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Energy



Energy Procedia 69 (2015) 663 - 671

# International Conference on Concentrating Solar Power and Chemical Energy Systems, SolarPACES 2014

# Technological perspectives of silicone heat transfer fluids for concentrated solar power

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### Abstract

Silicone based heat transfer fluids exhibit interesting properties for the application in solar thermal power plants like high thermal stability, very low freezing points and high environmental acceptability. In this paper, a new silicone based HTF (HELISOL<sup>®</sup> from Wacker Chemie AG) is investigated experimentally and economically in comparison to the eutectic mixture of biphenyl and diphenyl oxide which is currently the most important fluid for the heat transfer in solar thermal parabolic power plants. It was found that HELISOL<sup>®</sup> forms less low boiling and gaseous compounds at 425°C in comparison to currently applied HTFs at only 400°C. The techno-economic comparison shows that the LCOE can be reduced by 5% using the silicone fluid.

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Keywords: HELISOL®; DPO, BP, heat transfer fluid, HTF, CSP

## 1. Introduction

Organic heat transfer fluids (HTFs) are today used in any commercial scale solar thermal parabolic power plant. The most important fluid is the eutectic mixture of diphenyl oxide (DPO) and biphenyl (BP) which is known as Therminol<sup>®</sup> VP-1, Dowtherm<sup>TM</sup> A and Diphyl<sup>®</sup>. Despite of the widespread use of DPO/BP, alternative HTFs are requested for CSP applications as the maximum operation temperature of 400°C limits the efficiency of the plants. With molten salt maximum temperatures of 550°C are possible but so far no salts with low melting points around or

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below ambient temperatures seem to be accessible [1]. Hence, extensive freeze protection measures have to be foreseen. Corrosion is also an issue for molten salt in contrast to organic HTFs. Water is considered as an alternative as well but its high vapor pressure increases the costs for storage and the two phase flow in direct steam generation systems enhances the control demand considerably. In contrast to these alternatives, CSP plants with organic HTFs are easy to scale as proven technology is applied.

Organic HTFs for high temperature applications are predominantly produced from aromatic hydrocarbons and aromatic ethers due to their high thermal stability in comparison to aliphatic compounds [2]. The eutectic mixture of DPO and BP was patented in 1932 [3]. Since then no other fluid with carbon backbone has been described with higher stability despite intense investigation for the heat transfer in industrial heating or power generation [4,5]. Beyond DPO/BP only silicones like polydimethylsiloxane (PDMS) are applied at 400°C as HTF. In CSP technology PDMS is often used for test facilities as the fluid is not classified as hazardous material.

#### 2. Thermal stability evaluation

The thermal stability of HTFs is currently not a measurable value like the decomposition temperature. In order to evaluate the thermal stability, laboratory aging tests are applied to compare HTFs in terms of degradation at a particular working temperature. The degree of degradation after the aging is usually defined via the mass fraction of gaseous, lower or higher boiling and not volatile degradation compounds that have been formed.

HTFs in CSP plants are usually not exchanged during regular operation despite small quantities that arise from the draining of piping for service works. Due to the plant integrated HTF processing systems, degradation products with very low boiling points or insoluble products are removed. Some of the lower or higher boiling products in comparison to the fresh HTF are tolerated in the fluid. For DPO/BP this is the case for phenol, dibenzofuran, terphenyl and some higher oxygenated or all-hydrocarbon degradation products.

#### 2.1. Experimental approach

The thermal stability of the HTF samples was investigated in the style of DIN 51528 [6] for this study. This standard foresees the thermal storage of the samples in borosilicate ampoules at the intended operating temperature. The thermal degradation was evaluated subsequently via simulated distillation [7]. As the standard does not explicitly apply to silicon based HTFs, the aged samples were evaluated using tailor-made gas chromatographic analysis for specific compounds instead of using simulated distillation. As low boiling and gaseous HTF degradation products have to be removed from the HTF loop in regular intervals, the chemical analysis of the aged samples was focused on these compound classes. As hydrogen is a potential threat to the vacuum insulation of the heat collecting elements (HCEs) of a CSP plant, the formation rate of this gas is relevant for the lifetime of the HCEs [8]. Thus, the generation of hydrogen was analysed carefully although its mass is almost negligible with regard to the degradation products.

For kinetic aging tests a set of borosilicate ampoules was partially filled with HTF. (In preliminary tests different glass qualities like quartz and sodium-chalk glass had been compared to borosilicate 3.3 in order to prove that the latter does not affect the aging of the tested HTF qualities.) After cooling and repeated flushing with nitrogen and final evacuation, the ampoules were closed via smelting. The thermal storage was performed in specially prepared ovens to provide thermal stability and homogeneity with less than +/- 1 K uncertainty for all ampoules over months. The temperature of the samples was measured with calibrated PT-100 sensors and logged in 5 min intervals over the experimental time. After certain time intervals a set of three ampoules was removed from the oven and cooled down for analysis. The aging time was considered to be the time at the target temperature as the heating and cooling rates were high. The latter allowed neglecting the times at deviating temperatures. This approach enables excellent reproducibility among the tests in different ovens in contrast to the general procedure according to DIN 51528.

For chemical analysis of permanent gases and some low boilers (like small organosilanes) the samples were opened in a closed system that allowed for pressure measurement and gas composition analysis via micro gas chromatography. This analysis was performed as double determination. The third ampoule was opened at atmospheric conditions and complimentarily analysed for volatile compounds (like benzene in the case of DPO/BP).

#### 2.2. Results

The degradation of DPO/BP was investigated recently with regard to the formation of gases and volatile compounds in the range of  $400 - 450^{\circ}$ C [9]. The fluid does not form any coke over 1000 hours at these temperatures. In this study DPO/BP and HELISOL<sup>®</sup> 5 were heated to 465°C. While DPO/BP forms considerable amounts of coke-like products after a few days (fig. 1) at this temperature, HELISOL<sup>®</sup> 5 changes only from colourless to yellowish without any solid degradation products. This indicates that the silicone fluid withstands considerable overheating.



Fig. 1: Comparison of DPO/BP and HELISOL® 5 after 10 days at 465°C.

The formation of gaseous and low boiling degradation products of HELISOL<sup>®</sup> 5 was determined at 425°C for a time interval of 115 days and compared to DPO/BP at 400°C (figure 2). DPO/BP forms permanent gases like hydrogen, methane and carbon monoxide with increased rate on aging time. For HELISOL<sup>®</sup> 5 the amount of methane or hydrogen increases as well steadily but the initial formation rate is higher than after some aging time. In the case of hydrogen, the initial formation rate is lower for DPO/BP at 400°C as for HELISOL<sup>®</sup> 5 at 425°C but it increases for DPO/BP strongly with time. At 1340 hours the hydrogen formation of HELISOL<sup>®</sup> 5 at 425°C is equal to the value of DPO/BP at 400°C. At longer aging time the silicone fluid forms considerable less hydrogen as shown in figure 2.



Fig. 2. Formation of hydrogen from DPO/BP (green) at 400°C and HELISOL® 5 at 425°C (blue)

Gases and low boilers have to be separated in intervals from the HTF when it is operated at extreme high temperatures. The HTF system of CSP plants typically comprises an ullage and reclamation system for the separation of undesirable degradation products. While for DPO/BP beyond the gases benzene has to be removed for silicone oil low boilers like small organosilanes will most likely have to be removed. In figure 3 the mass of formed gases and compounds with normal boiling points below 100°C are presented for aging times up to 1000 and 3000 hours. Although DPO/BP was tested only at 400°C it forms about 8 fold more mass of these compounds in comparison to HELISOL<sup>®</sup> 5 at 425°C.



Fig. 3. Formation of relevant low boilers from DPO/BP (green) at 400°C and HELISOL® 5 at 425°C (blue)

#### 3. Techno-economic evaluation

For investors or owners of CSP plants the technical comparison of different HTFs is only one part of the whole figure. Typically they are interested also in key economic figures of the fluids or in other words: What's the economic benefit of using the one or the other HTF?

Annual performance simulations for different sites have been performed to compare HELISOL<sup>®</sup> 5, DPO/BP and HITEC<sup>®</sup> molten salt [10]. The latter one is considered in this comparison since molten salts are under discussion as HTF in order to increase the solar field outlet temperature considerably compared to the state-of-the-art. First test and demonstration plants with molten salt in linear concentrating systems are in operation.

Levelized costs of electricity (LCOE) are used as key figure for the comparison. This is a holistic approach to evaluate the utilization of HELISOL<sup>®</sup> 5 since several aspects are taken into account with opposed effects on LCOE.

For this study material data from the manufacturer were taken into consideration. They have been checked by DLR using methods like Calvet-DSC (heat capacity), volumetric expansion (density) and vibrational viscometry. The melting point of HELISOL<sup>®</sup> 5 is below -30°C, the pour point below -55°C according to Wacker Chemie.



Fig. 4. Material properties of HELISOL® 5 as a function of temperature (blue: density; red: heat capacity; green: viscosity)

#### 3.1. Yield analysis model and methodology

The results of the present paper are generated with an MS Excel based DLR-internal CSP plant model. The model is optimized for fast calculations of annual energy yields, and hence, is based on heat flows. Relevant CSP plant technologies with corresponding HTFs (such as synthetic oil, water/steam, and molten salt) are implemented in the model and their energy yields can be compared. Input parameters, such as solar field size, storage capacity and power block nominal output, can be varied easily and their influence on the electricity yield can be analyzed. Power block performance is modelled by using lookup tables. The steady state model considers startup losses of solar field and power block by correction factors reducing the heat actually used for electricity production. The Excel model is completed by VBA programs and DLLs for parameter variation and calculation of sun position.

One important step in such a techno economic comparison is the determination of-specific cost figures for all main plant components. Furthermore the major technical differences of power plants caused by the utilization of a certain HTF must be fixed prior to the annual performance simulations. The main figures are shown in table 1. All other specific cost and performance figures are kept identical for all three systems in this study. The nominal solar field outlet temperature has an impact on nominal live steam temperatures and thus on the power block efficiency, which increases with increasing live steam temperature. Specific investment costs for the solar field (including HTF system) are assumed to be identical for the DPO/BP and HELISOL<sup>®</sup> 5 plants but slightly lower for the molten salt systems. Actually specific costs for the sole solar field for molten salt systems are higher due to more expensive materials for piping, insolation and the need for freeze protection systems but these plants do not need a separate HTF system. Storage costs are decreasing with increasing temperature difference actually utilized. But in this study storage costs are not simply scaled with the reciprocal temperature difference because higher temperatures require more expensive materials for the storage systems. Actual costs for HELISOL<sup>®</sup> 5 are not available, thus the assumption is that they will be the same as for the DPO/BP fluid. It should be mentioned that the economic model adds a 30% surcharge on the total investment costs for construction, risks, etc. for all considered systems. The annual replacement rate for HELISOL<sup>®</sup> 5 is also not known currently; therefore we assumed 5% which is considered as conservative approach. This careful assumption is chosen in contrast to the finding that the new fluid forms less low boiling compounds (figure 3). In practice even lower exchange rates than 2 %/a might be necessary.

All plants are using Eurotrough collectors with 150m length and 817.5m<sup>2</sup> of aperture for a single unit. One loop consists of four collectors for the DPO/BP and the HELISOL<sup>®</sup> 5 solar fields and of six collectors for the HITEC<sup>®</sup> solar field. Receiver heat losses are calculated according to [11] valid for Schott PTR 70 vacuum receivers. The volumetric heat capacity ( $C_p \times \rho$ ) of the fluids at nominal mean solar field temperature is also given in table 1. This is a measure for the volume flow rate in the plants as the heat delivered by the solar field calculates according to (1).

$$\dot{Q} = C_p \times \rho \times \Delta V / \Delta t \times \Delta T$$

(1)

The volumetric heat capacity of HELISOL<sup>®</sup> 5 is about 75% of that of DPO/BP but this is almost exactly compensated by the increased temperature difference ( $\Delta$ T) between solar field inlet and outlet.

Thus the volumetric flow rate  $(\Delta V/\Delta t)$  for both systems is almost the same and since they are using the same receiver diameter (D) and loop length (l) with the same friction factor ( $\lambda$ ) and pressure loss coefficients ( $\Sigma \zeta_i$ ) the nominal pressure drop ( $\Delta p$ ) in the solar field is lower for HELISOL<sup>®</sup> 5. This is obvious from equation (2) as the density ( $\rho$ ) of HELISOL<sup>®</sup> 5 is considerably lower than the density of DPO/BP.

$$\Delta \mathbf{p} = 0.5 \times \mathbf{\rho} \times \mathbf{v}^2 \times (\lambda \times 1/\mathbf{D} + \Sigma \zeta_i) \tag{2}$$

Solar field parasitics are calculated from a conceptual solar field layout, according pressure drops and fluid properties. In the annual performance models specific parasitics in  $W/m^2$  of solar field aperture are used as shown in table 1. Nominal specific parasitics for the HELISOL<sup>®</sup> 5 plants are about 80% of the parasitics of DPO/BP plants while those of the HITEC<sup>®</sup> plants are about 43% compared to DPO/BP plants.

	Table 1.	Key in	put data	for 50N	ЛW pl	ants used	for t	he com	parisor
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Heat transfer fluid		DPO/BP	HELISOL <sup>®</sup> 5	<b>HITEC</b> <sup>®</sup>
	Unit			
Nominal solar field temperature	°C	393	430	510
Gross power block efficiency (wet cooling)	%	39.0	40.5	43.2
Gross power block efficiency (ACC)	%	37.7	39.2	41.9
Nominal specific solar field parasitics	W/m <sup>2</sup>	8	6.4	3.4
Specific investment solar field	€/m <sup>2</sup>	235	235	220
Specific investment storage	€/kWh	40	33	25
Specific HTF cost	€/kg	4	4	1
Annual HTF replacement rate	%	2	5	1
Mean volumetric heat capacity	$kJ/(m^{3}K)$	1871	1397	2787

A simple freeze protection concept is assumed and considered in the annual performance models. DPO/BP and HITEC plants have auxiliary heaters fired by natural gas which are operated once the HTF temperature falls below 60°C for DPO/BP and 200°C for HITEC respectively. The HELISOL<sup>®</sup> 5 plants do not need freeze protection since the freezing temperature is below -30°C.

The LCOE calculation is done according to the method proposed by Roy et al. [12], assuming a real interest rate of 8%, depreciation and life time of the plant of 25 years and annual insurance costs of 0.7% of the total investment costs of the plant.

In order to check whether the choice of HTF might have a different impact for different sites, solar resources or plant size, the comparison was done for three sites with different annual DNI sums and for 50 MWe and 150 MWe power plants. Table 2 shows a comparison of the three sites. Furthermore for the Spanish site a wet cooling tower was used for heat rejection whereas the other plants were assumed to have air cooled condensers (ACC). For the 150 MW plants no economy-of-scale was used except for the power blocks which are considered to cost 700  $\epsilon$ /kW for 150 MW instead of 750  $\epsilon$ /kW for 50 MW (with wet cooling tower) and 800  $\epsilon$ /kW instead of 850  $\epsilon$ /kW for plants with ACC.

Table 2.	Geographical	and meteorological	data of the	e three sites

Site		Guadix,	Daggett,	Riad,
	Unit	Spain	USA	Saudi Arabia
Latitude	°N	37.13	34.85	24.93
Longitude	°E	-3.06	-116.80	46.72
Altitude ASL	m	1100	586	612
DNI (yearly)	kWh/m	2052	2723	2328
Ambient temp. (mean/min/max)	°C	13.7 / -5.0 / 37.7	19.7 / -5.0 / 46.7	26.1 / 3.7 / 46.8
Rel. humidity (mean)	%	58	36	29

#### 3.2. Results

After a preliminary design of each plant for the individual site and HTF, several annual performance calculations were done with varying solar field aperture size and storage capacity in order to find the individual configuration with the lowest LCOE. Thus the CSP plants used for this comparison are not necessarily all of the same size but may differ since the HTF and the associated performance and costs may shift the LCOE minimum. Finally the optimization showed that the plants with DPO/BP and HELISOL<sup>®</sup> 5 will have the same solar field size for the same site but the storage size of the HELISOL<sup>®</sup> 5 plants will be somewhat larger (11 instead of 10 full load hours for the Daggett site). The molten salt plants show a LCOE minimum at larger solar fields and larger storage sizes (table 3). For the other sites similar conclusions are valid. Table 3 shows that increased solar field outlet temperatures are leading to lower annual heat production. But this will be over-compensated by higher power block efficiencies and thus the annual net electricity production is increased.

Table 3. Results of the techno economic comparison for 50 MW plants at Daggett, USA

Heat transfer fluid	Unit	DPO/BP	HELISOL <sup>®</sup> 5	HITEC <sup>®</sup>
Total aperture area	m <sup>2</sup>	539550	539550	549360
Storage capacity	h	10	11	12
Annual solar heat production	GWh	662	647	635
Annual net electricity production	GWh	219	226	243

Fig. 4 shows the calculated LCOE of the different plant variants considered in this study. One might easily recognize the impact of solar resource and maximum HTF temperature on electricity costs. The CSP plants at Daggett (USA) show the lowest LCOE values, while the plants at Guadix (Spain) show the highest LCOE values in this comparison. With increasing solar field outlet temperature the LCOE decreases too. If we take the plant with DPO/BP as reference at each individual site, the LCOE decreases by about 5% if HELISOL<sup>®</sup> 5 is used as HTF and by 15-18% if HITEC<sup>®</sup> is used. This is valid for the 50 MW plants. For the 150 MW plants the relation is similar for HELISOL<sup>®</sup> 5 but for HITEC<sup>®</sup> the difference is even higher (18-21%).



Fig. 5. Comparison of LCOE

Comparing the results, it is obvious that switching to molten salt as HTF is an attractive option but there are actually a couple of risks associated with this modification, e.g. freeze protection and corrosion issues. On the other

hand switching to HELISOL<sup>®</sup> 5 might also be attractive since it offers a 5% cost decrease while using equipment which is already available and proven at many existing CSP plants.

Since the techno-economic comparison is based on assumptions about several cost figures, a sensitivity analysis was performed to check the impact of individual cost assumptions. In figure 6 the results are shown. Interest rate shows the highest impact, followed by solar field investment costs. Increased solar field investment costs by 20% will lead to increased LCOE by about 11%. Storage and power block costs are of lower impact and HTF costs will only contribute by less than 1% increase in LCOE if they are 20% higher than assumed.



Fig. 6. Sensitivity analysis for the 50 MW plant with HELISOL® 5, Daggett

#### 4. Conclusions

The comparative thermal tests indicate clearly that HELISOL<sup>®</sup> 5 withstands considerably higher operating temperatures than DPO/BP with low tendency to hydrogen formation. The formation of other degradation products is low as well. Hence only low masses of separable compounds result for HELISOL<sup>®</sup> 5 in comparison to DPO/BP. Formation of hydrogen and low boiling degradation products at 425°C are lower for HELISOL<sup>®</sup> 5 than for DPO/BP at 400°C.

The techno-economic comparison shows that switching from DPO/BP to HELISOL<sup>®</sup> 5 can reduce the LCOE by about 5%. This value is valid for different sites and plant sizes. Although the utilization of molten salt promises higher LCOE reduction it is currently considered to imply higher risks. One important advantage of HELISOL<sup>®</sup> 5, compared to other alternatives, is that it might be used without major modifications in solar field design and with components which are used already in many other existing CSP plants.

#### Acknowledgements

This work has been funded by the German Federal Ministry for Economic Affairs and Energy, reference no. 0325453C.

#### References

- Raade JW, Padowitz D. Development of Molten Salt Heat Transfer Fluid With Low Melting Point and High Thermal Stability. J Sol Energy Eng 2011; 133(3): 031013-8.
- [2] Blake ES, Hammann WC, Edwards JW, Reichard TE, Ort MR. Thermal Stability as a Function of Chemical Structure. J Chem Eng Data 1961; 6(1): 87-98.
- [3] Grebe JJ. Composition of matter. US patent 1932; 1,882,809.
- [4] Rainey WT Jr.; Attrill JE, Yeatts LB Jr. Gas Chromatographic Analysis of Biphenyl Pyrolytic Products; ORNL-TM-523; Oak Ridge National Laboratory; 1963.
- [5] Adam AW, Niggemann RE, Sibert LW. Thermal Stability Determination of Biphenyl and the Eutectic of Biphenyl and Phenyl Ether in a Rankine Cycle System. In: Intersociety Energy Conversion Engineering Conference, New York, 1968; 1:398-406.
- [6] DIN 51528:1998-07, Testing of mineral oils and related products Determination of thermostability of unused heat transfer fluids.
- [7] DIN 51435:2010-03, Testing of petroleum products Determination of boiling range distribution Gas chromatography method.
- [8] Burkholder F, Brandemuehl M, Price H, Kutscher C. Parabolic trough receiver thermal testing, Proceedings of ES2007, June 27-30, 2007, Long Beach, California, US, ES2007-36129.
- [9] Jung C, Schmidt V, Senholdt M. Aging of organic heat transfer media. 18th SolarPaces Int. Symposium, September 11-15, 2012. Marrakech, Morocco.
- [10] HITEC<sup>®</sup> Heat Transfer Salt, Product data sheet, Coastal Chemical Co., L.L.C., 5300 Memorial Drive, Suite 250, Houston, TX 77007.
- [11] Burkholder F, Kutscher C, Heat Loss Testing of Schott's 2008 PTR70 Parabolic Trough Receiver, Technical Report NREL/TP-550-45633, May 2009.
- [12] Roy A., Meinecke W., Blanco Muriel M. (editors): Introductory Guidelines for Preparing Reports on Solar Thermal Power Systems, SolarPACES Report No. III-3/97, 1997.