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Qualification of Silicone Based HTF for Parabolic Trough Collector Applications

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Abstract. HELISOL[®] 5A has been subject to continuous research since 2012. This paper presents a selection of the most relevant test and measurement results gained along the parabolic trough collector application related qualification of this new HTF. HELISOL[®] 5A successfully demonstrated its loop scale functionality achieving the proof of concept at Plataforma Solar de Almería (PSA) after 480 hours of operation at 425 °C. The degradation processes induced formation of low boiling and gaseous products is shown for the aging tests in lab environment and for the loop scale application. In terms of operational safety five key investigations are presented. Three of which include the direct comparison with the commonly used mixture of diphenyl oxide and biphenyl (DPO/BP) the wick flame persistence test, the reaction of HELISOL[®] 5A and DPO/BP with molten salt and the spray ignition test. The other two tests cover the flammability of HELISOL[®] 5A in contact with hot (475 °C) surfaces and the worst case scenario of a tube rupture at collector level at 420 °C / 17 bar which both don't lead to ignition of the HTF.

INTRODUCTION

The silicone based heat transfer fluid (HTF) named HELISOL[®] 5A has been subject to continuous research in national and international research projects since 2012 [1],[2]. Lately it has received the SolarPACES Innovation Award [3] after a first commercial application was achieved with Royal Tech CSP Ltd. in Yumen City, China [4]. The new HTF holds suitable properties for parabolic trough collector applications and has clearly demonstrated its long-term applicability in different test loops at operation temperatures of 425 °C in China and in Europe. This substantial increase in temperature in parabolic trough (PTC) technology goes along with an acceptable hydrogen formation rate, a freezing point below -40 °C and a high occupational health and safety and environmental acceptability, at acceptable cost. This paper depicts several key investigations executed during the qualification process of HELISOL[®] 5A. Currently, there is no international standard available which would define the requirements for HTF in PTC application. Since April 2018 a national Spanish standard is available [5], which was elaborated based on the application of the commonly used mixture of diphenyl oxide and biphenyl (DPO/BP).

Thus, for the qualification of HELISOL[®] 5A two CSP unrelated national German norms DIN 51522 (for unused HTF) [6] and DIN 51529 (for used HTF) [7] were used as a reference/guideline. They comprehend qualifying examinations and requirements the HTF under investigation has to undergo or comply with. Based on the chemical properties and conditions some of the examinations (requirements) don't serve for silicone based HTF. Thus, inappropriate examinations were substituted by suitable ones, which were developed along with the qualification process of HELISOL[®] 5A. At least in terms of synthetic HTF it became evident, that responsible qualification activities must incorporate the fact that used HTFs differ significantly from their mint conditions. This fact leads to

the necessity of analyzing used HTF and consequently may have an impact on the “used HTF results” in terms of thermodynamic performance but surely in reliability of operation, occupational health and environmental safety.

TECHNICAL VIABILITY

Specific technical viability of a new HTF for parabolic trough collector applications can be achieved by fulfilling a variety of requirements/tests in order to ensure reliable long term operation of the HTF incorporating the containing installation itself. Corresponding lab investigations have been independently executed in laboratories at Wacker, DLR and elsewhere. These activities comprise the analysis of physical-chemical properties like freezing and boiling point, vapor pressure, density, heat capacity or enthalpy change, thermal conductivity and the solubility of gases like nitrogen in the temperature range of 20 °C up to 425 °C. Thermal aging is also relevant as it affects the maximum operating temperature of the HTF. Besides data of the fluid in mint conditions the properties of a typical used HTF environment were investigated in order to avoid any undesirable changes impairing the plant operation or durability of components. The loop scale functionality was demonstrated at Plataforma Solar de Almería while operational safety related investigations were mainly executed by DTM GmbH & Co. KG in cooperation with TÜV NORD Systems GmbH & Co. KG elsewhere.

Loop Scale Functionality and Applicability of HELISOL® 5A and Associated PTC Components at Temperatures up to 425 °C

The PROMETEO test facility (Fig. 9) consists of two east-west aligned parabolic trough collectors “Ibertrough” with eight 12 m long trough modules each (an aperture width of 7334 mm, focal length of 2172 mm) and the balance of plant. PROMETEO was erected in 2010 and refurbished in 2016. The latter happened in order to allow continuous operation under operating conditions with fluid temperatures up to 450 °C. For that purpose, new rotation and expansion performing assemblies (REPA) by Senior Flexonics and 70 mm diameter heat collecting elements (HCE) by RIOGLASS were installed. An additional TSK Flagsol designed buffer tank was integrated between collector outlet and balance of plant. This so-called retention line stores HTF for a variable time of about 4-9 minutes representing the residence time of HTF flowing through a typical header pipe in a 50 MW_e power plant.

HELISOL® 5A was used in solar operation in PROMETEO at 425°C during 480 hours. Including operation at lower temperatures app. 1100 hours of solar operation were accumulated. Daily operation was rarely interrupted by minor technical issues derived from the PROMETEO facility itself. Neither HELISOL® 5A nor the REPAs or the HCEs did show any behavior which may have prevented operation. During operation, an average volume of 3.5 m³ was kept at 425 °C inside the retention line while the total “hot” volume of the facility adds up to 6.7 m³ (expansion vessel excluded, retention line included). In terms of pressure, both the upper and lower pressure limits of the facility were operated at. This results in pressure values of 27 bar (425 °C) at the collector outlet or 15 bar (425 °C) at the same location. Especially operation at 15 bar did not lead to HTF boiling.

FORMATION OF GASES FROM HELISOL® 5A

Due to degradation processes low boiling and gaseous products like methane, ethane, hydrogen and alkyl silanes are formed from polydimethylsiloxanes like HELISOL® 5A. In laboratories, this formation can be quantitatively analyzed using an experiment on thermal aging of some grams of test material which is filled into test tubes made from borosilicate glass. The sealed test tubes have only negligible permeation for the products formed. The test tubes are kept for defined time intervals inside a special oven that allows for isothermal storage. Hence, the amount of gas per mass of heat transfer fluid (HTF) is to be considered as the amount that has actually been formed from the HTF within the considered period of time at a specific temperature. The amount of gaseous degradation products is determined by opening the test tube including the aged HTF sample inside a hermetic steel tube / container which is equipped with a valve. The contained gases are then mixed with a defined amount of carrier gas and then transferred into a micro gas chromatograph for compositional analyses. Taking volume, pressure, temperature and composition of the gas mixture into account the absolute amount of each gas can be calculated. Thus, the formed gases per mass of HTF are obtained. The gases formed per HTF (b in µmol/g) can be described with partial order reaction kinetics.

$$b = (A e^{-E_a/RT} t^{(1-n)} + b_0)^{1/(1-n)} \quad (1)$$

The parameters in (1) are the initial gas concentration (b_0 in $\mu\text{mol/g}$), the duration of ageing (t in hours), the general gas constant (R), the absolute temperature (T in K) and kinetic parameters comprising a pre-exponential factor (A in $\mu\text{mol}/(\text{g}^*\text{h})$), an activation energy (E_a in kJ/mol) and a reaction order (n) according to table 1. The latter are only apparent reaction parameters as they describe no single reaction. Due to the complex reaction situation this simplified evaluation gives no individual reaction orders, activation energies or pre-exponential factors of individual reactions processes but apparent kinetic parameters.

TABLE 1. Apparent kinetic parameters for the formation of gaseous degradation products from HELISOL® 5A between 425 – 465 °C

Gas	A in $\mu\text{mol}/(\text{g}^*\text{h})$	E_a in kJ/mol	n
Hydrogen	2,65E+29	416,7	-0,81
Methane	7,24E+26	373,8	-0,26
Ethane	2,62E+20	302,3	-0,25

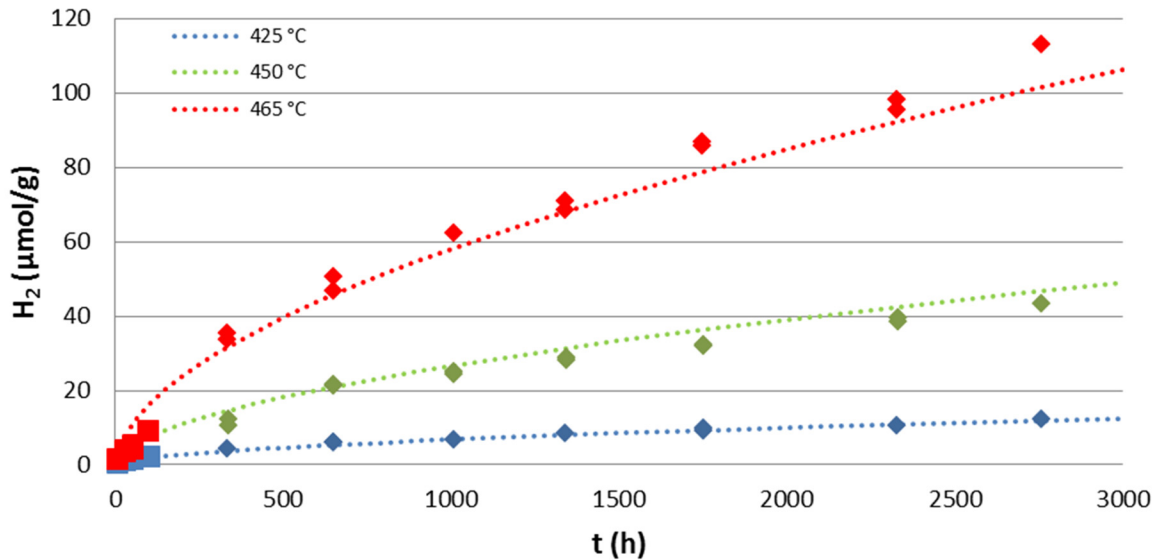


FIGURE 1. Hydrogen formation from HELISOL® 5A at 425°C, 450°C and 465°C in a lab experiment using borosilicate ampoules (filled diamonds) and simulated formation according to Equation 1 and TABLE 1 (dotted lines).

In contrast to lab experiments on the gas formation using glass ampoules the dissolved gas measurement of HTF in loop or full scale PTC systems is not exclusively determined by the formation of the gases according to the aging kinetics. The gases formed are distributed between the liquid HTF and gas spaces according to the gas solubility giving rise to considerably lower concentrations in comparison to the gas formation per mass of HTF in glass ampoules (see Fig. 1 – H₂ in $\mu\text{mol/g}$ in comparison to Fig. 2 – H₂ in $\mu\text{mol/Kg}$). Moreover, gases can be removed from a CSP system via venting processes, through leakages and by permeation processes. During the validation of HELISOL® 5A at PROMETEO test facility, samples of the HTF including the dissolved gases have been collected from the HTF circuit using a so-called cross-sampling device. Such device allows for flushing and filling steel sampling cylinders with hot and compressed HTF from the collector inlet (higher pressure) to the collector outlet. A representative HTF sample including all dissolved gases is obtained by closing the outlet of the filled sampling cylinder before closing the inlet. After cooling down and dismounting the cylinder from the sampling device, the separated sample is analysed in the lab. The quantitation of the dissolved gases is based on a combination of pressure measurement and compositional analysis using micro gas chromatography.

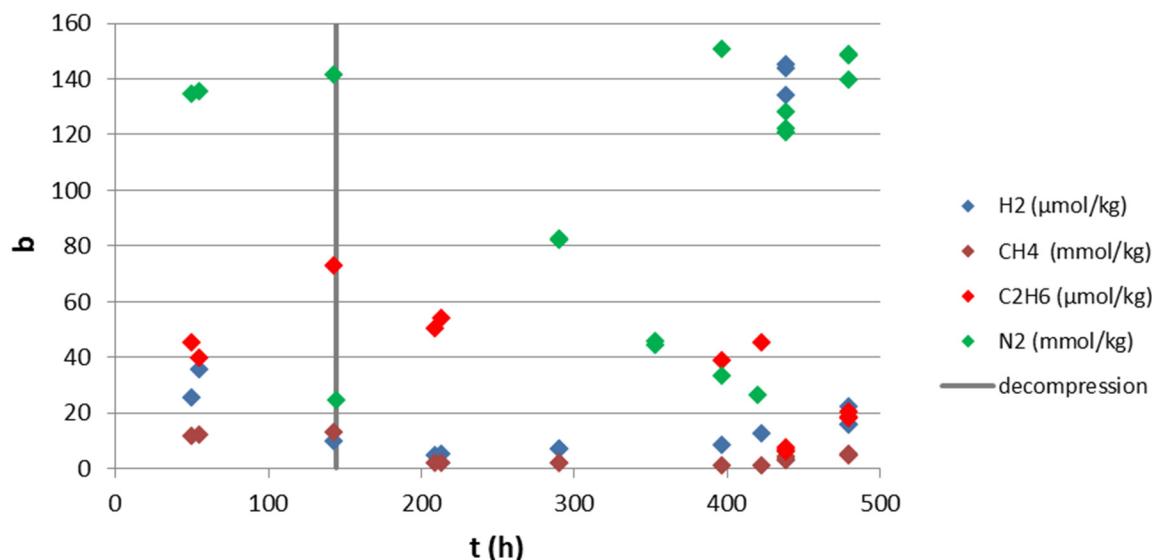


FIGURE 2. Dissolved gases in HELISOL® 5A during the validation test in the PROMETEO test facility (H₂: hydrogen, CH₄: methane, C₂H₆: ethane).

After 144 hours at 425 °C, the dissolved gases have been vented to the environment by decompressing the HTF circuit at a temperature of about 20 °C. The initially high concentrations dropped considerably by this measure as to be expected (see Fig. 2). Nitrogen had been replenished after the decompression and was then stepwise reduced again in order to check for potential effects on the plant operation resulting from low system pressure. Even the lowest system pressure (15 bar at 425 °C) correlating with a nitrogen concentration of app. 30 mmol/kg caused no obvious heat transfer problem or undesirable boiling of the fluid.

OPERATIONAL SAFETY

A series of different tests have been conducted at laboratory scale, pilot plant size and at loop scale in order to gain a detailed understanding of the HELISOL® 5A associated operational risks. The following investigations were selected to be presented in this paper:

- Wick flame persistence according DIN EN ISO 14935
- Reaction of HELISOL® 5A and DPO/BP with molten salt (NaNO₃/KNO₃, 60/40 wt.-%)
- Spray ignition test according DIN EN ISO 15029
- Flammability in contact with hot surface according DIN EN ISO 20823
- Tube rupture simulation / release test at 420 °C / 17 bar

The three tests according to DIN EN ISO standards are designed for petroleum products in other applications. They were used for HTF due to the lack of relevant standards for PTC applications. Thus, the transferability of the results in terms of pass to PTC applications is not valid. Still, said tests give basic information and enable the comparison of HELISOL® 5A to DPO/BP.

Laboratory Tests on Ignition and Fire Behavior of HELISOL® 5A and DPO/BP

The determination of the afterflame time of a HTF soaked wick was executed according to DIN EN ISO 14935. The HTF soaked wick is exposed at one end to an ignition flame for a defined period of time (2 seconds). The afterflame time is measured. Both HTFs did not pass the test. In both cases the entire wick caught fire and remained burning for more than 60 seconds. The fire behavior of HELISOL® 5A compared to DPO/BP can be described as “less energetic”. Flame appearance, flame temperature and fire duration seems to be more conservative. This observation correlates with the comparison of the combustion energy given in the data sheets of the HTFs (36 MJ/kg for DPO/BP, 26 MJ/kg for HELISOL® 5A).



FIGURE 3. “Wick flame test” according to DIN EN ISO 14935, left side HELISOL® 5A, right side DPO/BP. Both wicks caught fire entirely and remained burning for more than 60 seconds.

Some of the burning products of HELISOL® 5A (mostly silicium dioxide - SiO_2) are deposited on top of the wick and form a kind of barrier which gradually (after a few minutes) separates the flame from the soaked wick. When the layer is thick enough the HELISOL® 5A flame stops burning without outside influences. Figure 4 shows two different rock wool wicks after burning off equal amounts of both HTFs.

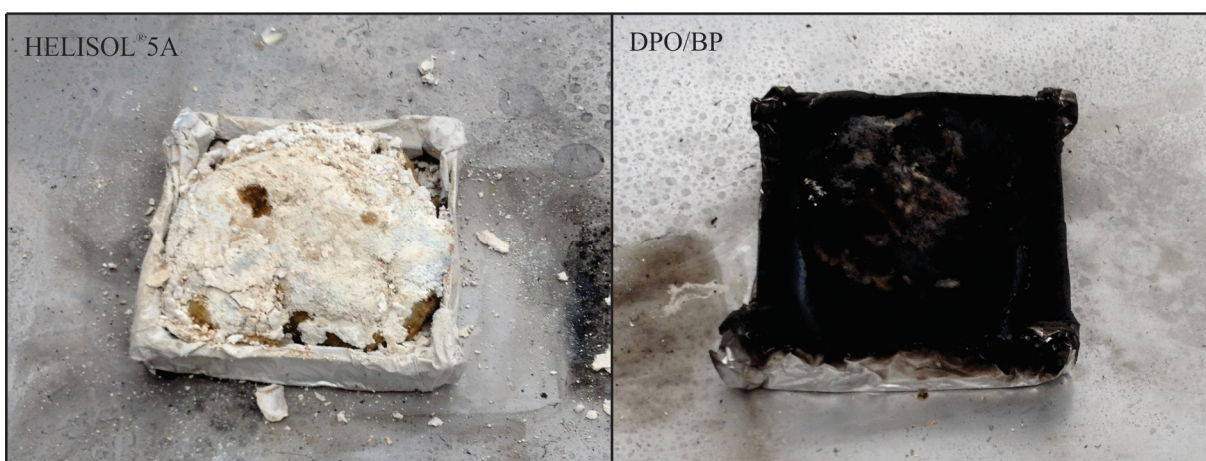


FIGURE 4. Wicks (rock wool) after burning off HTF: left: silicium dioxide (SiO_2) covering the rock wool wick, right: soot covering rock wool wick

Reaction of HELISOL® 5A and DPO/BP with Molten Salt Eutectic Mixture ($\text{NaNO}_3/\text{KNO}_3$, 60/40 wt.-%)

In the event of leakages between the HTF containing circuit and the heat storage circuit the HTF and the storage medium (molten salt) will be in direct contact. Therefore, an exothermic reaction between both compounds could occur. To analyze such situation, the reaction of both mixtures of HELISOL® 5A, as well as DPO/BP with molten salt ($\text{NaNO}_3/\text{KNO}_3$, 60/40 wt.-%) have been investigated via Differential Scanning Calorimetry (DSC) at temperatures up to 700°C (under nitrogen atmosphere). To compare the results, each HTF (DPO/BP, HELISOL® 5A and anhydrous molten salt) was measured individually. Water of crystallization had to be removed from the molten salt before conducting the measurements. Subsequently, the influence of the molten salt on the decomposition of the two HTFs was determined by measuring 1:1 mixtures of each compound. As reference points, the onset temperatures T_d of the exothermic decomposition of the pure HTFs were first determined (see blue arrows in Fig. 5

and Fig. 6). If the HTFs are treated with molten salt they will be oxidized at a certain temperature T_{ox} (onset) (see orange arrows in Fig. 5 and Fig. 6). These values at which oxidations occur were also measured and evaluated in comparison with the above mentioned onset temperature of the pure HTFs. For each measurement, milligram quantities of the test mixtures were heated at a constant rate (30 – 700 °C; 3 °C/min) and the resulting heat flows measured. The sample holder is a pressure-resistant DSC crucible, which eliminates the possibility of losses due to evaporation. Note that the exact onset temperature recorded in each individual measurement is depending on the precise initial weight of HTF and molten salt. In the presence of molten salt, the onset temperature for exothermal decomposition of DPO/BP is decreased compared to the neat HTF ($\Delta T = 110^{\circ}\text{C}$; $574^{\circ}\text{C} \rightarrow 464^{\circ}\text{C}$; see Fig. 5. According to [8], the probability of immediate decomposition is considered high once DPO/BP comes into contact with the molten salt, as the handling temperature during operation (395°C) differs from the onset temperature of decomposition (464°C) by less than 100 K.

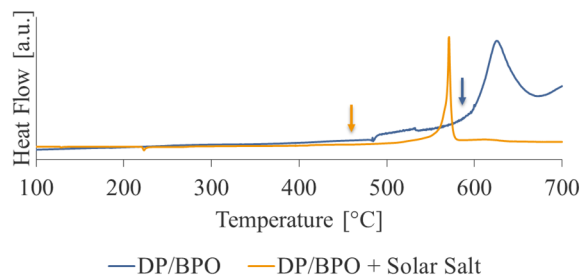


FIGURE 5. DSC-Measurements of a neat DPO/BP and a mixture of DPO/BP + molten salt ($\text{NaNO}_3/\text{KNO}_3$, 60/40 wt.-%) under N_2 atmosphere. Temperature range 100 to 700 °C; heating rate 3 °C/min. Both onset temperatures are marked. The features that can be seen at 125 °C and 203 °C belong to endothermic reactions of the pure molten salt.

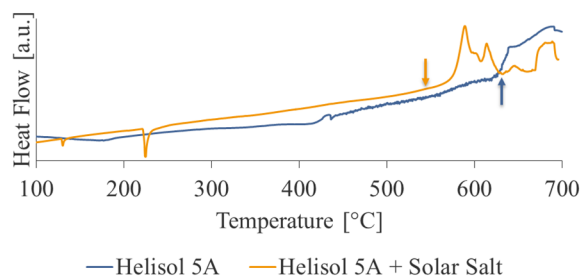


FIGURE 6. DSC-Measurement of neat HELISOL® 5A and a mixture of HELISOL® 5A + molten salt ($\text{NaNO}_3/\text{KNO}_3$, 60/40 wt.-%) under N_2 atmosphere. Temperature range 100 to 700 °C; heating rate 3 °C/min. Both onset temperatures are marked. The features that can be seen at 125 °C and 203 °C belong to endothermic reactions of the pure molten salt.

Similarly, the onset temperature for exothermal decomposition of a mixture of HELISOL® 5A and molten salt is also decreased compared to neat Si-HTF ($\Delta T = 82^{\circ}\text{C}$; $623^{\circ}\text{C} \rightarrow 541^{\circ}\text{C}$; see Fig. 6). In contrast to the reaction with the DPO/BP, the probability of immediate decomposition after contact is considered low, as the handling temperature during operation (425°C) differs from the onset temperature (541°C) by more than 100 K. In general, thermal decomposition of both mixtures (HTF + molten salt) occurs at lower temperatures than the thermal decomposition of the pure HTFs. The maximum possible energy released when the HTF oxidizes upon reaction with molten salt was estimated based on the heat of combustion ΔH_C . ΔH_C of DPO/BP is 36.0 MJ/kg, while ΔH_C of HELISOL® 5A is only 26.3 MJ/kg (both measured in accordance to DIN 51900 standard). As a result, the maximum exothermic reaction of HELISOL® 5A with molten salt is approx. 20% lower compared to DPO/BP.

Near to Realistic and Standard Fire Tests with HELISOL® 5A and DPO/BP

The “spray ignition test” according to EN 15029 (flame propagation and qualitative information on the fire behavior of the fluids) was carried out for both HTFs. According to the test specification an ignition flame (1500°C) is used to ignite a spray jet of the corresponding HTF. The test was performed with the pressures of 70 and 20 bar.

The test according to DIN EN ISO 15029-1 is passed, if the afterflame time of the “spray fire” after removing the ignition flame (see gas welding equipment) is max 30s for 10 repeated ignition tests (the ignition flame is moved from the far end to the spray device in defined steps). Both HTF did not pass the test. It was observed that HELISOL® 5A is less sensitive for ignition because the afterflame time was significant lower than the afterflame time of DPO/BP. Furthermore, it was observed that DPO/BP shows a more energetic afterflame than HELISOL® 5A.

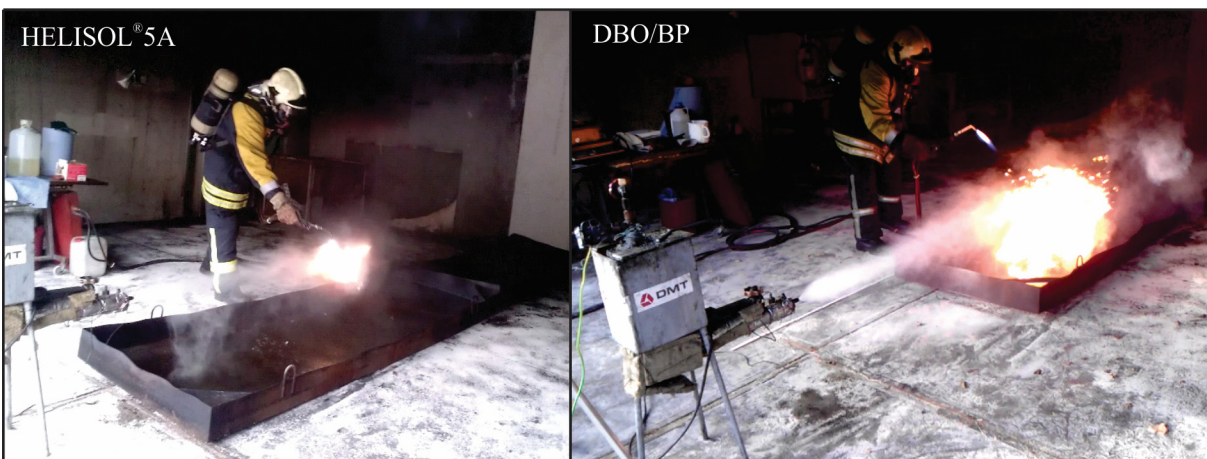


FIGURE 7. “Spray ignition test” according to EN 15029, left side HELISOL® 5A, right side DPO/BP under identical conditions

Flammability in contact with hot surfaces was investigated according to the DIN EN ISO 20823 standard. During this experiment a steel tube is heated at the inside by a resistance heater. Tube temperature can be adjusted by means of a temperature controller with an uncertainty of ± 5 K. Vertically above the steel tube a liquid dispenser is installed which releases (10 ml in 50 seconds) single HTF drops to the tube below. Starting off with a tube temperature below 400 °C the temperature was increased stepwise to 400 °C – 425 °C (see Fig. 8) – 450 °C – 475 °C and 500 °C. No self-ignition was observed at 475 °C or at temperatures below.

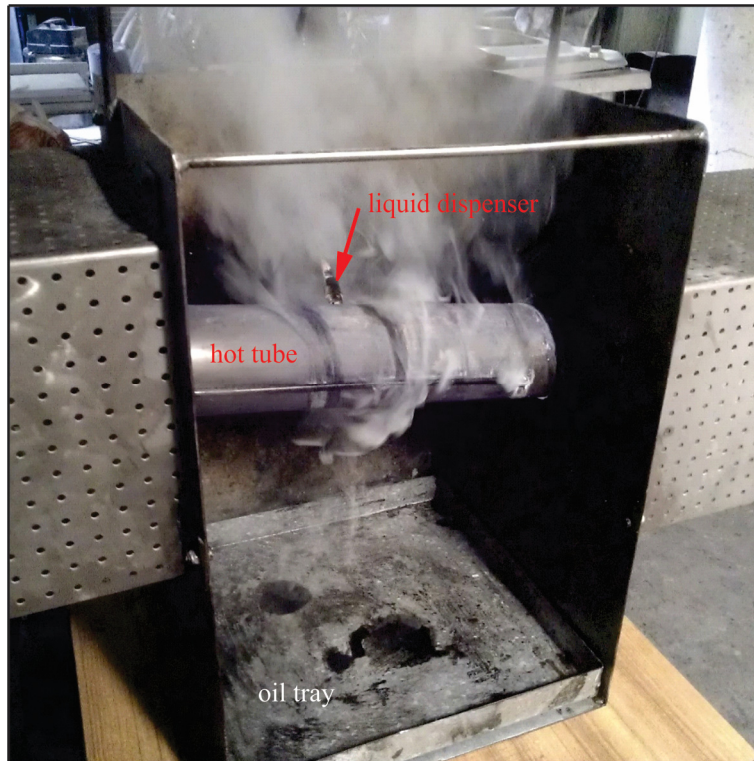


FIGURE 8. “Flammability in contact with hot surfaces test” according to DIN EN ISO 20823 with HELISOL® 5A at 425°C

Tube Rupture Simulation / Release Test at 420°C / 17bar

Organic and silicone based HTF in parabolic trough power plant applications can cause hazardous fire in case of leakages in combination with hot surfaces or other ignition sources. It was shown that the self-ignition temperature stated in the technical data sheet - which has been determined by analytical laboratory examinations according to DIN°EN 14522 - does not match with corresponding findings at test scale experiments (see flammability in contact with hot surfaces). These results have shown that HELISOL® 5A does not self-ignite under regular working temperature conditions (425 °C) although liquid and or gaseous HTF is in contact with hot surfaces. Subsequently, based on above findings a pipe rupture in a realistic plant surrounding and under full-scale conditions was simulated. Thus, an insulated 2" ring pipe was connected to the return line from the hot collector outlet of the PROMETEO test facility (Fig. 9). At a distance of 40 meters away from the PROMETEO test facility a fast release valve (opening and closing, each in 0.2 seconds) is installed. This valve is controlled remotely and closes automatically in case of energy loss. At the jet outlet, it is possible to mount exchangeable release nozzles with varying diameters ($\frac{3}{4}$ " and 2"). The release area was cleaned in terms of potential fire loads (biomass etc.). The sandy soil was smoothened in order to be easily removed after the release test.

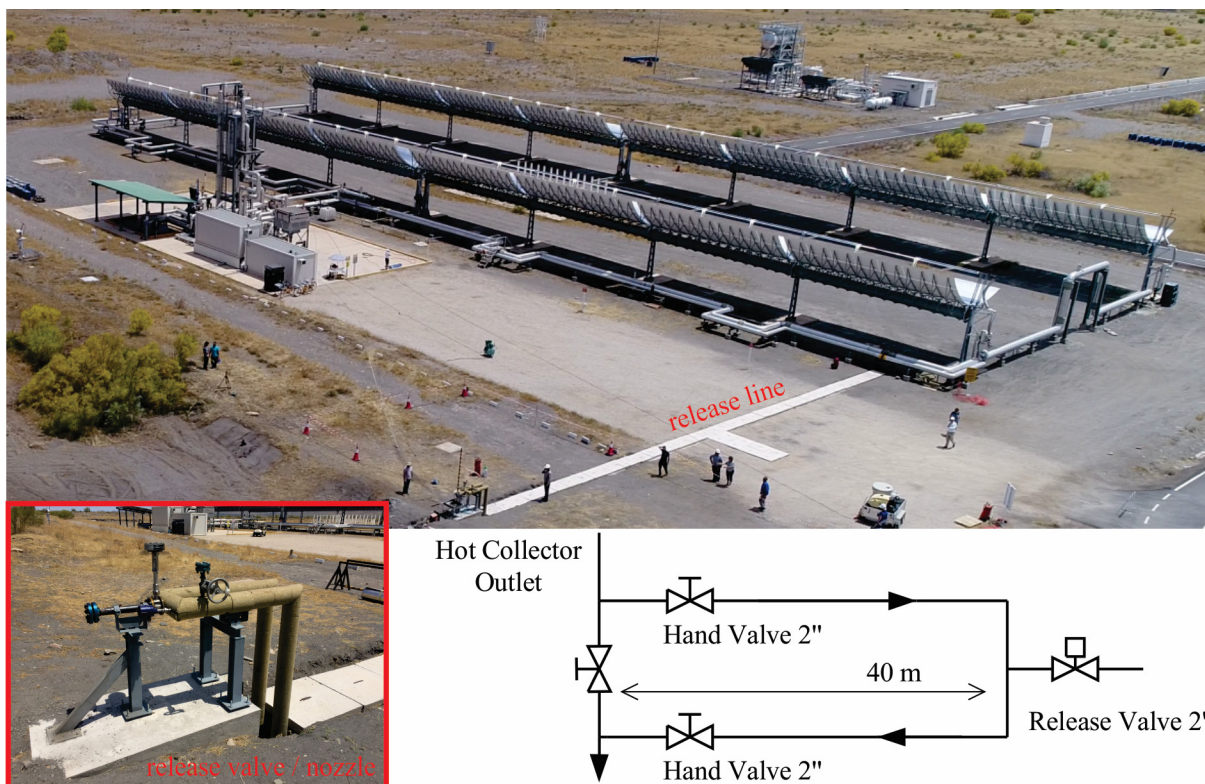


FIGURE 9. Aerial view of PROMETEO test facility with HTF release line, close-up of release valve and nozzle (red frame, bottom left), and flow sheet of release line (bottom right).

For the release test the PROMETEO facility was operated until a HELISOL[®] 5A temperature of 420 °C (± 3 K) was reached at both locations, the collector outlet and close to the release valve (see Fig. 9). The release valve was then remotely triggered and opened a 2" diameter cross section to the environment for 10 seconds until it was closed again. Figure 10 shows a picture series taken during the first 3 seconds of the release test until steady state conditions were met. The test demonstrated that no ignition occurs.



FIGURE 10. Photo series taken during the first 3 seconds (3 pictures / second) of the 2" HELISOL[®] 5A release test at 420 °C

A series of infrared pictures was taken by a THT70 handheld camera (HT Instruments GmbH) during the release test for the purpose of evaluating differential temperatures of the leaking and expanding HTF. Based on an IR picture taken about three seconds after the release valve opened (Fig.11) it can be stated, that the initial system / HTF temperature significantly decreases along the open jet. At a distance of about 10 - 12 meter the HTF vapor temperature is close to the surface temperature of the surrounding soil. A redundant temperature measurement with three thermocouples Type K (NiCr-Ni) was executed about 20 cm away from the orifice (horizontal distance) and inside the projected cross-sectional area of the orifice, thus inside the open jet. The three sensor readings are depicted in Fig. 11. It can be stated, that the HTF temperature inside the free jet drops about 50 K within 20 cm behind the orifice.

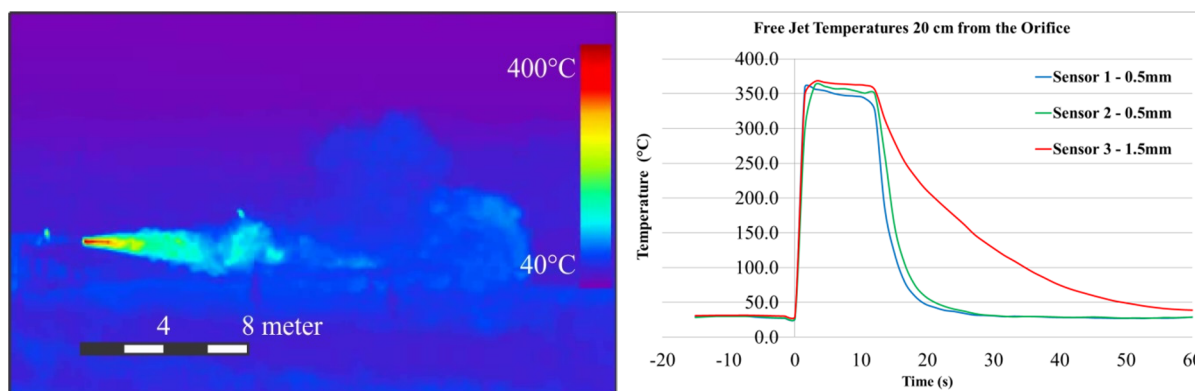


FIGURE 11. (left) Infrared image of the release test taken by a THT70 IR camera - HT Instruments GmbH, (right) temperature reading of three Type K thermocouples located inside the free jet during the HELISOL® 5A release test at 420 °C.

A thin film (1-2 cm) of soil has been wetted by condensing HTF during the release and was removed and packaged for adequate disposal afterwards.

Acknowledgments

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