THERMAL DECOMPOSITION OF THE SILICON PHOTOVOLTAIC CELLS COVERED WITH EVA AND ETFE FOIL

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Abstract

Photovoltaic panels are one of the most popular renewable energy sources. They can be found both in the traditional households and industrial facilities as well as the innovative applications in construction and automotive industry. The growing number of producing cells is strictly associated with the production of a large waste stream in the future. The photovoltaic modules are constantly being modified, and therefore it is required to include the influence of the applied materials to the environment during the whole lifecycle of the product. The final stages of the utilization of solar panels, including recycling, must provide the effective separation of the individual materials. It is critical for further processes. This paper presents the results of the thermal separation of the silicon cells and other materials used to produce photovoltaic panels. The aim was to determine the optimal process temperature for the most popular silicon module. The influence of the energy consumption and materials separation efficiency on the final thermal efficiency of the process were determined [4-7].

1   Introduction

Declining natural deposits of energy resources to encourage the use of natural and renewable energy sources, which are solar, hydro, geothermal and wind energy. One of the most developing branches of the renewable energy industry is the market connected with photovoltaics. The history of photovoltaics dates back to the 1930s. The production of solar panels on a commercial scale began already in the 1980s. The first items were based on crystalline silicon (mono- and polycrystalline cells) with a semiconductor connector formed. The next generations were based on thin-film technology using semiconductor materials based on amorphous silicon, cadmium telluride or metal blends - gal, indium, copper, diselen. The next generation is intensively developed and the European Union has recently included the PV waste into the new Waste of Electrical and Electric Equipment (WEEE) directive [19]. In detail, the EU imposes legal obligations on PV manufacturers, distributors and sellers to ensure take-

back and recycling of their waste products. Despite the regulations, WEEE continues to be not well managed and the percentage of recycling rate is extremely low around the World. Regarding the issues of the main technologies for recycling of PV waste, intertwined gaps, issues and complexities are often revealed. [19,33]

The main problem is multilayer material. There are many combined versions like: Dye-sensitized solar cell - Grätz's cells, multi-link cells (CPV), organic (OPV), polymeric and other [1,2].

Over the following years, many modifications to the construction of the photovoltaic panels produced so far have been created. This is due to both the need to reduce used natural materials (mainly silicon) in order to reduce production costs and, at the same time, improve the efficiency of solar energy conversion, panel weight reduction, and adaptation of cells for new applications [22-29.

The presented article presents a panel where the mass of monocrystalline silicon cells and thus the mass of use metals were reduced. In order to improve photovoltaic conversion, an EVA copolymer layer with a peroxyene dye was used and an ETFE polymer was used as the surface layer.

A panel composed of many layers of polymers forming a compact structure difficult to separate easily - this is due to the adhesives used and the vacuum closing of the cells. Many PV cells are now reaching the final stage of life cycle and are being replaced. The problem with proper its utilization is becoming serious. Many types of recycling are tested in order to make the best environmental performance including thermal recycling (energy recovery through combustion), chemical recycling (obtaining materials with other physical and chemical properties) and raw material recycling (degradation of polymer chains through physicochemical processes - e.g. pyrolysis) [17, 25,34].

2   Materials and methods

In this work an experimental pyrolysis was conducted, and chemical analysis of the remaining fractions. The material used for testing is a photovoltaic panel with a concentrator (perianol dye, perylene derivative). In this work an attempt was made to pyrolysis in an experimental pyrolysis chamber, followed by chemical analysis of the resulting fraction. The advantage of the pyrolysis chambers is the "transformation" of a heterogeneous mass of waste into volatile substances and a char. The use of the pyrolysis process allows a significant volume reduction of waste. The analysis covered the low-temperature pyrolysis process using a laboratory pyrolysis chamber. [16, 30, 31]

2.1   Materials

The material - PV panel with concentrator consisted of ETFE (ethylene-tetrafluoroethylene) layer, three layers of EVA (polyethylene-vinyl acetate), photovoltaic cell made of monocrystalline silicon, EVA layer saturated with perylene dye (being a concentrator, improving quantum yield of fluorescence. The last layer was a plastic based on a polyester resin reinforced with glass fibres. The cross-section of a photovoltaic panel with the use of peripheral dye is shown in Figure 2.1.1.
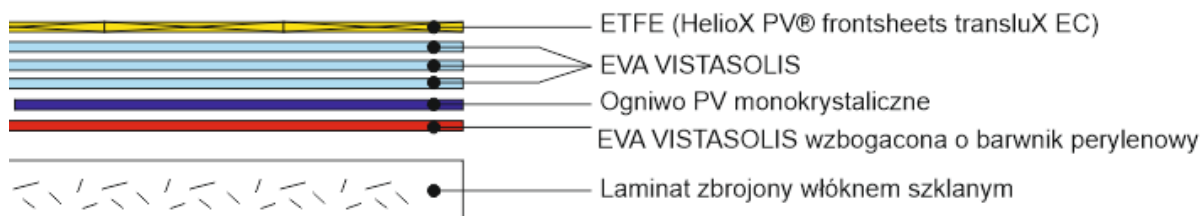

ETFE (HelioX PV® frontsheets transluX EC)
EVA VISTASOLIS
Ogniwo PV monokrystaliczne
EVA VISTASOLIS wzbogacona o barwnik perylenowy
Laminat zbrojony włóknem szklanym

Fig.2.1.1. Cross section of the panel with ETFE and EVA layer

2.2   Methods

2.2.1   Thermogravimetric

Thermogravimetric measurement was carried out using a Metaller TA1 thermobalance with a vacuum

system and the use of an inert argon Ar gas (5N purity). A sample weighed (sample weight 284.670 mg) was placed in an Al_2O_3 crucible (200,000 mg of melting furnace). During double pumping of gas from the system - gas exchange in the system from air to argon - a loss of sample mass equal to approx. 1.5 mg was recorded. On the TG curve, the course of mass change under the influence of sample heating can be observed. In order to improve the legibility of the TG curve, the first derivative of the thermogravimetric curve DTG is obtained in parallel with temperature (T). It indicates the rate of change and also allows estimation of the number of reactions. However, on the basis of thermal differential analysis (DTA curve differently: heating curves) one can assess whether the reactions were endo- or exothermic. Thanks to the DTA method, melting or confusion can be demonstrated (endothermic reactions).

2.2.2 Pyrolysis

Pyrolysis is a widely used process in the chemical industry, including for the production of charcoal, methanol, PVC, activated carbon and gasoline, as well as for the thermal treatment of waste. Pyrolysis is an alternative to the combustion process or it can be used as a supplement. The pyrolysis process is carried out under anaerobic conditions, which leads to liquid, gas and solid products [10]. The use of a moderate temperature regime (300-500°C) allows the production mainly of pyrolysis oil, while at high temperatures (500-900°C) gas generation is preferred [11].

The pyrolysis of the tested material was carried out in a laboratory pyrolysis furnace. The pyrolysis installation is shown in Figure 3.2.1. The furnace consisted of an electrically heated reaction chamber. In addition, water cooling of the outgoing gases was used, as well as the collection of liquid samples (filter flask) and gas samples (filter scrubbers and absorbent tubes with activated carbon and a polymer filter XAD-2).

3 Results and discussion

As a result of the thermal process, gas, liquid and solid products were obtained. The content of gaseous and liquid products was subjected to chemical analysis. The analysis also takes into account the energy consumption of the process by determining the consumption of electricity. As part of the analysis, thermogravimetric was also carried out to determine the temperature at which the mass of the panel being analysed is lost.

3.1 Thermogravimetric results

The recording of the TG and DTG measurement runs is shown in Figure 3.1.1. When analysing the TG curve, it can be concluded that during the heating of the sample there was a weight loss of 82.46% - the weight loss was 234.750 mg. The residue after the combustion process is 50 g.

From the presented thermogravimetric analysis (TG and DTG), it can be noticed that the slow mass decrease started already at about 180 ° C (loss of 1 mg). However, the fastest loss in mass occurred in the temperature range: from about 290 ° C to 565 ° C. From the automatically delineated DTG derivative temperatures were determined: 372.82 ° C, 416.93 ° C, 482.31 ° C and 538.87 ° C.

This is a basic study, however, to determine what compounds arise in the given phases of the processes, it would be necessary to perform additional extended thermal and chemical analyses (thermal analysis combined with mass spectroscopy).
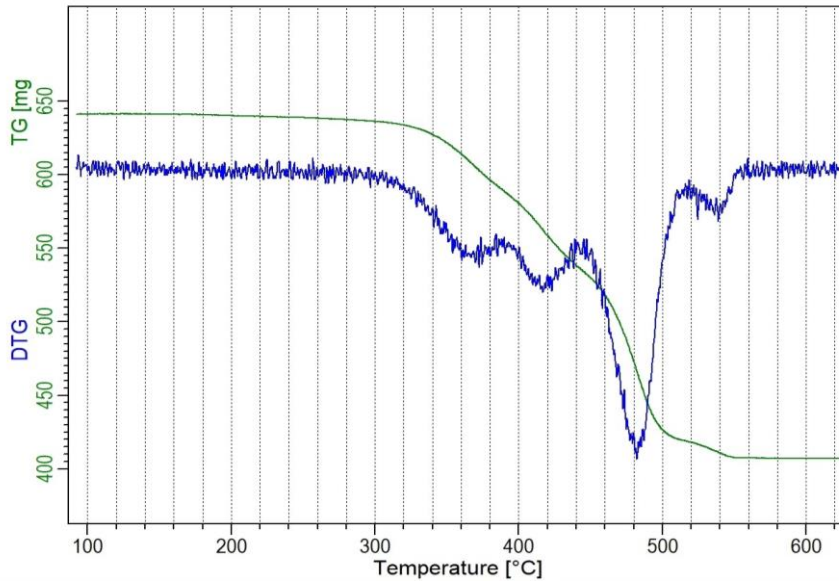
Fig. 3.1.1. Thermogravimetric of PV cell pyrolysis process.

3.2 Pyrolysis results

The proper pyrolysis process was preceded by a grinding process in a knife grinder using a sieve with a mesh diameter of φ6.0 mm. The material tested due to the presence of a large number of polymers (including ETFE, several layers of EVA film, polyester resin) required cooling before the grinding process. Liquid nitrogen LN2 was used to cool the sample. The material before and after grinding is presented in the figure 3.2.1.
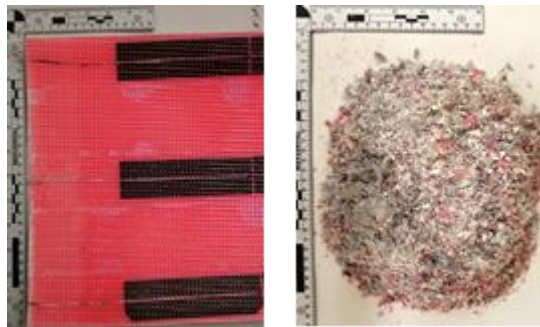

Fig. 3.2.1. Analysed panel with a concentrator before fragmentation and after grinding up to a grain diameter of φ6.0 mm

The sample weighing 0.589 kg in a 11.5 x 35.0 x 7.5 cm cuvette with a weight of 1.727 kg. After placing the sample in the oven, it was flushed with argon, monitoring O2 oxygen content using the Model 5200 Servomax analyser. The initial O2 content in the furnace chamber was 21.2%. After administration of argon, the oxygen content reached the level below the quantification, i.e. 0%. The reactor was heated to 500 ° C. During the test the furnace temperature (Temp.1), charge (Temp.2) and outlet gases (Temp.3) were measured. The test was carried out for one hour after the appearance of a condensed gas phase, which arose when the temperature of the batch reached a temperature of 300 ° C. In addition, the process was maintained under overpressure in the furnace. In table 3.2.1. the process parameters before and after pyrolysis are compiled.

Table 3.2.1. Process parameters before and after pyrolysis

Parameters	Unit	Before pyrolysis	After pyrolysis
Condition of the gas meter	m³	1.645	1.690
Gas temperature	°C	21	22

Furnace temperature	°C	27.4	507
The temperature of the batch	°C	18.8	480
Temperature of exhaust gases	°C	18.6	231
Weight of flask on the drain	kg	1.266	1.409
Weight of the cuvette with the sample	kg	2.316	2.003
Weight of the batch	kg	0.589	0.313
Oil weight	kg	-	0.143
The volume of oil	ml	-	115
Volume of scrubbers/Cl, Br, F	ml	-	220
The volume of gas produced	m^3	-	0.045

As a result of pyrolysis, 46.86% weight loss was observed (difference equal to 0.276 kg). The material balance from the pyrolysis process of 3 fractions is respectively 53.14% solid phase, 24.28% liquid phase, 22.58% gas phase.

As a result of pyrolysis, more than half of the charge (53.14%) was still in solid form. The remainder is primarily glass fibres made of laminate. The liquid and gas fraction constituted 24.28% and 22.58% of the feed, respectively.
During the test, the initial energy consumption was measured from the moment the furnace was switched on to the end of the test (time t = 75 min). The total electricity consumption measured for 75 minutes is 4.900 kWh (0.065 kWh / min).

The liquid fraction (pyrolysis oil) was directed to qualitative analysis, and the absorption tube with activated carbon and XAD-2 polymer (absorbed organic compounds) and the content of muds (presence of chloride, bromine and fluorine compounds) were directed to quantitative analysis. The results in the tables refer to the amount of gas obtained during the measurement, i.e. 0.045 m3.
In table 3.2.3. presents the results of the quantitative analysis of the absorption tube from activated carbon in order to determine the total hydrocarbon content using the gas chromatography (GC-FID) method for toulen (sample P1 / 1). The analysis was carried out using a gas chromatograph with a flame ionization detector with a DB-1 Elite capillary column. The total hydrocarbon content calculated as toulen in the sample tested was 136.76 mg ± 18.32mg.

In table 3.2.2., the results of quantitative analysis to determine the content of polycyclic aromatic hydrocarbons PAHs absorbed on the XAD-2 polymer substrate (sample P1 / 1 and P1 / 2) are presented. Liquid chromatography with fluorescence detection and ultraviolet (HPLEC-FLD / UV) was used for determinations. The analysis was performed using a liquid chromatograph with a gradient pump, FLD fluorescence detectors, VWD spectrometric detectors and ZPRBAX Eclipse PAH 4.6 x 150 mm, 5 μm column. In the P1 / 1 sample, the total hydrocarbon content per toluene was calculated and the value is 136.76 mg / sample. In the P1 / 2 sample, the highest concentrations were obtained for acenaphthene (79.42 mg / sample), acenaphthylene (18.96 mg / sample). The lowest concentrations were obtained for naphthalene (1.77 mg / sample) and fluoren (0.010 mg/sample). The content of other PAH hydrocarbons was below the limit of determination.

Table 3.2.2. Results of the quantitative analysis of the content of polycyclic aromatic PAHs

Sample number	Substance determined in the sample	Content in the sample [mg/0,045 m^3]	Markability [mg]	Analytical extended uncertainty [±mg]	Content of substance [mg/m^3]
P1/1	Total hydrocarbon content calculated as toluene	136.76	0.02	n.d.	3039.11
P1/2	Acenaftylen	18.96	0.02	2.838	3039.11
	Naftalen	1.77	0.03	0.269	421.33

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Acenaften	79.42	0.03	15.79	39.33
Fluoren	0.010	0.01	0.001	1764.89

In the case of pyrolysis oil, a qualitative analysis was performed, both for the gas phase over the liquid and for the substance itself. For the analysis, methods based on FTIR (Fourier Transform Infrared Spectroscopy) and liquid chromatography (HPLEC-FLD/UV) spectrometric techniques were used.

In the analysed sample after pyrolysis (sample P1/3) the presence of bands characteristic for ester compounds, carboxylic acids and aldehydes was found. These products are formed as a result of oxidation processes during pyrolysis. In the gas phase spectrogram, aromatic and aliphatic hydrocarbons were found from the sample surface. Chromatographic analysis showed the presence of acetaldehyde, propionaldehyde and traces of acrolein. In addition, GC/FPD analysis was carried out, which showed that the tested sample does not contain sulphur compounds.

Additionally, chemical analysis for halogen in the resulting gas was carried out: bromine Br, chlorine Cl and fluorine F. The concentrations obtained are presented in Table 3.2.3.

Table 3.2.3. The concentrations Br, Cl and F.

Sample number	Element	Concentration [mg/l]
P1/4	Cl	<0.40
	Br	2.00
	F	33.50

The high concentration of fluorine comes mainly from the decomposition of the ETFE polymer. It can contribute to the negative environmental impact of the considered method of recycling PV panels. However, an appropriate purification system can effectively remove this concentration, which will help to reduce the negative effect.

In order to make analysis as complex as possible the Low Heating Value (LHV) was determined using a calorimeter, the results of the analysis are presented in Table 3.2.3.

Table 3.2.3. LHV and moisture content of the carbonize.

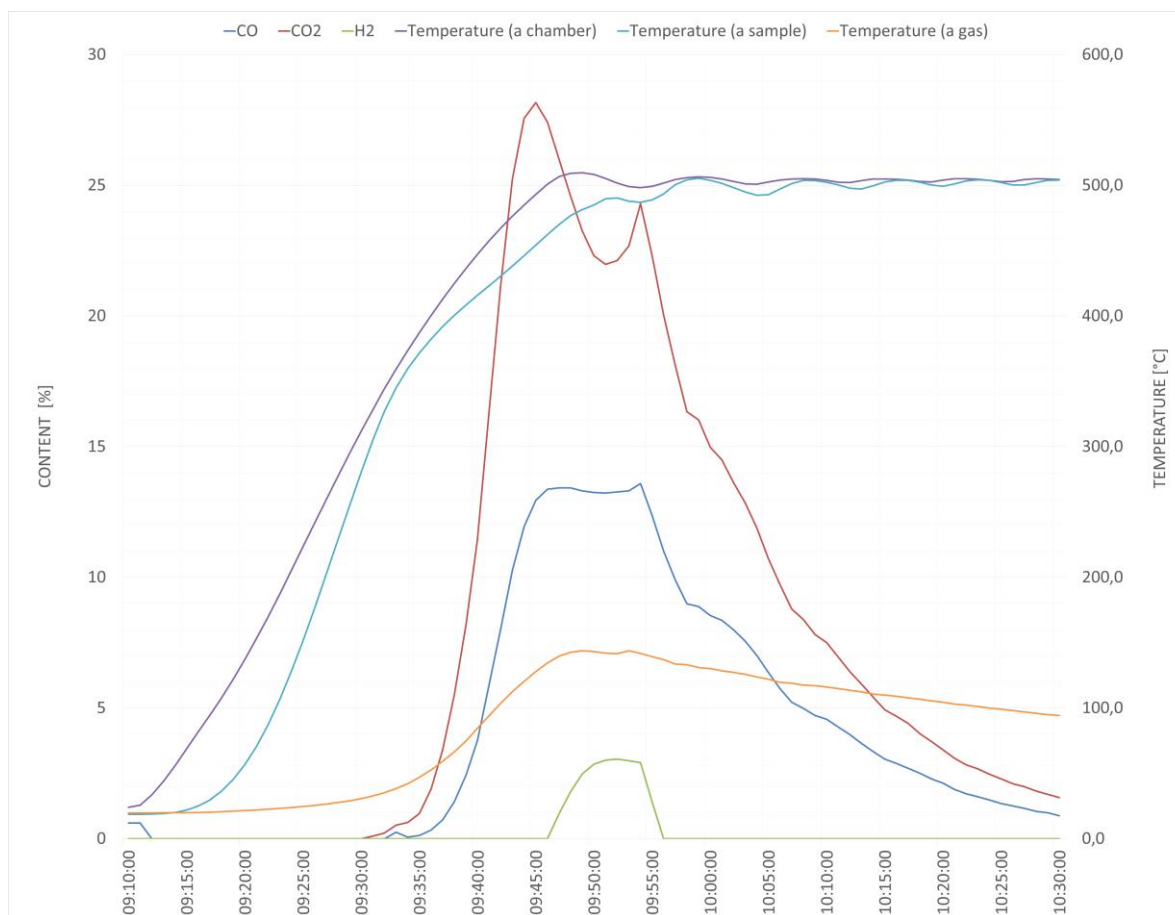|	Min.	Max.
LHV [MJ/kg]	10,69	11,023
Moisture content [%]	0,75	0,75

Fig. 3.1.1. The course of PV cell carbonization process.

4   Summary

The problem of recycling of PV cells is a very complex, especially due to the diversity of these cells. In the case of cells with a concentrator, the processing can be even more complicated due to the content of harmful substances. The high-temperature processes like pyrolysis, can help to solve this problem and demonstrate the high quality of end products.

The analyse carried could be used in order to determine possibilities of thermal treatment PV panels as a form of its utilization. It showed that pyrolysis process and the resulting products require further chemical analysis to optimize the process and places and forms of use of pyrolysis products.

The combustion heat of the char from the pyrolysis process is over 10 MJ / kg, and this value exceeds 6 MJ / kg. Therefore, the waste in this form provides autothermic combustion, it cannot be stored in a landfill, so you need to find a way to manage it.

In order to summarise the potential of pyrolysis in pv field more lab test should be taken. But for many reason it could be a valuable process.

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