheet) and 3.48% Si, 0.57% Cu, 0.01% Ag, 0.12% Sn and 0.07% Pb (solar cell). A thermal approach was used, and a pre-treatment of delamination was performed. The PV waste samples were positioned in quartz sample holders, placed inside the tubular furnace, and heated to 200 °C at a rate of 450 °C/h without gas flow. As a subsequent step, a thermal treatment was carried out, 24 L/h of gas was supplied, the reactor was warmed to the process temperature (500 °C) at a rate of 450 °C/h, and the temperature was maintained for 1 h. All the recovered materials showed a low carbon concentration, indicating the complete degradation of the polymer.

In [33], the process of pyrolysis in a fluidized bed reactor was used. The EVA was burned away in the air atmosphere or decomposed under nitrogen at temperatures of 450 °C and 480 °C, respectively, and 100% of the glass was recovered. As compared to a standard module, a module made of recycled wafers consumed 40% less energy per kWh. A total energy of 0.4 kWh was consumed per wafer during recycling.

In [34], the modules were polyc-Si PV with composition of 67.5% glass (front glass), 17.5% of Al (frame), 1.7% Cu, plastics, and adhesives (junction box and cables), 7% EVA (encapsulant), 1.05% PVF (back sheet), and 3.65% Si, 0.53% Al, 0.11% Cu, 0.053% Ag, and 0.053% Sn and Pb (solar cell). In this recycling procedure, the Al frame and the junction box were removed, and the sample was then cut with a circular saw and placed in a furnace under a stream of air, then heated to 600 °C, holding it there for 30 min. The rates of the material recovered were 99.97% of the Al, 100% of the Cu, 100% of the Si, 98% of the Pb, and 32% of the Ag.

A thermal method was proposed in [35] for the recovery of Si, glass, and metal from c-Si modules. The thermal process involved two steps of heating. First, the Tedlar layer was separated from the module back surface by heating it at 330 °C for 30 min. The second step involved burning out the EVA and Tedlar at 400 °C for 120 min. A two-step heating process was used to recover the glass plate. When the temperature is controlled, recycled glass can be used as a component for new modules. After its cleaning through
a chemical solution treatment, the obtained Si material was at least 99.999999% pure, having a recycling yield of 62%. A total of 85% of the Cu could be recovered through further acid treatment.

In [36], the modules used were c-Si PV with a composition of 16.13% of Al (frame), and a thermal approach was used. The rates of the material recovery were 99.97% of the Al, 100% of the Cu, 100% of the Si, 98% of the Pb, and 32% of the Ag. In [37], a thermal approach was used and the modules were c-Si PV, with the rates of the material recovered being 89% of the glass, 81% of the Al, 80% of the Si, and 89% of the Ag.

2.3. Chemical Approach

In this section, recycling processes using mainly a chemical approach are considered. In [38], a simulated leach solution was used for the experiment. An aqueous solution of nitric acid (HNO\textsubscript{3}) was prepared to dissolve Ag, Pb, Sn, and Cu pellets. The modules were c-Si PV with composition of 10% Al (frame), 3% Si, 0.6% Cu, 0.006% Ag, and 0.1% Pb. The rates of the material recovered were 83% of the Cu and 74% of the Ag.

In [39], it was found that HNO\textsubscript{3} has a better leaching performance on Ag and Al than sodium hydroxide (NaOH). A leaching rate of 99.89% was observed for Al, and a quality loss rate of 4.82% was observed for Si under optimal conditions. The precipitation process of Ag using hydrochloric acid (HCl)–ammonia dissolution was also found to be very efficient. An overall Ag recovery of 96.03% was achieved. Si wafers were purified using 20 wt% hydrofluoric acid (HF) etching, and the total recovery of Si was 96.03%. Therefore, the hydrometallurgical recycling of PV waste investigated in this study was proven to be efficient, and can be considered suitable for large-scale production. The process used non-green reagents, including HNO\textsubscript{3} and HF, and the recovered materials had a lower purity than the raw materials.

In [40], it was investigated using iodine–iodine as a lixiviant in place of HNO\textsubscript{3} for the leaching of precious metals from EoL PV modules. After that, OpenLCA was used to perform an LCA analysis. According to the study, the leaching efficiency of the iodine–iodine system is similar to that of HNO\textsubscript{3}, and the environmental impacts can be effectively reduced.

According to the study [41], compared to other reagents, potassium hydroxide (KOH)–ethanol is used, which is a green reagent with low environmental toxicity. In optimal conditions, layers of PV modules can be completely separated in 3 h, and the oxidation of the Si wafer can be controlled. Ultrasonic irradiation can accelerate the dissolution ratio of EVA. The drawback of aqueous alkali, such as NaOH or KOH, is that they are hardly able to penetrate the interlayer space, so the different layers must first be separated by pyrolysis. In this experiment, the plastic back sheet was removed during the cutting process into small square pieces. The separation efficiency of KOH–ethanol was higher than NaOH–ethanol and, therefore, the prior option was used. The separation ratio reached 100% under the following conditions: 200 °C reactor temperature, 3 h reaction time, KOH concentration of 0.2 mol/L, and the solid-to-liquid ratio of 55 g/L. A low surface oxidation of Si wafers was shown when compared to those recovered via pyrolysis. The recovery ratio of Si wafers reached 96.27%, and a closed-loop recovery process was proposed and proven feasible.

2.4. Mixed Approaches

In this section, recycling processes using a mix of approaches are considered, representing the most typical case.

In [42], thermal, chemical, and mechanical approaches were used. The modules were polyethylene terephthalate (PET)-based c-Si PV with a composition of 59.51% glass (front glass), 14.7% Al and 8.65% steel (frame), 1.9% Cu and 2.85% plastics and adhesives (junction box and cables), 4.52% EVA (encapsulant), and 1.91% PET (back sheet), and 1.82% Si, 2.01% Al, 1.99% Cu, and 0.12% Ag (solar cell). Several approaches were analyzed including thermal and chemical treatment and destructive and selective mechanical separation.
During the thermal and chemical treatment, a pyrolysis process was carried out at around 400 °C to break down the polymers (EVA and back sheet) and liberate the PV cells and glass layer. Further chemical treatment using HNO₃ allowed for the recovery of the metals from the PV cells (Cu and Ag). Through the thermal and chemical treatment, the rates of the material recovered were 98% for glass, 86% for Al, 85% for Cu, and 74% for Ag. When using the selective mechanical separation, the rates were 98% of the glass, 86% of the Al, 95% of the Cu, and 95% of the Ag.

In [43], three methods of recycling PV modules were analyzed: chemical, thermal, and mechanical. Thermal recycling was much faster, but it emits gases. The modules were Tedlar-based c-Si PV with a composition of 74% glass (front glass), 10.3% Al (frame), 1.16% plastics and adhesives (junction box and cables), 6.55% EVA (encapsulant), 3.6% Tedlar (back sheet), and 3.35% Si, 0.57% Cu, 0.17% Ag, 0.12% Sn, and 0.06% Pb (solar cell). The rates of the material recovered were 95% of the glass, 100% of the Al, 100% of the Cu, 81% of the Si, 50% of the Ag, 100% of the Sn and 100% of the Pb.

In [44], a physio-chemical process for recycling EoL PV modules was analyzed. The composition of EoL PV modules was considered to be 69.5% glass, 11.25% EVA, 10% Al (frame); 4.3% Tedlar (back sheet); 3.7% Si, 1.08% Cu, 0.12% Al, and 0.05% Ag. It was assumed that recyclers will receive a fee from the community, the PV collectors, and the PV manufacturers of about 0.25–0.50 $/kg of PV waste. It was assumed a recycling capacity of 79,200 Mton/year. A HNO₃ solution was used for the EVA decomposition. The analysis shows that about 33% of the total revenues come from the fees. Approximately 30% comes from the recovered Ag, and 37% comes from the other recovered materials. A total of 49% of the operating cost is labor dependent. The plant is expected to generate around 43% gross margins, and a payback time of 1.4 years.

In [45], polyc-Si PV modules were treated with a physical and a chemical process. The chemical process involved the use of solvents to separate the layers of glass, polyc-Si, and polymer. HNO₃ and H₃PO₄ were used to recover the Si layer at 400 °C. Furthermore, ultrasound and thermal pre-treatment were considered. The solvents could be recovered by evaporation and then condensation, with evident advantages. The physical process involved first dismantling the Al alloy, then cutting the modules, crushing/milling, sieving, and heavy medium separation were used. All the modules were preliminary cut into squares (mechanical approach) or stripes (chemical approach). In the physical route, crushing was the first step. Separation was then carried out first with water, then with sodium chloride, and then using sodium polytungstate. A total of 100% of the metals was recovered but with a low grade (around 67%, containing glass and EVA). A total of 76% of the glass was recovered, with a grade of 96%. In the chemical route, the stripes were firstly immersed in toluene, xylene, 2,4-trimethylpentane, n-heptane, and N,N-dimethylformamide. The best chemicals were found to be toluene and xylene. Thermal pre-treatment was irrelevant, and the power of the ultrasound did not affect the effect. Using toluene, the optimal conditions were found to be 60 °C, less than 60 min of residence time, use of ultrasound, and uses less pre-treatment.

In [46], an optical fiber pulsed laser was used to irradiate the solar cell from the back side, so that the EVA and the solar cell could then be mechanically peeled off easily without being damaged by the laser treatment. A perfect debonding effect was realized with a power density of 2.1 MW/cm² and a pulse repetition rate (PRR) of 50 kHz.

In [47], the modules were Al-based c-Si PV with a composition of 3% Si, 10% Al, 0.6% Cu, 0.006% Ag and 0.1% Pb (solar cell). No information for the rest of the module was given. Three steps were involved in the project: module recycling, cell recycling, and waste handling. Mechanically removing the junction box and Al frame from the PV module was the first step. Afterwards, the polymer layers of the cells (EVA and PVF) were melted in a furnace, acting as a source of heat. A string of interconnected cells remained after the glass was recycled after burning. During cell recycling, the interconnected cells were submerged in a leaching solution to dissolve Ag, Pb, Cu, and Sn. Electrowinning was then used to recover each of these metals from the leaching solution. To remove the Si nitride (SiNx)
layer and Al back electrode, the rest of the cells were submerged in an etching solution. Finally, the cell base was recovered as solar-grade silicon by submerging it in another etching solution that removed the emitter and back-surface field. The rates of the material recovered were 83% of the Cu, 90% of the Si SoG, and 74% of the Ag.

In [48], the modules were c-Si PV with a composition of 74% glass, 10% Al (frame), 0.6% Cu (junction box and cables), 6.5% plastics, adhesives, EVA and PVF (encapsulant and back sheet), and 3% Si, 0.006% Ag, and 0.1% Pb (solar cell). In this work, an automated procedure of thermal and chemical approaches was applied. The overall rate of recovered material was 95.7%: 94.3% of the glass (with 99.99975% purity), 100% of the Al, 100% of the Cu, and 72.8% of the Si. It was shown that PV modules made from newly produced solar cells need three times more energy than a module of equal capacity manufactured with solar cells made using recycled materials. The same values reach four times in [49].

In [23], the modules were c-Si PV. Using a thermal process, the EVA-laminated cells were separated in a fast, simple, and inexpensive manner in the first stage. In the second stage, Si (powdered Si) and sheets were recovered using chemical processes. The overall rate of the material recovered was 88.9% and the energy used for this method was 76 MJ per 1 m² of PV panel.

In [50], a new recycling method was developed. It consists of recovering the tempered glass using organic solvents, removing EVA by thermal decomposition, and recovering Si through chemical etching. The tempered glass was separated using toluene at 90 °C for 2 days of immersion. To remove completely the EVA resin from the PV cell, the cell was heated at 600 °C for 1 h under argon (Ar) gas. Finally, the PV cell was immersed in a chemical etching solution of hydrofluoric acid (HF), nitric acid (HNO₃), sulfuric acid (H₂SO₄), acetic acid (CH₃COOH), and distilled water, immersing at room temperature for 20 min. Toluene was chosen because it is cheap, stable, and able to dissolve the EVA completely. Adding the surfactant to the chemical etching (20% in weight), a Si yield of 86% was achieved. The purity of the obtained Si was 99.999%, and after eliminating the impurities, the recovered Si was found to be the same as the merchandise Si wafer.

The PV modules in [20] were multic-Si and thermal and chemical recycling approaches were used. Furnaces, afterburners, and washers all consume energy during thermal treatment. Chemical treatments were performed on the recovered cells, which required different chemicals. Afterwards, the chemicals used for etching were treated chemically and physically, and the resulting sludge was disposed of. For each module recycled, 92 kWhel were consumed.

In [51], the modules were polyc-Si PV with a composition of 74.16% glass (front glass), 10.3% Al (frame), 1.91% Cu, plastics and adhesives (junction box and cables), 6.55% EVA (encapsulant), 3.6% PVF (back sheet), and 3.48% Si (solar cell). This procedure involved manual removal of the Al frame and the junction box from the panel, identification of a representative sample including a single cell, and cutting and cleaning the sample in order to prevent contamination by the use of a saw. It was then heated from 20 °C (the initial temperature) to 600 °C and held at this temperature for 30 min. The thermal treatment left behind a coarse-grained residue. After passing the solid through a 0.5 mm sieve, the filtered mass (ashes) was collected for further characterization. The coarse portion of the sieve mainly contained Si, glass, and metal electrodes, so those were manually separated and weighed. The rates of the material recovered were 99.97% of the Al, 100% of the Cu, 100% of the Si, 98% of the Pb and 32% of the Ag. The required energy was 25.6 kWh/m² of PV waste. Recycling c-Si PV modules requires about 300 kWh/ton of energy when considering plants and processes dedicated specifically to recycling PV modules [52].

In [53], the modules were c-Si. Two steps were involved in the process. First, pyrolysis was used to recover c-Si wafers from PV modules. In this process, the EVA layer is vaporized by pyrolysis in an inert atmosphere at about 500 °C. The second step is chemical etching, which removes metal coatings, anti-reflective coatings (ARCs), and diffusion layers. Common acidic chemical etching mixtures are based on HF–HNO₃–
H₂O solutions. The EPBT could be decreased from 2.5 years to 0.6 years in sunny regions and from 4.3 years to 1.14 years in continental regions if recycled modules were used instead of standard modules.

In [54], the extraction of Ag from waste PV modules was evaluated. The average Ag content in c-Si PV modules was 630 g/t. This concentration is comparable to a United States high-grade Ag reserve (1100–800 g/t). Furthermore, two methods for concentrating Ag from waste PV modules were investigated, as well as the use of pyrolysis. The first method involves milling, sieving, and leaching the modules in 64% HNO₃ solution with 99% sodium chloride (hydrometallurgical). The Ag concentration yield was 94% after this procedure. The second method involved milling, sieving, pyrolysis at 500 °C, and leaching in 64% HNO₃ solution with 99% sodium chloride and 92% Ag concentration yield was achieved. Because the first method consumes less energy and yields more Ag, it is preferred. The results of this study showed that pyrolysis does not aid in the extraction of Ag. The recovery of Ag should therefore be carried out before the use of pyrolysis in PV module recycling.

In [24], the laminate was first burned off to ease manual separation. In the case of c-Si cells, the metallization, antireflective coating, and p/n-junction were removed subsequently by etching. Etching can be used on a technical scale to recycle solar cells. The EPBT of recycled PV modules was 2 years as opposed to the 7 years of the original modules. The overall recycling rate is 76.4%.

In [35], silica nanoparticles were recovered from PV waste using chemical and thermal treatment with a yield greater than 99.9%. These particles could be used in applications such as molecular imaging, biomedical, chemical sensing, and ink printing.

In [56], new approaches using high-voltage pulse discharge in water, called high-voltage fragmentation (HVF), were discussed. From an energy consumption point of view, the optimal condition was found to be 160 kV for 300 pulses, crushing the PV panels into particles of 4.1 mm on average. The energy consumption was 192.99 J/g.

Some studies have estimated the recovering and recycling rates of materials for different recycling processes and the composition of PV waste. The ranges of those values are summarized in Table 1.

### Table 1. Mass composition and recycling yields of materials of c-SI PV modules.

<table>
<thead>
<tr>
<th>PV Module Part</th>
<th>Material</th>
<th>Mass Share %</th>
<th>Recycling Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Range</td>
<td>Study</td>
</tr>
<tr>
<td>Front glass</td>
<td>Tempered glass</td>
<td>54.70–80.00%</td>
<td>71.57%</td>
</tr>
<tr>
<td>Frame</td>
<td>Aluminum</td>
<td>8.00–20.00%</td>
<td>8.29%</td>
</tr>
<tr>
<td></td>
<td>Silicon</td>
<td>1.82–5.00%</td>
<td>3.48%</td>
</tr>
<tr>
<td>Solar cell</td>
<td>Tin</td>
<td>0.02–0.20%</td>
<td>0.12%</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>0.01–0.1%</td>
<td>0.07%</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>0.006–0.12%</td>
<td>0.01%</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>0.11–1.99%</td>
<td>0.57%</td>
</tr>
<tr>
<td>Junction box &amp; cables</td>
<td>Copper</td>
<td>0.45–1.90%</td>
<td>1.20%</td>
</tr>
<tr>
<td></td>
<td>Plastic</td>
<td>1.16–2.85%</td>
<td>2.55%</td>
</tr>
<tr>
<td>Encapsulant</td>
<td>EVA</td>
<td>4.52–11.25%</td>
<td>6.53%</td>
</tr>
<tr>
<td>back sheet</td>
<td>Tedlar</td>
<td>1.00–4.30%</td>
<td>3.60%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>83.79%</td>
<td></td>
</tr>
</tbody>
</table>

1 The output purity can be > 99.999%. 2 The output purity can be > 99%. 3 Energy can be recovered by incineration.
2.5. The FRELP Process

The FRELP process is a mixed process using mechanical, thermal, and chemical approaches. The FRELP project was financed by the European call LIFE+ and it was ran from 2013 to 2017. It had a budget of almost 5 million € and the main participating partners were Sasil Spa, SSV, and PV CYCLE. The project aimed to test and demonstrate the application of existing technologies to recycle 100% of EoL PV modules (both mono- and polycrystalline) in an economically viable way. The aims were the recovery of high-quality extra-clear glass to be employed in the hollow and flat glass industry and the recovery of metallic Si to be employed as ferrosilicon or transformed into amorphous Si to be used in thin films. For the FRELP process, a thermal treatment was used for glass separation, pyrolysis was used for plastic while recovering energy, and finally, acid etching was used to separate Si from the other metals. Selective electrolysis was used to filter and recover the other metals. Finally, an LCA was performed in collaboration with the Joint Research Centre (JRC).

Report [8] presents an overview of the technology and research carried out in the field of recycling PV modules. The report analyses the trends of patents developed around the world. Included in the technology reviewed, there is the FRELP process. According to this report, FRELP is comprised of the following steps. A machine first removes the Al frame and junction box from the PV modules. Afterwards, the laminated structure is heated to 90°C–120°C and the glass is separated and recovered. As a next step, the remaining structure containing the encapsulation, Si cells, electrodes, and back sheet is heated to 500°C and the metals are separated. The waste gas from burning polymers is then recycled for combustion, and the separated metals are treated chemically. Si cells are etched with HNO3, and the Si is recovered. Afterwards, electrolysis and calcium hydroxide treatment are used to recover other metals (Ag and Cu). A comparison was made between the FRELP process and the current recycling process used in other European WEEE recycling facilities in studies [15,57]. Recycling processes were evaluated for their resource efficiency, environmental benefits, and burdens. According to the studies, the FRELP process has higher impacts, but also higher benefits, across all impact categories. By pre-treating PV waste locally and treating it further in a centralized facility, highly efficient logistics could significantly reduce the environmental impact of the FRELP recycling process. Lastly, the low quantity of PV waste collected so far discourages investments in industrial PV recycling processes.

The LCIs for five different processes of recycling PV modules are developed in report [58], including the FRELP process. In the FRELP process, approximately 88% of the input material and 95% of the glass was recovered in good quality (the incinerated polymers make up about 7% of the input mass). It has been reported that the three recycling processes consume between 50 and 100 kWh/ton of module input for the mechanical processes, and 494 kWh/ton for the PV recycler that uses fine milling to increase glass and metal yields. FRELP consumed about 50 kWh/ton of electricity for its mechanical process and 76 kWh/ton equivalent of natural gas for its thermal and incineration processes, for a total of 126 kWh/ton. The glass yield ranged from 59% to 75% and non-ferrous metals were recovered at a rate between 13.5% and 21.8%. Similar results were shown in [15,26,57].

3. Proposed Energy Model and PV Manufacturing Comparison Model

Figure 1 shows the general system considered in this study. The system includes the main steps of recycling c-Si PV modules: component separation (dismantling, EVA delamination), material recovery (cell recycling), and material purification. The study excludes the transportation of PV waste to recycling facilities. Furthermore, the study does not consider what happens to the materials after they are separated, extracted, or purified. The functional unit consists of 1000 kg of c-Si PV modules, both monocrystalline and multicrystalline, reaching EoL. The back sheet is composed of PVF, also known as Tedlar, with an Al-based back surface field (Al-BSF).
Based on the FRELP process (developed by Sasil Srl) [2,57], the specific system was developed (shown in Figure 2). Two processes were added, the back sheet removal and Si purification, which were the main modifications. To avoid harmful emissions of burning Tedlar (PVF) containing fluorine, the back sheet is removed before the EVA layer is delaminated. Through electrochemical refinement, Si is purified to a solar SoG level (different from the metallurgical grade of FRELP) in order to be used to produce new PV modules.
In this section, a conceptual model to compare PV modules manufactured using recycled materials or raw materials is schematized. This model is referred to as the “PV manufacturing comparison model”. Figure 3 shows the simplified life cycle of PV modules. The proposed model can also be correlated with those proposed by other authors. In [59], the life cycle of PV modules is analyzed. In [60], the material flow of PV recycling processes is shown, considering thermal and chemical recycling processes. The studies [61–63] show the flow charts of manufacturing c-Si PV modules. System boundaries for LCA analyses were analyzed by [64,65]. In [66], two simplified LCA system boundaries were defined both for closed-loop and open-loop material systems. LCA data on the FRELP process can be found in [15,67]. These studies also contain information on LCI that could be compared when an LCA needs to be performed. Note that the cycle shows a simplified version of the life cycle of PV modules and that further considerations should be made in order to implement an LCA and avoid phenomena such as double counting. In the PV manufacturing model, note that every box represents a process of the chain. Every box is subject to material and energy flows, both in and out, and emissions flow. Note also that the cycle refers to PV modules only. BOS, inverters, batteries, and other components are excluded for simplicity although they are essential for PV modules to function during their operational life. As it is shown in Figure 3, recycling ideally allows the omission of two steps in the life cycle of PV modules: the extraction of raw materials, and the treatment and disposal of PV modules that reach the EoL. In reality, these two processes are still present in the case of recycling, as not all materials can be recovered from EoL PV modules and not all the materials of PV modules can be recycled. The PV manufacturing comparison model focuses only on one part of the life cycle, i.e., the manufacturing stage of PV modules. The aim, as discussed previously, is to understand how the manufacturing stage of PV modules can be compared if raw or recycled materials are used. Therefore, the use, decommissioning, treatment, and disposal phases are not considered in this model. The latter could be introduced in life cycle analysis or be used to conceptually represent the material flows of the two different manufacturing approaches: manufacturing PV modules from raw materials or recycled materials.

Figure 3. Simplified life cycle of PV modules.

The PV manufacturing comparison model is shown in Figure 4. Two different manufacturing lines can be seen. The first one is called “Raw”, where c-Si PV modules are produced using raw materials. The other one is called “Recycled”, where c-Si PV modules are produced using recovered materials through the recycling process proposed in the previous section (represented in the picture by the orange contour box called “Recycling process”). Furthermore, in the recycled path, there will be waste related to materials that cannot be recycled. The raw materials are shown in the purple boxes. Materials such as EVA for the encapsulating layer and the Tedlar back sheet are needed also in the recycled path as they are not recovered by the recycling process. This is shown in the purple box called ”Missing raw materials”. The two approaches can be compared as they produce
the same output, which represents the functional unit: 1000 kg of c-Si PV modules with similar performances, layouts, and compositions. Theoretically, as the output represents the functional unit, it is possible to estimate the missing materials and their quantity, as can be seen in Section 4.

Figure 4. PV manufacturing comparison model. The “Raw” approach shows the manufacturing of PV modules starting from raw materials. The “Recycled” approach shows the manufacturing of PV modules using materials recovered from the recycling process considered for this study and the other raw materials needed.

4. Results

Based on the general system considered, Table 1 shows the composition of c-Si PV modules and the recycling yields of the different materials.

According to the specific system considered, the total energy consumption was 185.15 kWh/ton of PV waste treated. Table 2 shows the energy flows of the FRELP process obtained from [27] and the values of the added processes. Using electrochemical refining from [68], the energy required to purify Si is estimated to be 63.4 kWh, while the energy required to remove the back sheet is estimated to be negligible. The amount of Si to be purified is equivalent to 31.7 kg/t (= 34.8 kg/t * 91%), as shown in Table 1. Approximately 34% of the total energy consumed is required to purify silicon from MG (metallurgical grade) to SoG; 31% is used to recycle solar cells via processes such as cutting, sieving, acid leaching, filtering, and electrolysis; and 26% is used to delaminate the EVA layer (see Figure 5). A total of amount of 1.14 L of diesel fuel was considered to be equal to 11.4 kWh of energy, according to [58]. Moreover, around 69 kWh of electricity and 140 kWh of thermal energy can be recovered from incinerating the polymeric materials contained in 1 ton of PV waste. As a result, the net electricity consumption would be equivalent to 105 kWh/ton of PV waste. The process considered in this study would consume about 52% more energy than FRELP, but it can be considered to be a complete upcycling process. By comparing the general system to the specific one, as well as comparing it with the literature reviewed, it was found out that the energy consumption of recycling the first-generation c-Si PV modules, obtaining a recycling
yield similar to the one of our studies, i.e., about 84%, with the recovered Si of SoG purity can reach values as low as 130 ÷ 300 kWh/ton of PV waste treated. Those values are in agreement with those found from direct estimations.

Table 2. Energy flows of the considered system.

<table>
<thead>
<tr>
<th>Energy Flow</th>
<th>Process</th>
<th>Energy Type</th>
<th>Unit of Measure</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy A (Input)</td>
<td>(1)</td>
<td>Diesel fuel</td>
<td>Liters</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>(2), (2a)</td>
<td>Electricity</td>
<td>kWh</td>
<td>5.33</td>
</tr>
<tr>
<td></td>
<td>(3)</td>
<td>Electricity</td>
<td>kWh</td>
<td>0</td>
</tr>
<tr>
<td>Energy B (Input)</td>
<td>(4)</td>
<td>Electricity</td>
<td>kWh</td>
<td>48.01</td>
</tr>
<tr>
<td></td>
<td>(5)</td>
<td>Electricity</td>
<td>kWh</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>(7), (8), (9), (10), (11)</td>
<td>Electricity</td>
<td>kWh</td>
<td>56.76</td>
</tr>
<tr>
<td>Energy C (Output)</td>
<td>(2b)</td>
<td>Electricity</td>
<td>MJ/kg of incinerated polymer</td>
<td>2.86</td>
</tr>
<tr>
<td></td>
<td>Heat</td>
<td></td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>Energy D (Output)</td>
<td>(4), (6)</td>
<td>Electricity</td>
<td>MJ/kg of incinerated polymer</td>
<td>3.48</td>
</tr>
<tr>
<td></td>
<td>Heat</td>
<td></td>
<td></td>
<td>7.03</td>
</tr>
<tr>
<td>Energy C+D (Output)</td>
<td>(2b), (4), (6)</td>
<td>Electricity</td>
<td>MJ</td>
<td>248.84</td>
</tr>
<tr>
<td></td>
<td>Heat</td>
<td></td>
<td></td>
<td>502.84</td>
</tr>
</tbody>
</table>

1 They are the new processes implemented in the proposed model.

It was also found in the literature that the energy needed to produce a PV module using recycled materials could be as low as 1/10 (according to [69]) of the energy needed to produce a PV module with equivalent characteristics using raw materials; however, values around 1/3 and 1/4 are more common in the literature. Consequently, recycling could reduce the EPBT of PV modules made from recycled materials. Therefore, recycling c-Si PV modules is feasible and may lead to many benefits from an energy perspective.

Figure 5. Energy consumption of recycling by process.

Concerning the comparison of PV modules manufactured using raw and recycled materials, the material flows are summarized in Table 3. To calculate the “missing raw materials” for the “Recycled”, the recycling yields considered for this study were used. In particular, because it is assumed that the highest recycling yield is represented by the Al (see Table 1), equal to 100%, Al would be the limiting material, i.e., the material that is not missing and that is exactly equal in quantity to the material needed to produce the functional unit. If the output is set at 1000 kg of c-Si PV modules of the layout,
performance, and composition considered in this study (see Table 1), this would mean that the Al needed both for the Al frame and the solar cell is equal to 103.0 kg (8.29% of 1 ton for the Al frame + 2.01% of 1 ton for the solar cell). All the other recovered materials could be quantified by multiplying the recycling yield by the composition mass share and the functional unit. The remaining materials needed to reach the final composition must come from raw materials. The results are shown in Table 3. It can be seen that the total amount of missing raw materials to manufacture 1000 kg of c-Si PV modules in the “Recycled” scenario is equal to 162.06 kg, with a significant fraction coming from the plastic materials that are not recycled. This means that if all the materials that are recovered through the proposed recycling process are used to manufacture new PV modules of the same composition of the initial ones, there would be still 162 kg of raw materials needed. This value is therefore representative of the PV modules and the recycling process considered in this study.

Table 3. Material flows in the PV manufacturing model.

<table>
<thead>
<tr>
<th>Material</th>
<th>Functional Unit = 1000 kg of c-Si PV Modules</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>“Raw” Scenario</td>
</tr>
<tr>
<td>Tempered Glass</td>
<td>715.70</td>
</tr>
<tr>
<td>Aluminum</td>
<td>103.00</td>
</tr>
<tr>
<td>Silicon</td>
<td>34.80</td>
</tr>
<tr>
<td>Tin</td>
<td>1.20</td>
</tr>
<tr>
<td>Lead</td>
<td>0.70</td>
</tr>
<tr>
<td>Silver</td>
<td>0.10</td>
</tr>
<tr>
<td>Copper</td>
<td>17.70</td>
</tr>
<tr>
<td>Plastic</td>
<td>25.50</td>
</tr>
<tr>
<td>EVA</td>
<td>65.30</td>
</tr>
<tr>
<td>Tedlar</td>
<td>36.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1000.00</strong></td>
</tr>
</tbody>
</table>

5. Improvements

Finally, improvements are suggested considering also the design of PV modules (eco-design). The suggestions were divided into general and technical suggestions to improve c-Si PV module recycling. These suggestion have been developed based on the literature review described in Section 2. In terms of general suggestions, they include reducing the administrative burden, disincentivizing landfills (e.g., raising landfill taxes), and tagging modules with recycling and composition information. Additionally, improvements need to be made to the collection network; improved transportation modes and reverse logistic mechanisms should be considered [70,71]. In addition, our suggestions include favoring high-value recycling; increasing the amount of research on degradation mechanisms, failure modes, module composition, and future trends; and recycling Si powder instead of intact wafers. Our final suggestions include increasing the life-span of PV modules, updating and improving LCA data, and treating different types of PV modules to achieve economies of scale [17].

Technical suggestions include: heating the EVA layer uniformly to avoid cracks that may result in breakage and make further recycling steps more difficult [72] and examining electrostatic separation in order to recycle PV modules [29]. In addition, hydrofluoric acid
(HF) should be avoided, the possibility of recovering chemical solvents (by evaporation and then condensation) should be analyzed, and the use of solvents with high environmental impact should be reduced [73]. Our suggestions also include preferring an inert atmosphere when pyrolyzing [32], preferring Ag recovery before pyrolyzing, using O-dichlorobenzene as an organic solvent for pyrolyzing EVA, and investigating universal etching solutions to treat different types of modules [74,75]. Finally, it is recommended to always have a long-term vision when choosing which technology and approach to follow (as PV modules have a very long lifetime) and to examine whether achieving a closed-loop life cycle for PV modules is the right path to take.

Finally, eco-design features are suggested to improve PV module recyclability. It is possible to achieve eco-design features by substituting, removing, or changing the layout of the encapsulating layer because its separation is one of the most difficult steps of recycling. Alternative materials include thermoplastic silicone elastomer (TPSE) and thermoplastic polyolefin elastomer (TPO) [76]. Potentially harmful materials (toxic, hazardous, rare, precious, etc.) should be eliminated or substituted. It is also important to increase the use of PET-based back sheets, as well as back sheets with low F content in general [77]. In accordance to [78], design for recycling (DfR) practices include labeling PV modules, substituting Ag with Cu and nickel-based materials (although this may reduce recycling economic feasibility), and using frameless modules, which may simplify recycling but also increase the risk of breaking cells or glass. Finally, simplifying module architecture could facilitate recycling processes and even reduce energy consumption.

6. Conclusions

This study may be used to better understand the issues associated with PV waste management, especially recycling, from the technical processes to the economic implications. Several significant documents have been reviewed, presenting a reference of scientific knowledge on recycling c-Si PV modules. Moreover, the energy consumption information can be used for future LCAs considering the end-of-life phase. The study estimates that the energy consumed to recycle c-Si PV modules could reach values as low as 130 ÷ 300 kWh/ton of PV waste treated. Of the total energy consumed, 34% is used to purify the Si, 31% is used to recycle the solar cell, and 26% is used to delaminate the EVA layer to separate the glass. The overall recycling yield of the proposed recycling process was estimated to be around 84%. When comparing the manufacturing phase of c-Si PV modules, it was found that in the case of manufacturing PV modules using all the recycled materials obtained from the proposed process, around 162 kg of raw materials are still needed to produce 1000 kg of c-Si PV modules of the same composition as the initial modules considered. Note that this value strongly depends on the assumptions made in this study and it could be further improved using more advanced processes. Finally, ideas for the improvement of the recycling of c-Si PV modules and their EoL management in general may be deduced from this study.

7. Further Developments

In order to understand the methods by which research on recycling PV modules is conducted and its evolution over time, it might be useful to first make analytical considerations of the literature reviewed: comparing the years, the countries, and other information from the documentation. Secondly, the obtained results can be compared to real recycling processes and used to develop an LCA analysis of c-Si PV modules that considers the end-of-life phase as well. Lastly, the methodology could be enriched by examining other recycling processes and reaching a deeper level of detail with the help of players in the industry.

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Nomenclature

PV Photovoltaic
Polyc-Si Poly-crystalline Silicon
EoL End-of-Life
FREL Photovoltaics End of Life
LCA Life Cycle Assessment
EVA Ethylene Vinyl Acetate
PVF Polyvinyl Fluoride
PET Polyethylene Terephthalate
SoG Solar Grade

References


