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Hydrogen Monitoring and Control in the Heat Transfer Fluid of Parabolic Trough Plants

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Abstract. In this study hydrogen concentrations in the heat transfer fluid (HTF) of parabolic trough systems were analyzed and hydrogen control by venting was practically tested in several plants. Concentrations between 10 and 800 µmol/kg and decreases of hydrogen by venting between 10 - 75% were found. A model consideration is presented that clearly demonstrates the impact of equilibrating HTF from the solar field with the fluid in vessels on hydrogen concentration. Concentrations could be reduced more than 80% in the solar field if equilibrium of the gas with gas spaces in vessels was achieved. Hydrogen formation rates of used HTF with up to nine years of service life were checked with lab tests. These indicate increasing hydrogen formation of up to eightfold compared to unused fluid which gives rise to re-consider recommendations of maximum tolerable concentrations of low and high boilers in used eutectic mixtures of biphenyl and diphenyl oxide.

INTRODUCTION

Diphenyl oxide (DPO) and biphenyl (BP) as a eutectic mixture is the most commonly applied heat transfer fluid (HTF) in parabolic trough power plants. [1] The maximum operating temperature of the fluid is limited to 400 °C but slow degradation already occurs within the typical operating range of 293 – 393 °C.

Among the degradation products hydrogen is particularly important as it permeates into the vacuum insulation of the heat collecting elements (HCEs). The HCEs are equipped with getter materials that reversibly bind hydrogen to avoid the formation of a heat conducting atmosphere inside the glass envelope of the HCEs. This protective principle works as long as the getter capacity is not exceeded. In order to ensure sufficiently long lifetimes of the HCEs, the hydrogen permeation has to be kept within tolerable limits by controlling the hydrogen concentration in the HTF. [2,3]

In this study, the hydrogen concentrations in solar thermal trough plants have been examined using hot and pressurized HTF samples that were extracted from the systems during operation. The samples have been analyzed at DLR's lab with respect to all dissolved gases using a combination of pressure measurement and compositional gas analysis via gas chromatography.

The hydrogen formation rates of the HTF of numerous plants have been monitored as well by lab tests to evaluate the potential benefit of HTF processing to achieve some hydrogen formation rate control.

HYDROGEN MONITORING IN PARABOLIC TROUGH SYSTEMS

The analytical procedure used in this study includes the extraction of HTF samples without any change of fluid and gas composition as a first step. For this purpose, hydrogen-tight steel cylinders equipped with high temperature valves are used and directly connected to the HTF system. The filling of the containers with HTF is performed via pressurized flushing in flow-through mode using cylinders with two valves, or by filling the pressurized HTF into evacuated cylinders equipped with only one valve. After cooling the closed sample to ambient temperature, the cylinders are disconnected from the system and shipped to DLR's lab for evaluation. The analysis of the HTF can be focused on dissolved gases or any other of the fluid's ingredients using gas chromatographic techniques adapted to

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the required analytical parameter. The outcome of the gas analysis is the total amount of each gas per mass of HTF sample (typically µmol gas per kg HTF). [4]

For comparison with the hydrogen concentration limit of 0.3 mbar given by receiver manufacturers in terms of pressure [5], the conversion according to Henry's law (1) as well as the comparison with a hydrogen atmosphere with identical volumetric density like in the liquid HTF at operation condition are considered.

$$p_{H_2} = H \cdot x_{H_2} \tag{1}$$

According to earlier studies [6] the Henry constant of hydrogen in BP/DPO is about 2300 bar at 400 °C. A relation of concentration and pressure can be calculated from the Henry relation (2). At 400 °C about 0.8 µmol/kg correspond to 0.3 mbar.

$$p_{H_2} = H \cdot b_{H_2} \cdot M_{HTF} \tag{2}$$

The Henry pressure relates to a gas phase which is in equilibrium to the liquid. As there is no significant gas phase to be expected in HCEs, the transport of hydrogen is expected to be driven by hydrogen dissolved in the liquid HTF. The density of hydrogen in the fluid is expected to correlate with the permeation rate. The pressure of gaseous hydrogen atmosphere with the same volumetric density like in the liquid HTF (3) can be considered as an estimate of the driving force of this process as long as there no experimental data on the hydrogen permeation from liquid HTF are available. According to this estimate the hydrogen limit of 0.3 mbar would be reached at about 8 µmol/kg.

$$p_{H_2,\text{ideal gas}} = b_{H_2} \cdot \rho_{HTF} \cdot R \cdot T \tag{3}$$

In a Spanish plant samples have been analyzed continuously for almost two years so far. In this specific plant, the hydrogen levels are about two times higher in summer compared to winter operation (**Fig. 1**). Higher concentrations are generally to be expected in summer due to the higher operating temperatures and longer operational periods.

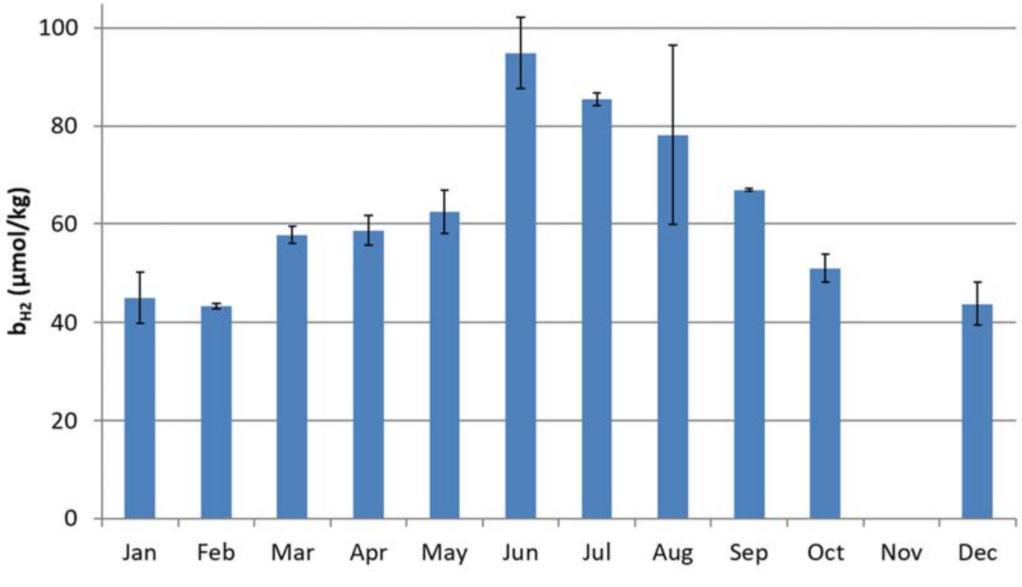

FIGURE 1. Averaged monthly hydrogen concentrations in the HTF of a Spanish parabolic trough plant over 21 months (and deviations from the averages as error bars).

Depending on the applied conversion the hydrogen concentrations of the Spanish plant are 4(40) – 13(130) times above the limit. In other systems lower concentrations in the range of 30 µmol/kg were found in summer, others had concentrations of several 100 µmol/kg. The span of the lowest concentrations in summer within all tested plants is about 10 to 800 µmol/kg. The lowest concentrations are moderately high compared to the limits under consideration while readings above 100 µmol/kg are clearly above any limit. The very large span of readings in technically similar plants illustrates that hydrogen concentration depends a lot on the operation of a plant. The balance of hydrogen formation, distribution of hydrogen within the HTF system and removal of hydrogen out of the system results in a specific hydrogen concentration.

MONITORING OF HYDROGEN FORMATION RATES

Hydrogen formation rates of samples in this study are determined by aging tests analogous to DIN 51528. [7] In contrast to the standard test three test temperatures between 390 – 410 °C are applied and a set of five samples is used in order to collect them from the furnace after 72 – 480 h. Hydrogen is quantified by determining the pressure and composition of the gases formed per mass of HTF. The amounts of hydrogen per HTF increase at constant rates for used HTF samples at these temperatures and comparably short aging intervals (**Fig .2**) whereas at larger aging intervals or higher temperatures exponential increases had been observed in previous studies. [8] The formation rates (r_{H_2}) are determined from the slopes of lab studies with 15 used HTF qualities and with unused eutectic BP/DPO mixture. All data derived for a specific HTF quality were evaluated with an Arrhenius approach to allow for interpolation of formation rates at least within 390 – 410 °C.

$$r_{H_2} = A \cdot e^{-\frac{E_a}{R \cdot T}} \tag{4}$$

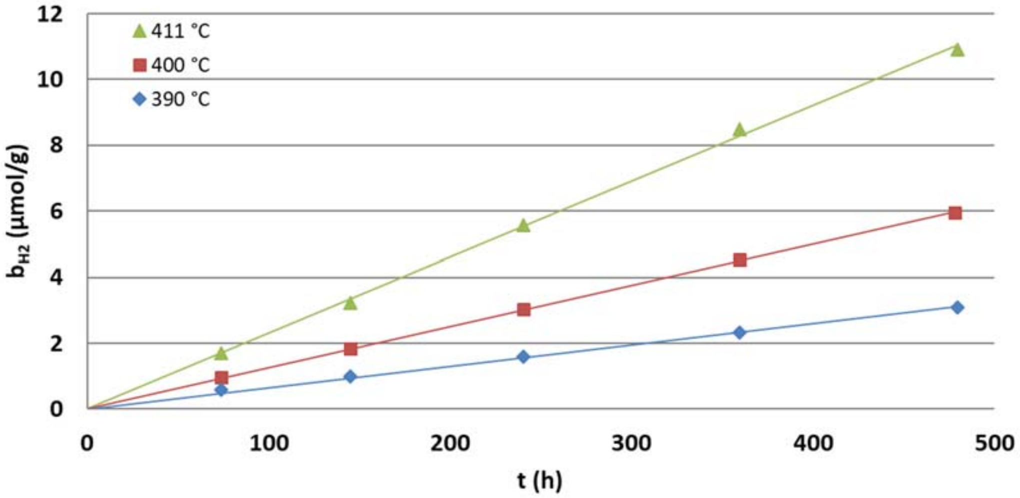

FIGURE 2. Hydrogen formation of a used HTF sample at three temperatures with increasing aging time (dots: determined amounts hydrogen per mass of HTF, lines: linear fit of formation).

Used HTF samples were collected from power plants with one to nine years of service life of the HTF and the formation rate of hydrogen was calculated for 393 °C which is typically the maximum operating temperature of parabolic trough systems.

Although the parabolic trough plants tested within this monitoring program have various set-ups, sizes and operating conditions, there is a clear trend of increasing hydrogen formation rate at 393 °C after longer service life of the plants (**Fig. 3**). After nine years of service life up to eight times of the initial hydrogen formation rate of unused fluid has been found so far.

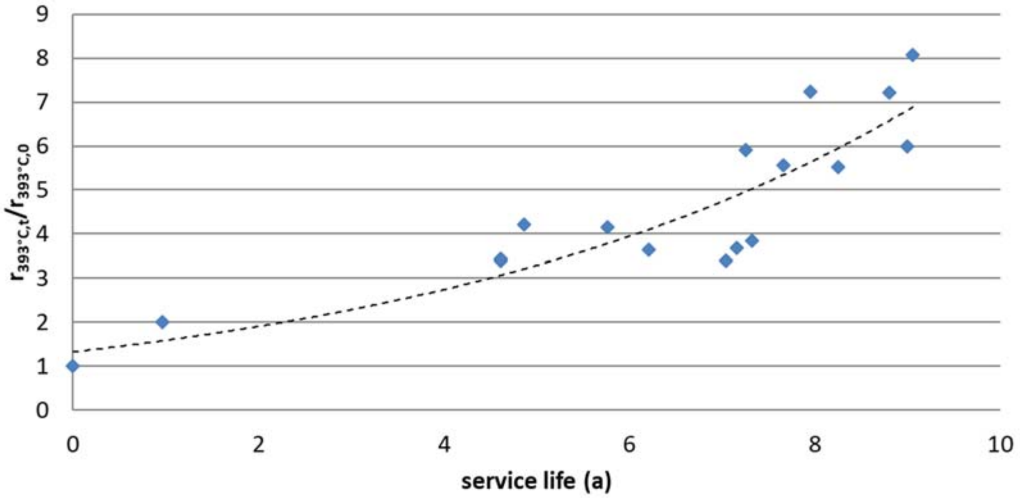

FIGURE 3. Hydrogen formation rate of used BP/DPO in terms of service life relative to unused fluid (dots: calculated from Arrhenius parameters, dotted line: exponential trend).

The cause of increasing hydrogen formation rate is the accumulation of degradation products as recently shown. [8] According to the data obtained in this study, steadily increasing hydrogen formation rate is to be expected when no countermeasures against the accumulation of degradation products are applied. Manufacturers recommend to keep low boilers below 5 % and high boilers below 10%. [9] These recommendations obviously had not been designed in terms of hydrogen control and keeping the fluids' condition closer to the unused HTF would obviously reduce hydrogen formation considerably.

DISTRIBUTION OF HYDROGEN WITHIN PARABOLIC TROUGH SYSTEMS

Hydrogen formation depends exponentially on temperature according to (4). Hence, only HTF at maximum temperature i. e. in hot header piping contributes significantly to hydrogen formation. An additional small contribution is to be expected from the HTF at the end of loops. All other HTF can be ignored in terms of the formation reaction.

To illustrate the potential of equilibration of the hydrogen between the liquid HTF and the gas phases of HTF vessels a model system is considered. In this model only the HTF inside the hot header piping forms hydrogen during the operational day. A formation rate of 5 µmol/(kg*h) is assumed which corresponds to a system at 393 °C with 5 – 7 years of service life. The HTF is considered to be operated between 293 – 393 °C during the day for 10 hours and to cool down isothermally to 150 °C at night. At this lowest temperature it is assumed that hydrogen would perfectly equilibrate between the liquid HTF and all gas spaces available in any vessels taking a Henry constant of 3000 bar into account. [6] The total mass of HTF is assumed to 2300 t and the volumes of piping and vessels given in **Tab. 1** is considered.

TABLE 1. Volume of vessels and piping at low, intermediate and high temperature

Piping section	Volume (m^3)	HTF mass, day (t)	HTF mass, night (t)
HTF, cold	725	597	688
HTF, intermediate	750	574	712
HTF, hot	725	513	688
Vessels	1200	616	212

As indicated in **Fig. 4** (blue line) the total amount of hydrogen increases in this model day by day as no hydrogen is considered to be lost from the system. As perfect equilibration is assumed to happen at 150 °C during the night, most of the hydrogen is shifted to the gas spaces in the vessels. In this model only 14% of the hydrogen formed remain in the HTF and obviously causes correspondingly low concentrations. If there was no equilibration, the hydrogen concentration would be about seven times larger.

This model consideration clearly shows the relevance of exchanging HTF from the solar field with HTF in vessels for hydrogen concentration control. Poor exchange will result in considerably higher hydrogen concentrations in the solar field.

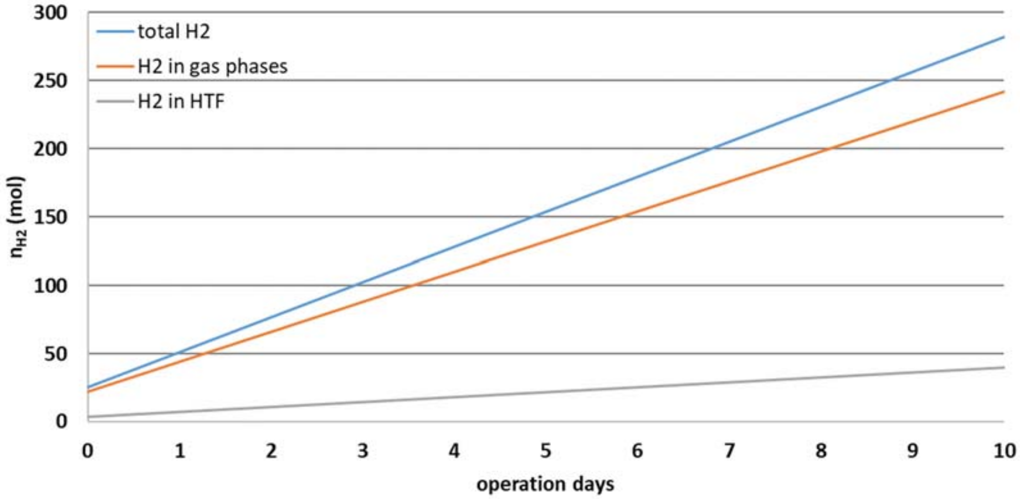

FIGURE 4. Increase of hydrogen in a model system with assumed equilibration of hydrogen between liquid HTF and gas spaces of HTF vessels (blue line – total amount of hydrogen formation, orange line – amount of hydrogen in gas spaces, grey line – amount of hydrogen in liquid HTF).

VENTING TESTS IN PARABOLIC TROUGH SYSTEMS

According to the findings of the monitoring program hydrogen concentrations differ strongly between different plants. Although there are technical differences e. g. in terms of controlling the flow through vessels in all of them nitrogen can be released from the system at least to some extent. When gas is vented off the HTF system some hydrogen is lost as well and accordingly the concentration in the HTF can be decreased by that measure.

The impact of nitrogen release from the HTF system on the concentration of hydrogen in the solar field has been tested in several plants so far. For this test some HTF samples had been collected in the afternoon of the first day. During the night or during the start-up on the next day nitrogen was vented off and after reaching production conditions in the morning another set of HTF samples was collected for hydrogen analysis.

The reduction of hydrogen concentration depends strongly on the extent of nitrogen release and on the exchange of HTF from the field with the vessels. Basically, three cases have been observed (**Fig. 5**). In some plants moderate decrease of hydrogen was observed in the range of 10%. In most plants significant reductions of about 40% could be shown and in a few a decrease by more than 70% was achieved with one single venting event.

Hence, by optimizing the venting process some control of hydrogen is possible with comparably low effort.

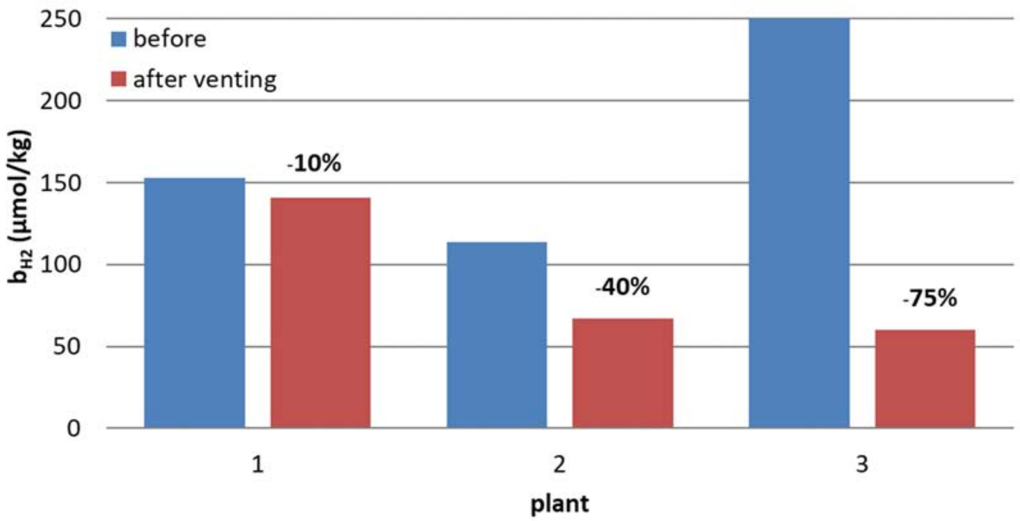

FIGURE 5. Hydrogen concentration in some plants before (blue) and after (red) exchange of nitrogen (with hydrogen) from the HTF system (averages over plants with low, medium and high impact of the exchange process on the concentration of hydrogen).

CONCLUSION

Hydrogen concentrations in HTF of the solar field of parabolic trough plant can be very high if no or insufficient countermeasures against hydrogen accumulation are applied. Up to 800 µmol/kg dissolved hydrogen in HTF samples have been found in this study.

Hydrogen concentrations in the solar field are a consequence of formation in the hottest parts of the system. Lab tests with HTF from various parabolic trough plants demonstrated clearly that hydrogen control is to be expected to getting harder with used HTF. This is as hydrogen formation rates up to eightfold compared to unused fluid have been found after nine years of service life. Degradation products of BP/DPO have been shown to be the cause of increasing formation rate. Thus, the limits for high and low boiler accumulation should be critically re-considered to keep hydrogen formation rates closer to unused HTF.

By equilibrating the HTF of the solar field with the HTF inside vessels, hydrogen can be significantly shifted into the gas spaces of vessels. As shown with model considerations in this study, this could reduce hydrogen concentrations more than 80% in the HTF if equilibrium between all HTF and the gas spaces was achieved.

Removal of hydrogen out of the system can be achieved by decompression or venting off blanket gas from vessels. Accordingly, hydrogen that was successfully shifted to the gas spaces can be removed from the HTF system by venting. Venting alone without careful exchange of HTF from the solar field with the HTF in vessels will have limited effect on hydrogen concentration. Venting tests in this study demonstrated hydrogen decreases between 10 – 75% depending on the intensity of the decompression and exchange efforts. In parabolic trough plants that perform regular venting hydrogen concentrations below 100 µmol/kg are typically found. Some plants keep the concentration significantly below 30 µmol/kg. Recommended hydrogen limits are smaller. Nevertheless, they have been set-up with gas mixtures and hydrogen permeation out of hydrogen solutions in HTF might be smaller as some competition of HTF molecules and hydrogen on the adsorption sites of steel surfaces can be assumed. Hence, hydrogen pressure limits should be evaluated in terms of resulting permeation rate in the future to avoid unnecessarily strict targets for hydrogen control.

NOMENCLATURE

TABLE 2. List of abbreviations

Parameter	Definition
A	Pseudo pre-exponential factor*
b_{H2}	Molality of hydrogen in HTF/ hydrogen formed per mass of HTF
E_a	Pseudo energy of activation*
H	Henry coefficient
M_{H2}	Molar mass of hydrogen
p_{H2}	Partial pressure of hydrogen
R	ideal gas constant
ρ_{HTF}	Density of liquid HTF
r_{H2}	Formation rate of hydrogen
t	Aging time
T	Absolute temperature
x_{H2}	Molar fraction of hydrogen in HTF

* These parameters refer not to individual reactions but to complex consecutive processes. Accordingly, they are not constant but will be only valid within the investigated time frames.

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