Development of a Hybrid Collector for an Innovative Energy Supply System Using Molecular Solar Thermal Energy Storage

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Abstract

An innovative system for chemical heat storage using photo-induced isomerization will be presented. For this process, also known as molecular solar thermal energy storage (MOST), a special collector was developed. The initial small collector was scaled up to hybrid collector of a size of 0.5 m². This collector consists of a transparent front part for the photo-induced isomerization, but this process does only absorb a small spectral part within the UV region of the solar energy spectrum. Therefore, the back part of the hybrid collector is similar to a conventional flat plate solar collector to absorb the remaining solar energy. The paper covers the special requirements for materials and geometries for an optimum and most efficient operation. The biggest challenge in the development at the first stage of the project was the necessity to use of a solvent as a carrier for the molecules with the photo-induced isomerization properties which was not compatible to any usual materials. Furthermore, the paper describes the upscaling process, the testing and the installation of the first complete full-scale prototype of the hybrid collector in a complete MOST system, consisting of the collector, pumps, storage tanks, heat release device and heat exchangers.

Keywords: hybrid collector, molecular solar thermal energy storage, MOST, photo-induced isomerization, norbornadiene–quadricyclane, chemical heat storage

1. Introduction

Conventional solar thermal systems are state of the art for regenerative heat generation (Alexopoulos and Kalogirou, 2022; Stieglitz and Heinzel, 2013; Tiwari and Tiwari, 2016). The solar cover ratio, which is defined by the ratio of heat requirement e.g. of a building to solar generated heat is limited by the size of the collector, the size of the thermal heat storage and the maximum temperature of the fluid. The solar-generated heat is thereby stored as sensible heat. This means that there are always thermal losses in the thermal heat storage. This paper describes the development of a hybrid collector which design and requirements differ significantly from conventional solar thermal collectors. This collector is part of a new innovative system for solar energy generation using photo-induced isomerization for energy storage, which enables almost loss-free long-term energy storage.

A first concentrating solar collector with a reflector size of approx. 900 cm² for photo-induced isomerization is presented in (Wang et al., 2019). The idea of and the first lab scale prototype of a hybrid collector is described in (Orrego-Hernández et al., 2020). In this paper we describe the development of a full-scale hybrid collector which is almost ready to the market and embedded in a complete MOST system for outdoor tests under real conditions.

This innovative energy efficient energy storage has the potential to be a key technology for solar regenerative energy supply.

2. Photo-induced isomerization

The photo-induced isomerization process used here for chemical energy storage is based on norbornadiene–quadricyclane derivatives. These molecules absorb the UV part of the solar insolation and store this energy by

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changing their molecular structure and were dispersed in an UV transparent liquid, together called MOST liquid (MOST = Molecular Solar energy Storage System). The energy storage density is up to 103 kJ mol^{-1} respectively 396 kJ kg^{-1}. After the photo-induces isomerization the MOST liquid can be stored in tanks for days or even weeks. The back reaction for the heat release can be triggered either using catalysts (Gimenez-Gomez et al., 2023; Magson et al., 2024) or a heat pulse. The energetic principle of this process is shown in Figure 1 (Dreos et al., 2017): by absorbing solar energy the parent molecule in Fig. 1 is lifted to an energetically excited intermediate state (parent* in Fig. 1) and then converts into a long-term stable photoisomer. When the isomer overcomes the energetic barrier ΔH^{++} (through the addition of heat or a catalyst), the back conversion to the original molecule takes place whereby $\Delta H_{storage}$ is released as heat.

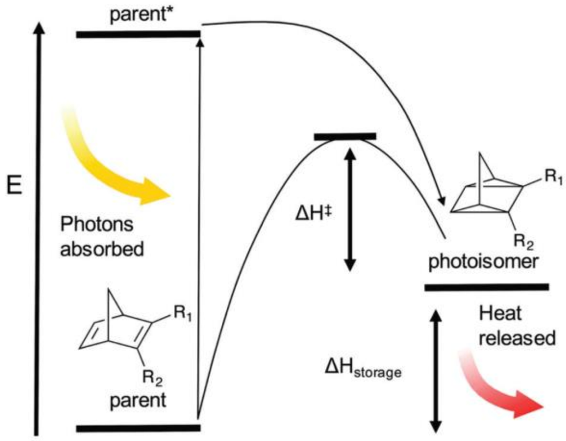

Figure 1: Schematic energy chart of the norbornadiene–quadricyclane molecular solar thermal energy storage system.

3. Principle of the molecular solar thermal energy storage system

A complete MOST system for renewable energy generation consists of a hybrid collector, the heat release device, a consumer and various storage units. A simplified representation of such a system is shown in Figure 2.

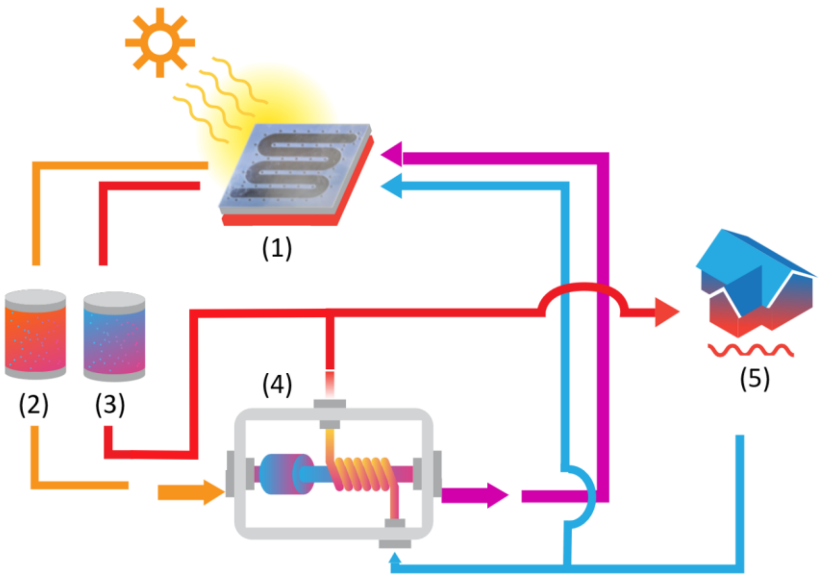

Figure 2: Simplified scheme of a MOST system, consisting of a hybrid collector (1), MOST storage (2), thermal storage (3), heat release device (4) and a heat consumer (5, building only as an example).

The aim is to develop and demonstrate an emission-free solar energy storage system. The MOST system is based on a molecular system that can store solar energy for very long periods of time. This corresponds to a closed cycle of energy generation, storage and release.

In simple terms, the MOST system works as follows: In the hybrid collector (1 in Fig. 2), the UV spectrum of the solar irradiation stimulates photo-induced isomerism in the MOST liquid; the remaining solar irradiation is converted into heat in the rear part of the hybrid collector and dissipated by a thermal fluid. The MOST liquid and the thermal fluid are stored in separate tanks (2) and (3), whereby the MOST liquid can be stored over a long period of time without any heat losses. The heat can be utilised either directly from the thermal storage tank or via the MOST liquid, which is fed into the heat release device. In this device, the reverse reaction is triggered via a catalyst, the chemically stored heat is released again and dissipated via a heat exchanger. MOST liquid and thermofluid are then fed back into the collector.

As part of the MOST project, the molecular systems as well as the associated catalysts and other devices are being tailormade for this world first outdoor installation of a complete MOST System. Catalysts and devices will be developed beyond the state of the art.

4. Demonstration Stages

Four steps, so-called demonstration stages, were planned for the development of the overall system with hybrid collector (MOST collector + solar thermal collector) (see Figure 3). Since only part of the solar spectrum is absorbed for photo-induced isomerization, (typically wavelengths between 320 nm and 400 nm,), it is necessary to have a hybrid collector for a maximum solar efficiency as a development goal. This consists of two functional layers (demonstration stage III and IV): the first layer contains the MOST liquid and must be as transparent as possible for the entire solar spectrum. the second layer then utilizes the emitting spectrum and largely corresponds to a normal thermal flat plate collector.

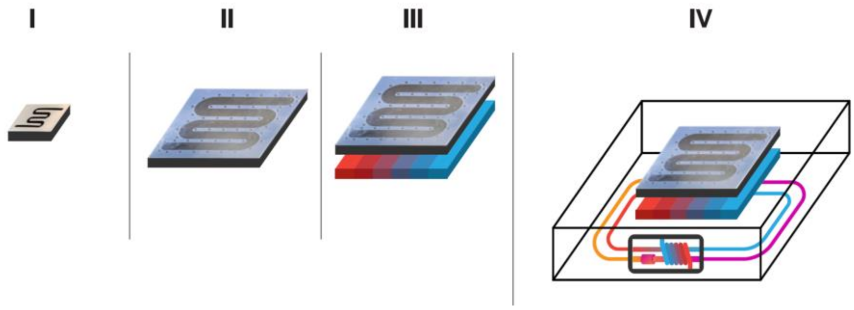

Figure 3: Device Development stages. I) Small “pre-devices”, II) MOST devices in lab-size, III) Hybrid MOST-TES, still lab-size, IV) integrated system according to Figure 2 with hybrid collector in full size.

4.1 Stage I - Small pre-devices

First development step I were solar collectors with a size of approximately (2 x 2) cm², which is a standard size that fits into smaller lab-scale solar simulators to carry out first tests of the photo-induced isomerization. These pre-devices are of low complexity and should allow rapid screening of MOST materials and catalysts without consuming large amounts of material. The collectors were developed and constructed at the Center for Applied Energy Research, in Würzburg (Germany), the isomerization tests were carried out at the University of Copenhagen (Denmark) and University of La Rioja (Spain).

The following technical requirements and problems arose during the development:

The carrier material in which the MOST molecules are dissolved can have a considerable influence (usually negative) on the photoisomeric properties of the MOST molecules. At the beginning of development, toluene was used as a solvent. In addition to the easy flammability, there was the further problem that many of the materials required for the collector, (especially adhesives, sealants, hoses and connectors) are not compatible with toluene in the long term. Only metals, glass and a few plastics with fluorine content were usable for the implementation of the first laboratory scale prototype. Further research revealed that a special epoxy resin (EPO-TEC® 377) and a ceramic adhesive (RESBOND® 940 HE and RESBOND® 940) are resistant to toluene. This has opened up further possibilities to consider adhesive bonds as well as clamped bonds.

Because of the development aim of a hybrid collector as mentioned above, the glass panes of the collector should have the highest possible UV transmittance in the wavelength range of approximately 320 nm to 400 nm. For the subsequent application of a hybrid collector with solar thermal energy, the MOST collector should have a very high surface transmittance of the radiation in wavelengths above 400 nm, too.

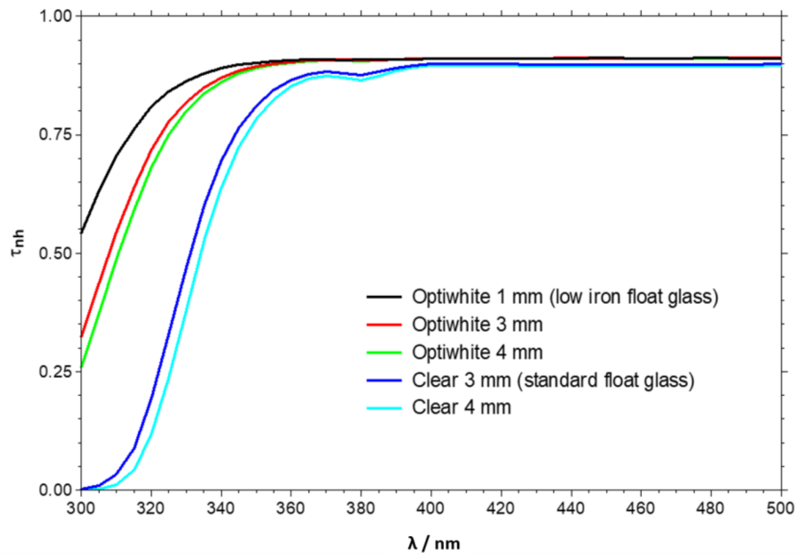

Figure 4: Overview of the wavelength-dependent normal-hemispherical transmittance τ of typical white glass panes and standard float glass panes at different glass thicknesses as a function of wavelength.

Usual plate glass (also known as float glass) with no special properties is not sufficiently suitable for this application due to its low UV transmittance in the wavelength range from 320 nm to 360 nm ("Clear 3 mm" and "Clear 4 mm" in Fig. 4 (IGDB, 2024)). White glass, produced using quartz sand with a low fraction of Fe_2O_3 (less than 0.03 % in mass) shows significantly higher transmittance values within the relevant wavelength range, even at a thickness of 3 mm to 4 mm (Optiwhite® in Fig. 4).

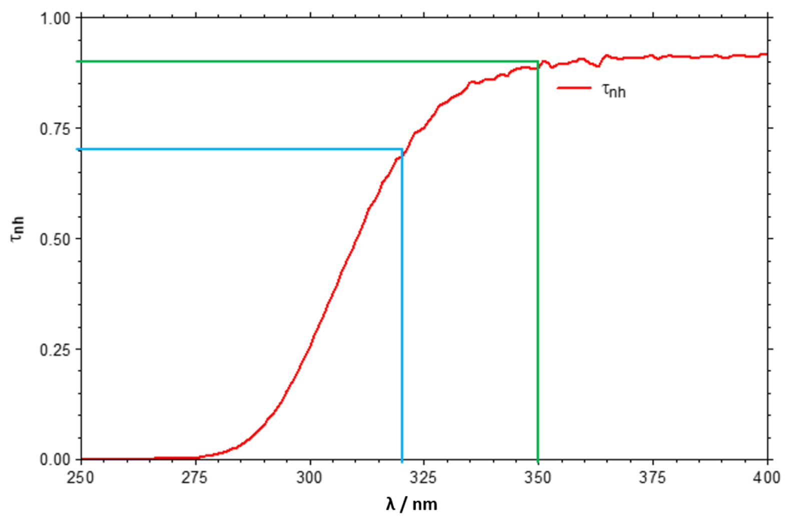

Figure 5 : Measurement of the normal-hemispherical transmittance τ_{nh} of a white glass pane "Guardian Optiwhite" with a thickness of 2.9 mm as a function of the wavelength λ within the relevant ultraviolet spectral range. A transmittance of approx. 70 % was measured at 320 nm and of approx. 90 % at 350 nm.

The commercially available white glass Guardian Optiwhite® from Guardian Industries Holdings (LLC) with a thickness of 2.9 mm confirmed the values in the database in the laboratory measurements (see Figure 5) and was therefore suitable. A UV transmittance of approx. 70 % at 320 nm and 90 % at 350 nm was measured. This glass type was therefore used for almost all prototypes shown below. Even higher transmittances can only be achieved with pure quartz glass (laboratory glass). However, this glass is extremely expensive compared to white glass and only available in certain smaller sizes.

The toluene-resistant material PTFE (Polytetrafluoroethylene), also known as Teflon®, was used as the inlay for the prototype (Fig. 6). Further advantage of PTFE is the permanent temperature resistance until 260 °C. The use of an inlay in combination with extremely low flowrates ensures, that a uniform turbulent free flow is ensured, so that each part of the fluid absorbs the same amount of solar radiation. Laser processes were used for cutting the inlay. In some cases, the same results can be achieved with waterjet processes.

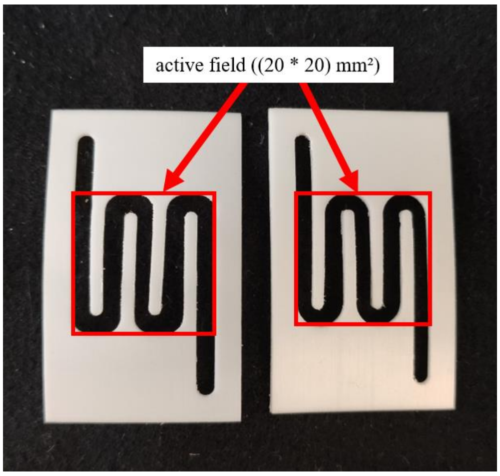

Figure 6: Lasered meander inlay made of PTFE (active field (20 x 20) mm²). Different layouts were tested, the right one has rounder bows.

A clamping method was realized as a very small laboratory scale collector (20 x 20) mm² in order to fixate the inlay between two panes of white glass. With the existing clamping process, due to the tolerances of the glass panes and the caused bending of the glass panes during the clamping, tightness could not be achieved.

The bonding process could be used for small laboratory scale collectors and larger prototypes. For smaller laboratory prototypes, edge bonding only should be sufficient.

For larger prototypes, a solution must be found to prevent the pane tolerances and deflections of the glass panes. In addition to glass edge bonding, the glass pane would also have to be bonded in the surface.

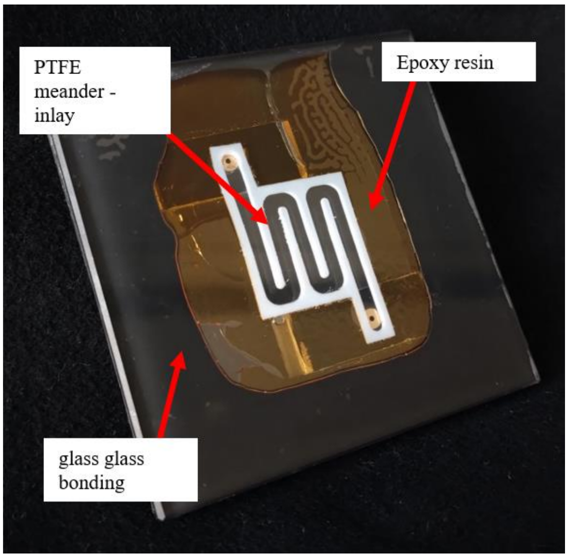

Figure 7: The first functional prototype resistant to the solvent toluene ((76 x 76) mm²) – active field (20 x 20) mm².

Figure 7 shows the first functional prototype filled with the solvent toluene. A meander inlay made of toluene-resistant PTFE was selected as the inlay in order to realize a very slow and uniform flow of the MOST fluid. The edge areas were bonded with a flexible glass-glass bonding. The prototype was then filled with epoxy resin around the meander inlay. The inlet and outlet connectors made of brass are at the back side. For safety, the filling side was then masked again with flexible glass-glass bonding. For testing it in lab scale sun simulators, the whole collector is covered with a metal mask so that only the active field in the middle is exposed to irradiation.

4.2 Stage II - MOST devices

In development stage II, the focus of the collector design was on functional testing of the systems and an initial performance evaluation (flow rates and photo-isomerisation conversion rates). This collector development had to be carried out with an intermediate step in the panel size 0.09 m² due to the change in the adhesive. Using toluene as a solvent, several bonding options, e.g., ceramic adhesives or indium compounds, were tested without permanent sealing success.

The next intermediate stage of the collector is larger and is dimensioned in such a way that two of them placed next to each other already reach the size of the last development stage.

Meanwhile, the project partners searched intensively for a different carrier fluid due to the design problems and the fire hazard of all organic solvents, especially toluene. It turned out that a commercially available thermal oil from the company Duratherm Extended Life Fluids (USA) was suitable as a carrier fluid. This opened up many new possibilities for collector bonding.

Instead of the opaque PTFE, now a transparent ETFE film (Ethylene tetrafluoroethylene from Nowofol Kunststoffprodukte GmbH & Co. KG, Germany) was used for the meander-shaped inlay, increasing the gain of the thermal part of the hybrid collector. The solar transmittance of this ETFE in a thickness of 500 µm is 83.3 % according to the manufacturer’s datasheet. The film is specified by the manufacturer as resistant to toluene, but this requirement has been dropped in the meantime.

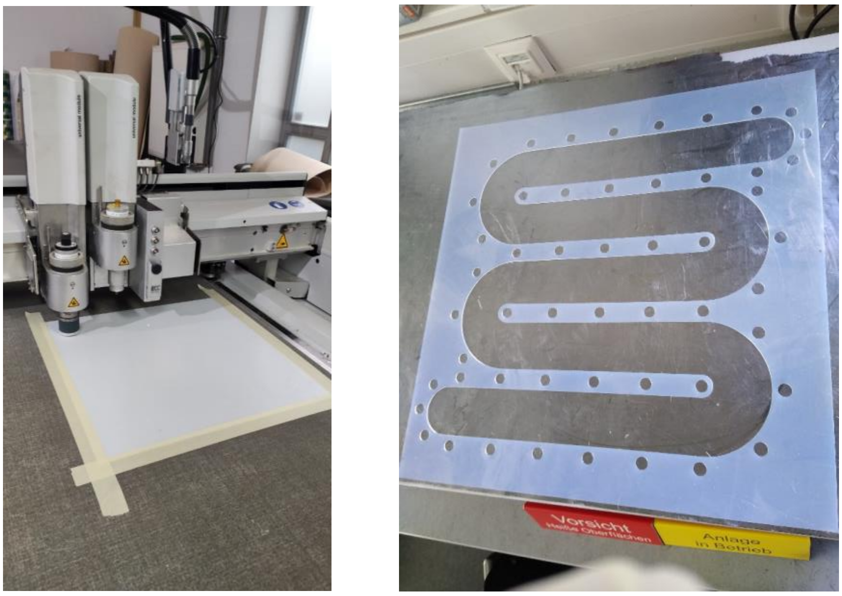

Figure 8: Left: Successful cut plotter tests with 500 µm Teflon film (PTFE); Right: ETFE film with very precisely cut out adhesive dot circles, again performed with a cut plotter.

Both films with a thickness of 500 µm could be accurately processed with the cut plotter (see Figure 8). However, the ETFE film was clearly easier to process due to its flat contact surface compared to the slightly wavy Teflon film.

Additionally, at this stage several adhesives/glues were tested (Fig. 9). Three of them passed the 8 weeks tightness test successfully (Tab. 1). Tests were carried out with glass specimens, consisting of two edge glued glass panes (76 x 76) mm² filled with the Duratherm oil.

The thermal test was 55 cycles of:

- stay for 20 minutes at 30 °C
- heat up to 80 °C within 20 minutes
- keep at 80 °C for 20 minutes
- cool down to 30 °C within 120 minutes

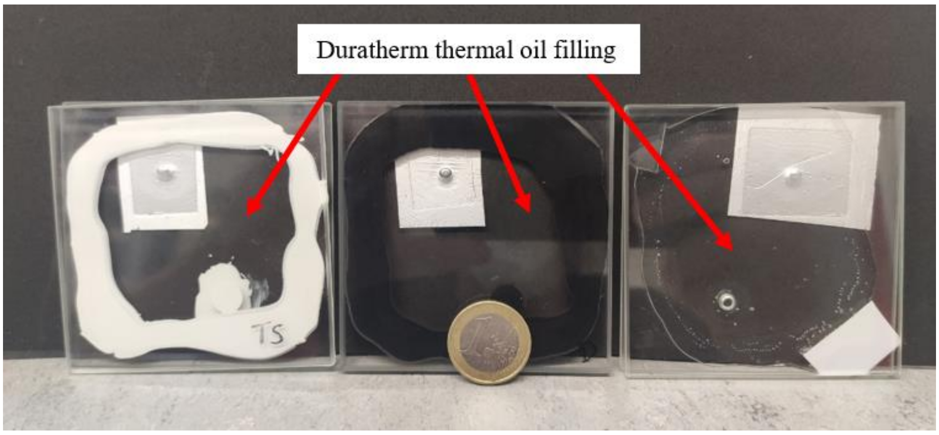

Figure 9: Test specimen of various adhesives with Duratherm oil filling. after 8 weeks with thermal cycle tests. Left: Torr Seal bonding, middle: DELO PUR 9694 bonding, right: transparent DELO PHOTOBOND GB368 bonding. All passed the testing.

Tab. 1: Manufacturer and product name of the adhesives which passed the test.

Manufacturer:	Product name:
Agilent Technologies, USA	Agilent Torr Seal Low Vapor Pressure Resin Sealant
DELO Industrie Klebstoffe GmbH & Co. KGaA, Germany	DELO® -PUR 9694
DELO Industrie Klebstoffe GmbH & Co. KGaA, Germany	DELO® PHOTOBOND® GB368

The two major changes in collector construction (partially transparent inlay and transparent bonding) significantly increased the solar transmission of the whole MOST collector. This will increase the performance of the hybrid collector (MOST + solar thermal collector) in the later stages of development.

For the search for new solvents, collector flow simulations with the dynamic viscosity as parameter was performed for the MOST collector. For the flow velocity a typical value of 0.035 mm * s^{-1} was chosen.

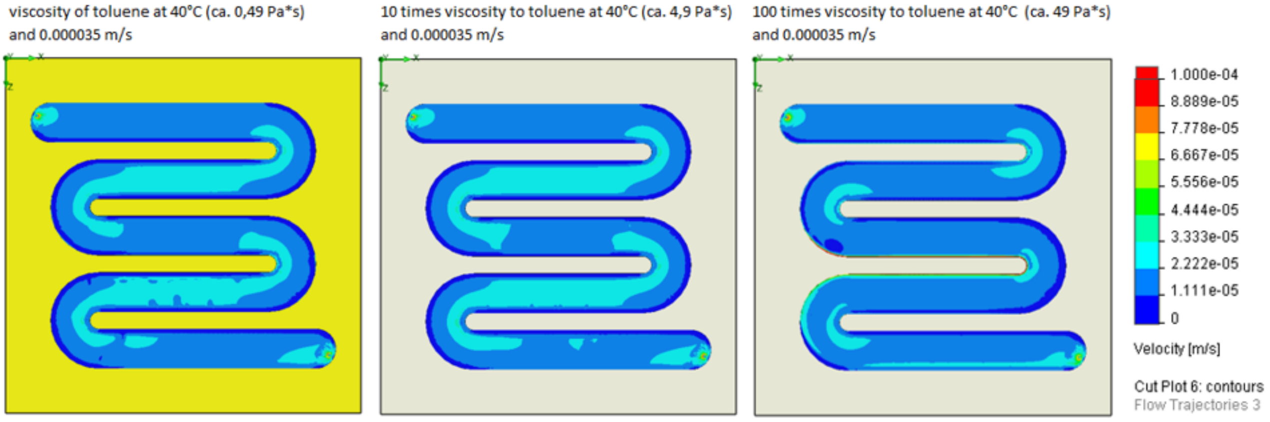

Figure 10: Volume flow simulation for the prototype at different viscosities of the MOST solvent.

The viscosity of Toluene (η = 0.49 Pa * s) was taken as the initial value, because the new solvent was not determined at this stage of the project, and the viscosity was increased by a magnitude each step (4.9 Pa * s and 49 Pa * s). There were only minor differences of the fluid velocity in the 45 mm wide channels of the meander shape. Thus, it can be concluded that the function of the collector is not affected at viscosities at least up to 49 Pa * s (see Figure 10). Further result is, that there are no dead edges with stagnation of the MOST fluid.

Figure 11: Almost fully transparent thermal oil resistant collector with DELO PHOTOBOND GB368. For better visibility, the edges of the collector are marked with a dotted line.

The MOST collector was tested for tightness with the new solvent Duratherm oil fluid over 3 months (see Figure 11). The very good transparency indicates a very high efficiency of the solar thermal collector (note the MOST logo behind the collector).

4.3 Stage III - Hybrid MOST collector

In development stage III, a hybrid collector was developed. This consists of a MOST collector as the outer layer and a thermal flat-plate collector underneath. The collector is an intermediate step with a square area of 0.09 m². The size was specified by the maximum dimensions of the solar simulator at the project partner University of Copenhagen. As thermal flat-plate collectors of this size are not commercially available, the entire hybrid collector was handmade, details are shown in Fig. 12.

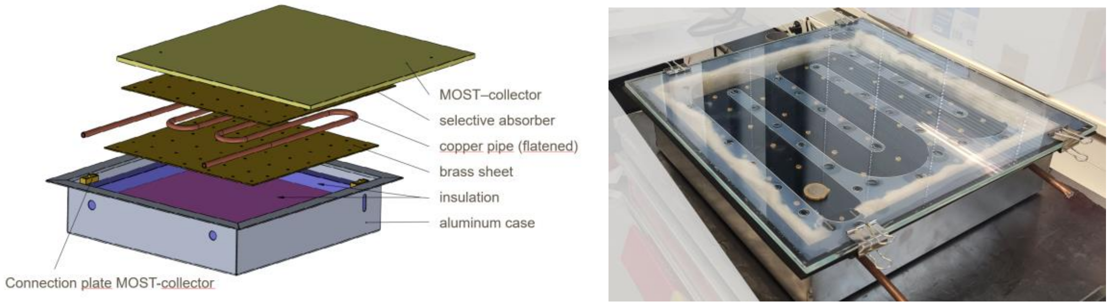

Figure 12: Left: Exploded view drawing of the first hybrid collector (MOST collector (top) + solar thermal collector (below); right: Picture of the finished hybrid collector.

An important point in the development was that even with a high thermal load, the temperature in the MOST collector does not rise to the temperature limit where the back reaction is thermally activated. The following tests were carried out to ensure this. The collector was exposed to an irradiation of around 1000 W * m^{-2} in a solar simulator. The temperature of the thermal collector was kept at 80 °C using a thermostat and then even at 90 °C.

The ambient temperature was kept at 35 °C and then at 36 °C. The temperature of the most collector was measured at three points (centre inside, centre outside, corner inside). In the first case (with 80 °C in the thermal collector), all temperatures in the MOST collector were approx. 54 °C, in the second case (with 90 °C in the thermal collector) at 57 °C (Fig. 13). This was still within the tolerable range as the critical temperature for triggering the back reaction is approx. 65 °C.

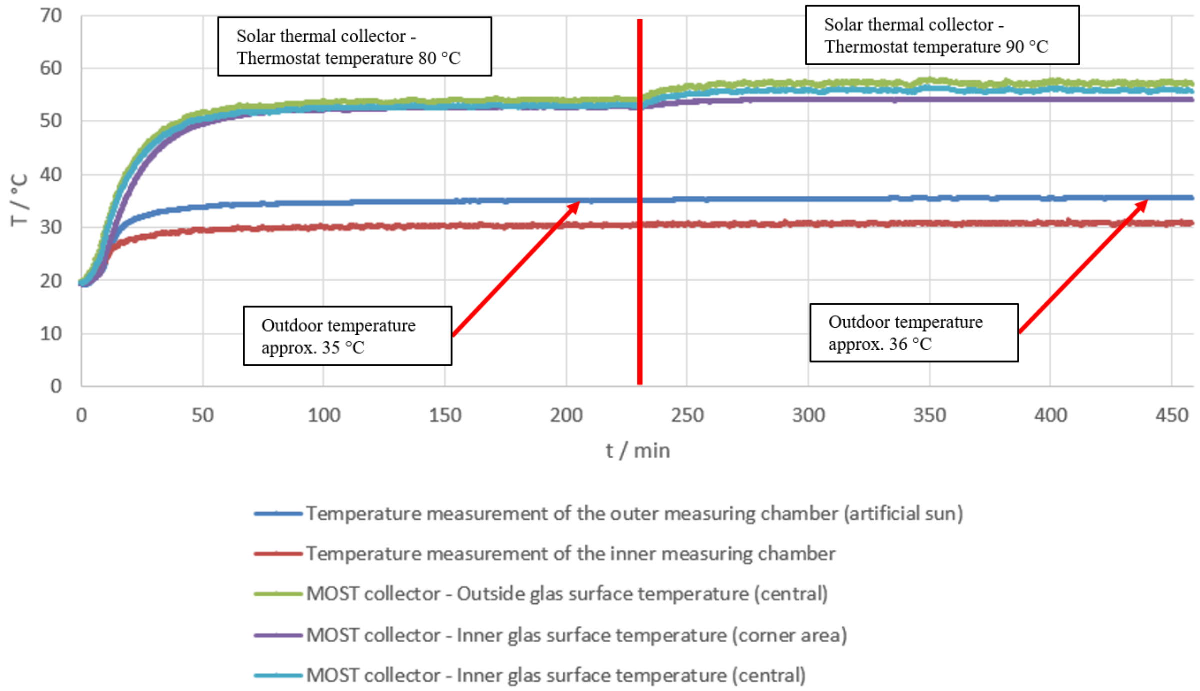

Figure 13: Temperature results of the solar simulator test for the hybrid collector.

The final stage of upscaling of the collector was a near-series hybrid collector with size of (50.8 * 105.5) cm² (Fig. 14 and 15). The size of the collector results to the use of a slightly modified commercially available flat plate collector for the thermal part of it (FK 8000 from GREENoneTEC Solarindustrie GmbH (Austria)).

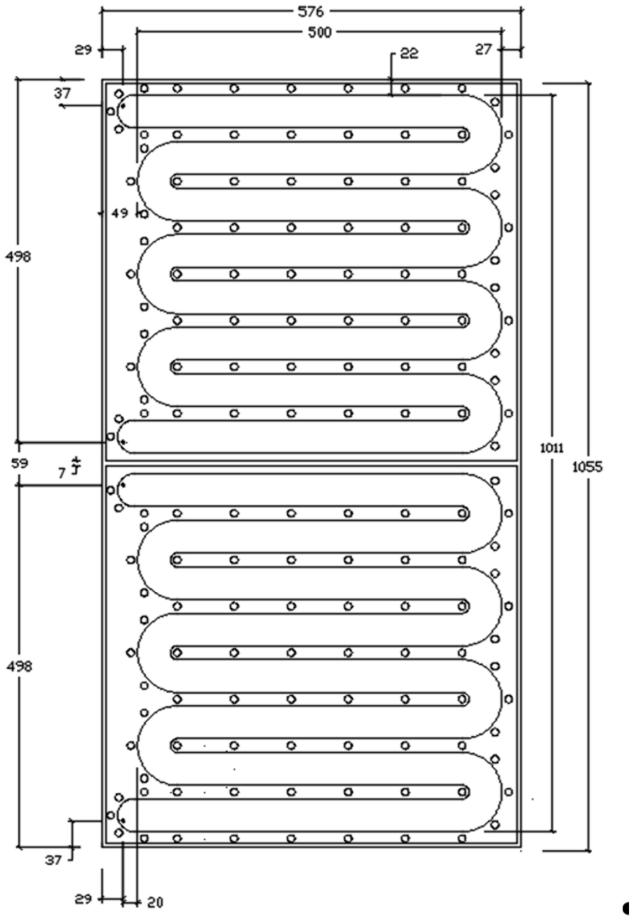

Fig. 14: Technical drawing of the final hybrid collector

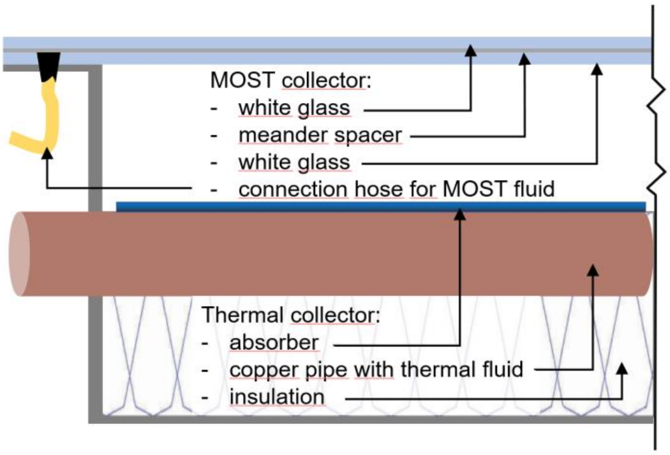

Fig 15: Cross section (schematic) of the final hybrid collector.

The MOST collector here is divided into two test areas of 0.25 m² each for mechanical reasons. Additional advantage of this is, that there are direct comparisons between different fluids, different flow rates or different operation modes possible. The design of the hybrid collector is almost close to series production, resistant to UV, storm and frost and for a high cycle capacity. The hybrid collector was extensively tested in an indoor solar simulator for tightness and stability for three weeks without intermission (Fig. 16). When performing the tests, water was flowing through the thermal part of the collector and Duratherm oil (without any photoisomeric molecules because there were not available in a sufficient amount at this stage of the project) was flowing through the MOST layer of the collector. The tests were therefore related to mechanical stability, tightness to water and oil and thermal performance, especially testing that the MOST layer is not getting to hot which would trigger the back reaction inside the collector.

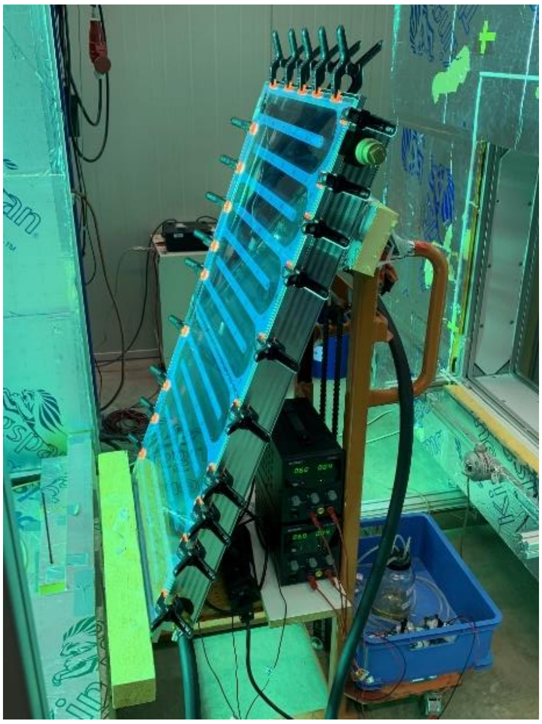

Figure 16: Sun simulator tests of the hybrid collector before the MOST-collector was finally bonded with the thermal collector. Instead, it was fixed with several clamps.

The testing was carried out at a surrounding temperature of 24 °C, the water in the thermal part of the collector was kept at 85 °C. Within the MOST layer the Duratherm oil was pumped through the MOST layer with a flow rate of approx. 5-10 ml/min.

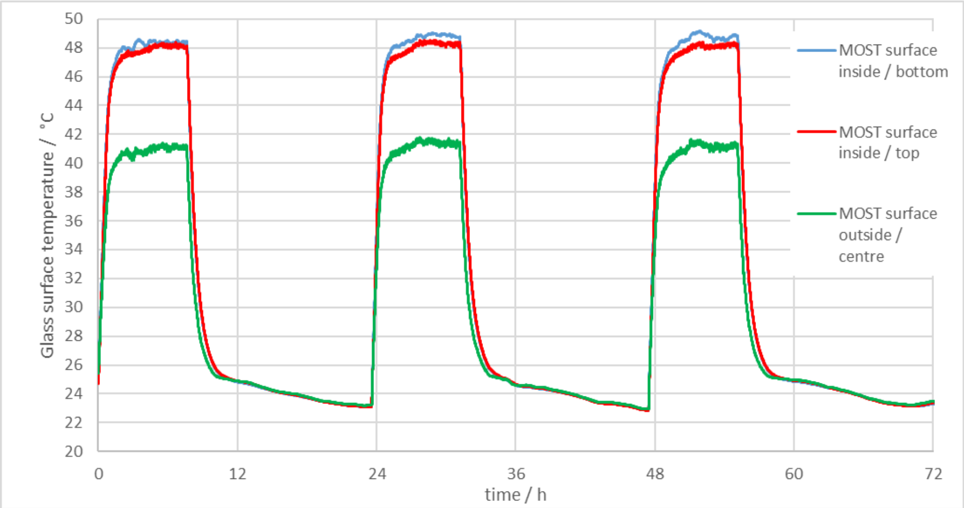

Figure 17: Glass surface temperatures of the MOST part (first collector-layer) when tested at the solar simulator. Red/blue line: temperature at the inside glass pane (pointing to the thermal collector); green line: temperature at the outside glass pane.

As a result, all parts or the collector stayed tight and the glass pane surface temperature of the MOST layer pointing to the solar thermal collector is approx. 48-49°C (see Fig. 17) which is not critical to trigger the back reaction.

The glass panes were glued in with special silicone for outdoor use. Experience from the small version with regard to production processes and connections could be usefully incorporated here.

In January 2024, two hybrid collectors were shipped to the Universitat Politècnica de Catalunya in Barcelona (Spain) for real monitoring of the overall system in Stage IV.

4.4 Stage IV - Integrated system

In the final development stage, a complete MOST system is developed and constructed in accordance with Fig. 2 with all associated components. The setup is supplemented by a normal thermal flat-plate collector whose output is measured in parallel operation. The system is realized as an outdoor test stand on the roof of the Universitat Politècnica de Catalunya in Barcelona (Spain). The system is south oriented with a variable slope for the collectors. The Hardware setup is completed (Fig. 18), software for controlling the MOST system and data acquisition is under development by Fraunhofer ISE in Freiburg (Germany). The MOST system will go into operation under realistic conditions like changing insolation, changing outdoor temperature and changing heat demand (simulated with a chiller unit) in September 2024.

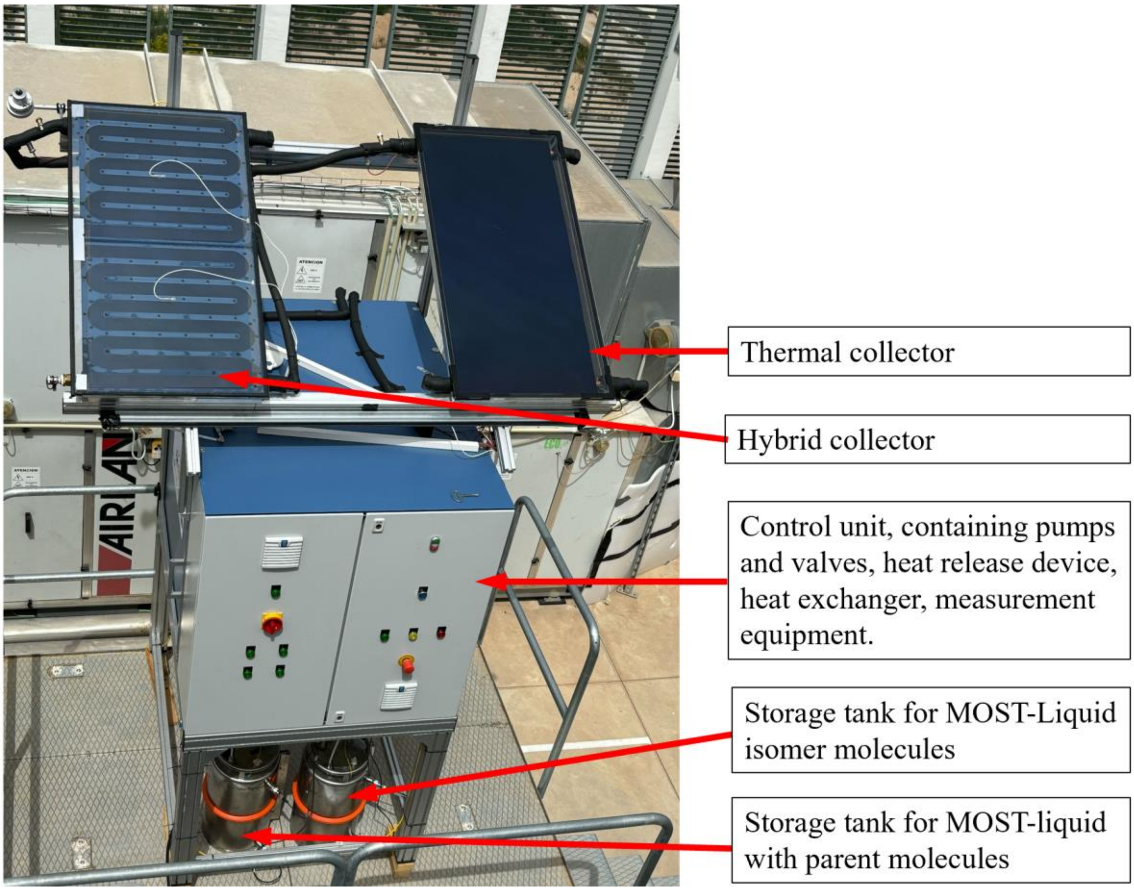

Figure 18: MOST-system at the roof of the Universitat Politècnica de Catalunya (UPC) - Barcelona Tech in Barcelona; on the left the hybrid collector (solar thermal + MOST) and on the right a normal solar thermal collector for comparison.

5. Summary

A small MOST collector was initially developed for the first laboratory-scale tests. This was scaled up in several stages into a near-series hybrid collector. The initial major problems with the choice of materials, caused by toluene as the carrier liquid, have now been solved. The hybrid collector has been tested for permanent leak-tightness and all components are UV-resistant.

The upper layer of the hybrid collector (the MOST collector) is almost completely transparent, so that as much of the energy of the solar spectrum as possible still reaches the second thermal collector layer.

The world's first complete MOST system with a close to series production collector has been installed at the Universitat Politècnica de Catalunya in Barcelona and will go into operation in September 2024.

6. Acknowledgments

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Special thanks to our colleagues Leslie Ullerich, Thomas Will and Johannes Wachtel for contributing their skills to the construction of the different stages of the collector.

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