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Christian Jung and Marion Senholdt

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Comparative Study on Hydrogen Issues of Biphenyl/Diphenyl Oxide and Polydimethylsiloxane Heat Transfer Fluids

Christian Jung[a)] and Marion Senholdt[b)]

German Aerospace Center (DLR), Linder Hoehe, 51147 Cologne (Germany)

[a)]Corresponding author: christian.jung@dlr.de
[b)]marion.senholdt@dlr.de

Abstract. The formation of hydrogen from new and several used qualities of eutectic biphenyl (BP) and diphenyl oxide (DPO) mixture was investigated with an established lab experiment in the range of 380 – 410 °C and 410 – 430 °C respectively. Kinetic evaluations show that hydrogen formation increases not only with temperature but also with time. Field samples extracted after 5 and 10 years' operating time confirm an increase of hydrogen formation with operating. A thermal aging study at 430 °C for 480 hours with a series of samples composed of new BP/DPO each doped with a degradation product indicates that the formation of phenol is the mayor driving factor for steadily increase with time. The impact of hydrogen formation on the concentration in the fluids of parabolic trough systems was checked with a simplified model that takes volumetric dimensions, residence time at maximum temperature, back mixing with fluid from overflow vessels and some assumed hydrogen removal step into account. New BP/DPO at 400 °C and polydimethylsiloxane (PDMS) at 425 °C is compared. After initially higher formation of hydrogen, in the long term low hydrogen formation is reported for PDMS. Although PDMS is considered at significantly higher operating temperature lower hydrogen concentrations are to be expected for this fluid after a starting-up phase in the model system. Accordingly, hydrogen control with PDMS is expected to be easier with PDMS fluids like HELISOL® 5A as no steady increase of effort on hydrogen removal will be required.

INTRODUCTION

The mixture of 26.5 % biphenyl (BP) and 73.5 % diphenyl oxide (DPO) still is the heat transfer fluid (HTF) most commonly applied in parabolic trough systems. [1] Its maximum operating temperature is 400 °C according to several manufacturers. [2-4] Nevertheless, even below this limit slow thermal degradation occurs leading to the formation of gases like hydrogen, carbon monoxide and methane, low boilers like benzene and phenol as well as high boilers like terphenyls, phenoxybiphenyls, quaterphenyls, phenoxyterphenyls and others. [5]

Hydrogen formation is not relevant in classical applications but in solar thermal parabolic trough systems it is a threat to the vacuum insulations of the heat collecting elements (HCEs). [6] Control strategies have been proposed for avoiding excessive hydrogen accumulation as the latter causes heat losses due to early exhaustion of the capacity of the getters that are included in HCEs for absorbing hydrogen that permeates into the vacuum insulation.

It could be shown that BP/DPO mixtures form hydrogen at steadily increasing rate but the factors that drive this apparently self-amplifying process have not been investigated so far. [6] Obviously, the active removal of hydrogen could be operated less intensive if the factors that drive the hydrogen formation rate could be controlled as well. Therefore, the impact of the degradation products on the formation of hydrogen rate has to be examined.

Polydimethylsiloxanes have been known for many years as heat transfer fluids as well but only recently, HELISOL® 5A has been introduced to the CSP market as a new product with enhanced thermal stability compared to BP/DPO mixtures at comparable costs. [7-8] Previous studies had shown that HELISOL® 5A forms less hydrogen than BP/DPO in the long term operation. Initially, the hydrogen formation rate is even higher than for BP/DPO

when the maximum operating temperatures of 425 °C and 400 °C are compared but in contrast to the organic fluid its formation rate slows down at increasing operation time.

In this study, the hydrogen formation and hydrogen formation rate of various BP/DPO qualities (new, used from different CSP plants and new fluid doped with degradation products or impurities like water or typical particles) are compared with polydimethylsiloxane (PDMS) like HELISOL® 5A. Both HTF classes are evaluated in terms of required hydrogen control measures in a parabolic trough model plant.

EXPERIMENTAL METHODS AND MATERIALS

Materials

A mixture of biphenyl (26.5%) and diphenyl ether (73.5%) was used as reference material without further purification. Purity of at least 99.5% was confirmed with gas chromatograph analysis with flame ionization detection (GC-FID). HTF samples from CSP plants were extracted by direct transfer into steel cylinders during regular operation. Sufficient amount of fore-run was taken to ensure compositions representative for the bulk fluids. These samples were used for the aging test in this study without any pre-treatment unless otherwise stated. Gases (nitrogen, helium, hydrogen and oxygen) were applied with purity of 99.999%.

Aging and Analytical Evaluation of Heat Transfer Fluid

Isothermal aging of HTF samples was performed according to DIN 51528 using ampoules made of Duran® glass tubes. [9] In order to keep the test temperature constant within less than 1 K deviation a fan convection oven was equipped with a carousel. The samples rotated inside the furnace during the experiment and the temperature was recorded within the orbit of the sample using a calibrated Pt-100 sensor. Temperature deviations less than 0.5 K were achieved using this set-up within aging times up to 3000 hours. After specific time intervals samples were taken out of the furnace in order to receive a series of samples aged for increasing time intervals at a specified temperature. For quantifying the formation of gases formed per mass of HTF the ampoules were opened in special containers that allowed for expanding the gases into a calibrated volume for determination of pressure and temperature. The gas composition was determined with micro gas chromatography. The total amount of gas was calculated using ideal gas laws taking the partial pressure according to the chemical analysis into account.

RESULTS AND DISCUSSION

Aging of BP/DPO

The eutectic mixture of pure BP/DPO was aged up to 3000 hours at 380 °C, 395 °C and 410 °C. The amount of hydrogen formed per mass of HTF increases exponentially (Fig. 1) and the development of the amount per HTF can be described with the fractional order kinetic equation (1) with satisfying accuracy within the investigated range.
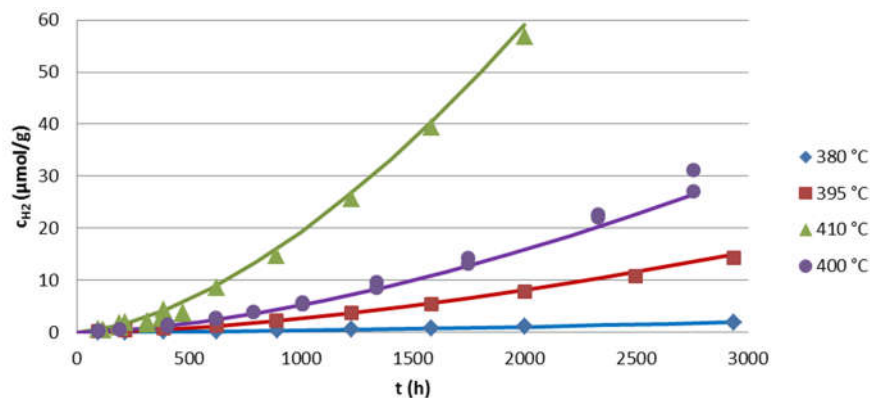

FIGURE 1. Formation of hydrogen from fresh BP/DPO (dots) and simulation according to kinetic equation (1) (lines)

$$b_{H_2} = (4.28 \cdot 10^{21} \cdot e^{-\frac{311.7}{R \cdot T}} \cdot t \cdot)^{1.6136} \frac{\mu mol}{g} \tag{1}$$

The initial rate cannot reasonably be determined with equation (1) which predicts zero formation for t = 0. For short duration of aging linear approximation of hydrogen formation represents the data well up to 400 hours particularly within the range of 380 – 400 °C according to the kinetic equations given in Fig. 2.
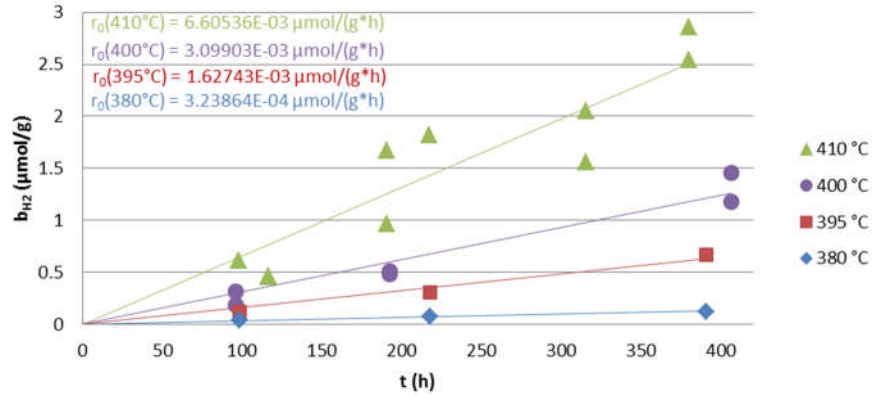

FIGURE 2. Formation of hydrogen from fresh BP/DPO (dots) with linear approximation up to 400 hours (lines)

Evaluation of the reaction rates presented in Fig. 2 with Arrhenius rate law allows for calculating the initial hydrogen formation rate of new eutectic BP/DPO mixture in the range of 380 – 410 °C according to equation (2).
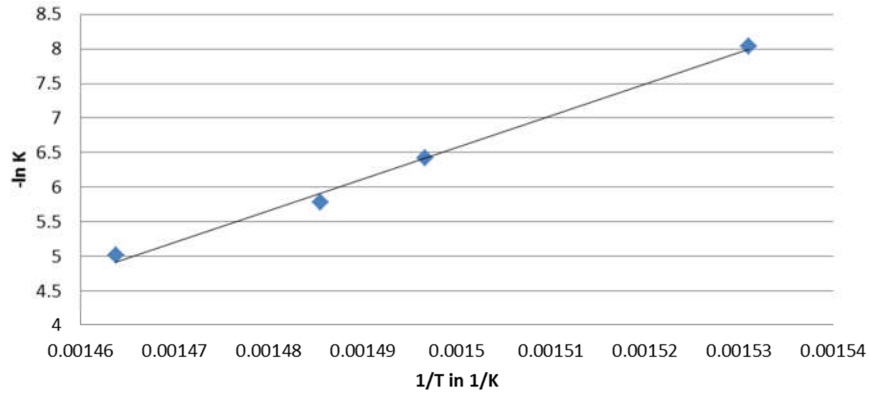

FIGURE 3. Arrhenius plot of the initial formation of hydrogen from fresh BP/DPO

$$r_0 = 6.87 \cdot 10^{26} \cdot e^{-\frac{379}{R \cdot T}} \cdot \frac{\mu mol}{g \cdot h} \tag{2}$$

While the initial rate can be calculated with equation 2, the rate on prolonged aging is available as derivative of equation 1. In Fig. 3 the results of these calculations are plotted in terms of time.
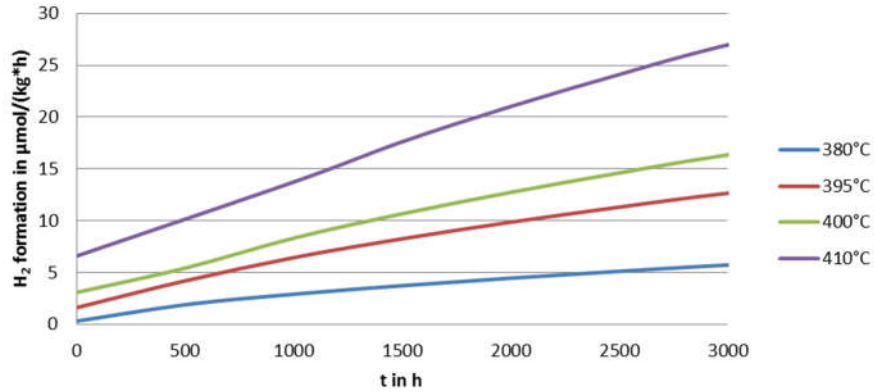
FIGURE 4. Formation rate of hydrogen from fresh BP/DPO in terms of time calculated according to equations 1 and 2

In contrast to the lab experiment, HTF in a CSP plant is neither operated in a closed system nor in isothermal condition. Typical annual exchange rates of used against fresh HTF are 1-3% per year. Moreover, some of the degradation products can be selectively removed by the ullage and the reclamation unit of the plant.

At a good solar site about 3500 operation hours at maximum temperature of the HTF can be expected at the outlet of the solar field. As shown below in this article about 25% of the total mass of HTF is at maximum temperature in operation condition. Accordingly, about 875 hours of isothermal aging in the lab experiment would correspond to one year operation in a parabolic trough plant assuming the same maximum temperature.

The aging rate of HTF samples from parabolic trough plants after prolonged operation was tested for comparison. Accelerated aging lab tests at 410 °C, 420 °C and 430 °C were used. Samples were supplied from three facilities with about five and ten years' operation time but no information was available on the duration of operation at the maximum temperature of about 390 – 395 °C.

As to be expected from the aging study of new BP/DPO the HTF qualities from the plants reveal significantly higher aging rates than the fresh fluid in this test. In Fig. 5 the hydrogen formation at 410 °C is shown. Although the samples are from different plants and from different sites the increase of hydrogen formation rate is 0.002 μmol/(g*h) per year at 410 °C. This indicates that the HTF qualities were operated and processed under comparable conditions.
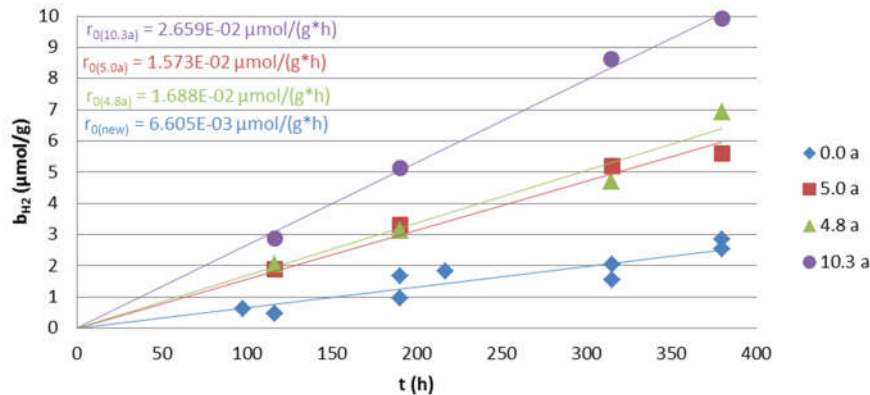

FIGURE 5. Formation of hydrogen at 410 °C from used BP/DPO (dots) with linear approximation up to 400 hours (lines)

The formation rates of each fluid were evaluated according to Arrhenius law (Fig. 6) and rate equations 3- 5 were derived.
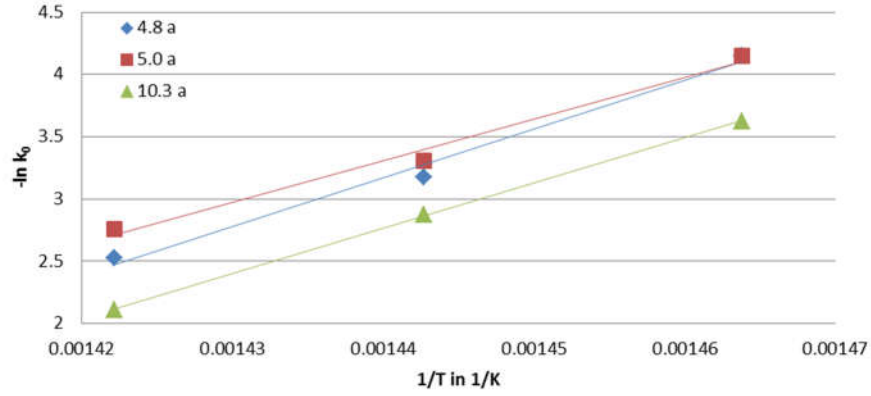
FIGURE 6. Arrhenius plot of the formation of hydrogen from used BP/DPO

$$r_{0,4.8a} = 1.26 \cdot 10^{23} \cdot e^{-\frac{325}{R \cdot T}} \cdot \frac{\mu mol}{g \cdot h} \tag{3}$$

$$r_{0,5.0a} = 3.01 \cdot 10^{19} \cdot e^{-\frac{278}{R \cdot T}} \cdot \frac{\mu mol}{g \cdot h} \tag{4}$$

$$r_{0,10.3a} = 3.81 \cdot 10^{21} \cdot e^{-\frac{303}{R \cdot T}} \cdot \frac{\mu mol}{g \cdot h} \tag{5}$$

With equations 2 - 5 the rates of hydrogen formation can be extrapolated down to 390 – 400 °C. According to Fig. 7 the rate increases about linearly with operating time. Compared to the isothermal lab test case (Fig. 4) the rates found for the HTFs from the CSP plants are significantly lower. The fluid sample with 10 year operation time forms 5.3 µmol/(kg*h) at 390 °C while in the isothermal case this rate is already reached at 380 °C after 3000 hours which corresponds to only 3.4 years of operation. Lower maximum operating temperature, lower annual operation hours, and higher exchange rates of HTF and selective removal of degradation products will have positive effects on hydrogen formation. Accordingly, the HTF in the tested facilities seems to have been less intensively aged compared to the fluid in the closed system lab test.
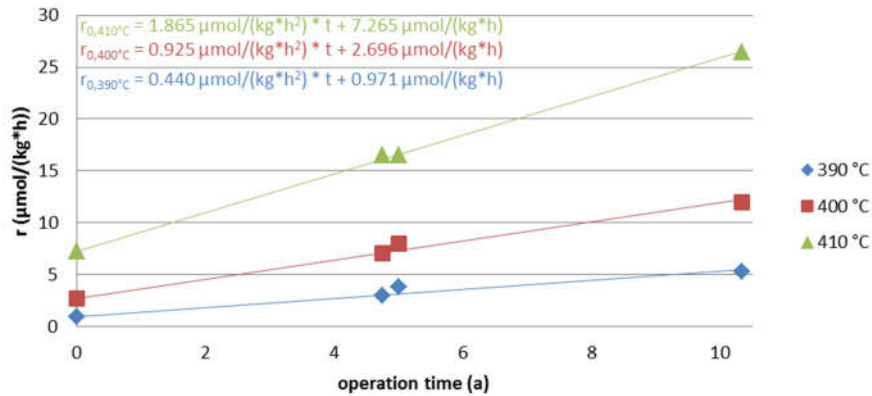

FIGURE 7. Calculated initial rates of hydrogen formation for new BP/DPO and HTF qualities from CSP plants with 5 and 10 year operation time (dots) and linear fits (lines & equations)

If the relation of hydrogen formation rate and compositional condition was known, the current hydrogen formation rate could be calculated according to a compositional analysis of the HTF. As a first step the impact of specific degradation products on hydrogen formation is examined in this study. BP/DPO samples were prepared

each doped with 1 % (m/m) of a specific degradation product and aged at 430 °C for 480 hours. The amount of hydrogen formed per mass of HTF was analyzed for each case.

According to Fig. 8 hydrocarbons like benzene and ortho-terphenyl have only negligible effect on hydrogen formation. Dibenzofurane seems to cause some amplification but phenol is obviously the strongest factor as it enhances hydrogen formation by 50% in this test while all the other test compounds reveal much weaker amplification by only 3-11%.
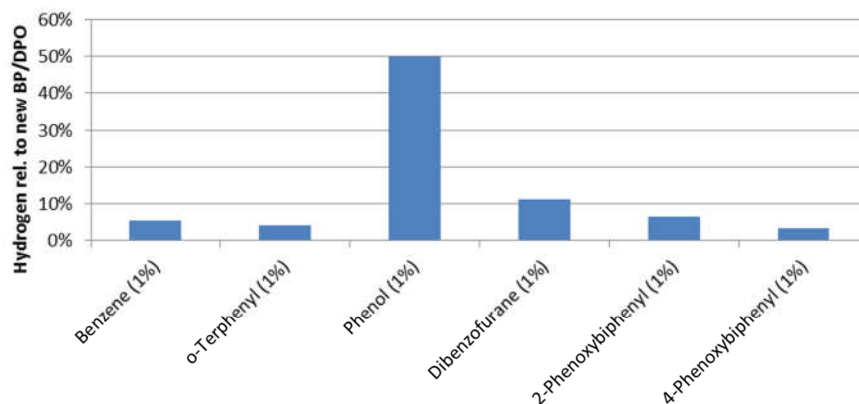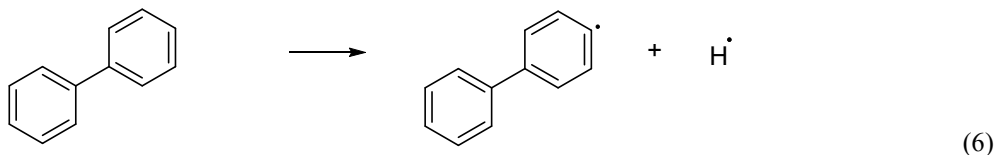

FIGURE 8. Formation of hydrogen at 430 °C for 480 hours from BP/DPO with dopants relative to pure BP/DPO

Formation of molecular hydrogen from BP/DPO is caused by radical chain reactions. The initial step of the chain is formation of aromatic and hydrogen radicals (H·) by thermal bon dissociation.

$$(6)$$

These radicals can add to aromatic compounds causing the cleavage of the bond to aromatic substituents. [10] The products will be an aromatic cleavage product with saturated valence and an aromatic radical that maintains the chain of reaction.

$$(7)$$
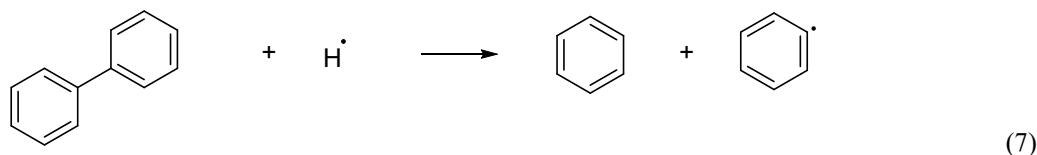
Alternatively, hydrogen radicals can subtract a hydrogen atom from any C-H bond of a compound in the HTF giving rise to formation of molecular hydrogen and a product that maintains the chain.

$$(8)$$
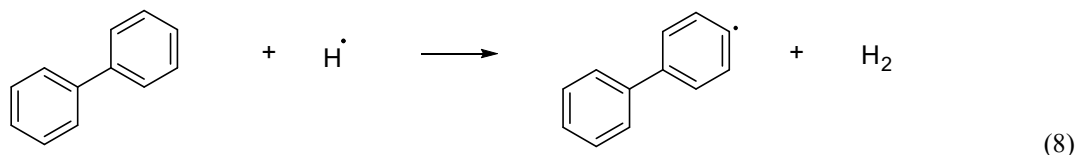
When to radicals combine the chain is terminated. This is an unlikely process compared to any chain reaction according to the extremely low concentration of radicals in the HTF at moderate temperatures.

The bond dissociation energy of the O-H bond in phenol is only 363 kJ/mol compared to 472 kJ/mol of aromatic C-H bonds. [11] Accordingly, the likeliness of hydrogen radical formation increases when phenol accumulates in the HTF. Thus the accumulation gives rise to steadily increasing hydrogen formation rate.

Aging of PDMS

The lab experiment described in this article had been used in a previous study to determine the formation of hydrogen from a new PDMS quality called HELISOL® 5A. The experimental data set covers 425 – 465 °C and aging up to 2800 hours. [7-8]. Formation of hydrogen from this fluid is initially faster and slows down on prolonged heating. The formation of hydrogen can be calculated by the equation 9 and the parameters given in [8].

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

(9)

Equation 9 is only validated below 3000 hours. In the long term it is to be assumed that the formation of hydrogen reaches a constant value at a specific temperature rather than decreasing steadily. In Fig. 9 the data given in literature are evaluated with a linear fit for the aging range of 400 – 3000 hours. The linear fits do not match zero as the initial formation rate is enhanced compared to the constant rate after some 100 hours above 400 °C.
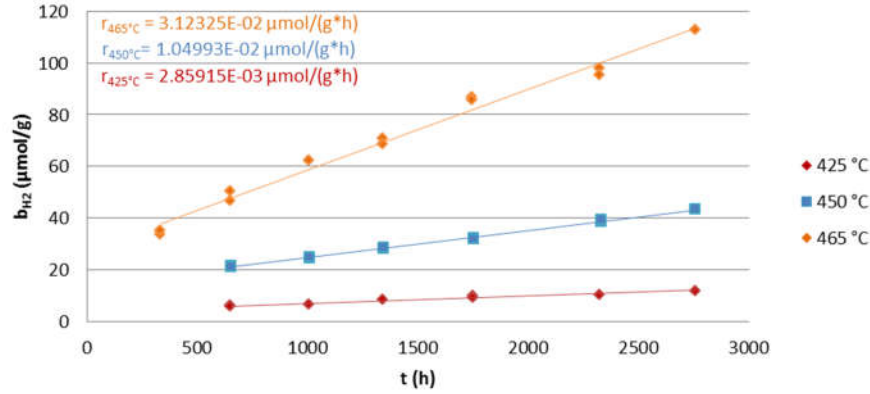

FIGURE 9. Formation of hydrogen from fresh HELISOL® 5A (dots) [7] with linear approximation after prolonged aging (lines)

The long-term rate of hydrogen formation is 2.86 µmol/(kg*h) at 425 °C for HELISOL® 5A which is lower than the initial hydrogen formation rate of 3.10 µmol/(kg*h) of BP/DPO at only 400 °C.

By evaluating the rates given in Fig. 7 with Arrhenius law parameters equation 10 is obtained that allows for calculating the long-term rates of hydrogen formation of HELISOL® 5A at least within the range of 425 – 465 °C.

$$r_{>600h,H5A} = 3.24 \cdot 10^{19} \cdot e^{-\frac{251.8}{R \cdot T}} \cdot \frac{\mu mol}{kg \cdot h}$$

(10)

Simulation of Hydrogen Accumulation in Parabolic Trough Systems

The hydrogen concentration in the HTF system of a parabolic trough plant has to be kept below acceptable limits. Several manufacturers of receivers specify a maximum effective hydrogen pressure of 0.3 mbar. [12] Hydrogen concentration in the HTF is to be considered as a balance of formation in the HTF, distribution in the system and removal out of the system. For evaluating the impact of BP/DPO or PDMS as HTF on the hydrogen concentration of parabolic trough systems model plants are considered (Table 1-3). The system set-up is relevant for analyzing the amount of HTF in the various parts of the system and the concentration changes within idealized operation days. No weather data are taken into account for this comparison.

In the cold condition 37.8 °C (100 °F) and during night time 150 °C is assumed for both models in any compartment of the HTF system. The hot or steady state operating condition is 300 °C inlet temperature in each case. The outlet temperature in the case of BP/DPO is 400 °C and 425 °C in the case of HELISOL® 5A. Each HTF is assumed to have the inlet temperature in the cold headers and the vessels, the outlet temperature is assumed in the hot headers and average of inlet and outlet temperature in the loops.

TABLE 1. Volumetric model system for the operation with BP/DPO and PDMS

Plant component	BP/DPO		PDMS	
	Elements	Volume (m³)	Elements	Volume (m³)
Cold piping		1300		1300
Hot piping		1300		1300
Loops	302	640	302	640
Expansion vessels	1	300	1	300
Overflow vessels	6	1800	8	2400

TABLE 2. Volumetric model system and distribution of HTF with BP/DPO

Plant component	HTF, cold condition		HTF, night condition		HTF, hot condition	
	(t)	(rel.)	(t)	(rel.)	(t)	(rel.)
Cold piping	1369	39.2%	1246	35.7%	1040	29.8%
Hot piping	1369	39.2%	1246	35.7%	876	25.1%
Loops	671	19.2%	610	17.5%	470	13.5%
Expansion vessels	79	2.3%	72	2.1%	60	1.7%
Overflow vessels	0	0%	352	9.0%	1043	29.9%

The consideration assumes that cold and hot headers have equal volumes and that the expansion vessel is operated with 25% filling degree all the time while the overflow vessels have no filling in the cold condition. Higher expansion due to decreasing density is compensated by more vessels in the case of PDMS.

Only formation of hydrogen by aging of HTF at maximum temperature is considered as aging processes at lower levels will be negligible due to the exponential dependency on temperature. Daily operation of 10 hours with steady state condition in terms of temperature is considered ('hot condition'). At the end of an operation day cooling down of all HTF to 150 °C is assumed ('night condition').

TABLE 3. Volumetric model system and distribution of HTF with PDMS

Plant component	HTF, cold condition		HTF, night condition		HTF, hot condition	
	(t)	(rel.)	(t)	(rel.)	(t)	(rel.)
Cold piping	1214	39.3%	1076	34.8%	854	27.6%
Hot piping	1214	39.3%	1076	34.8%	594	19.2%
Loops	595	19.2%	527	17.0%	358	11.6%
Expansion vessels	70	2.2%	62	2.0%	49	1.6%
Overflow vessels	0	0%	352	11.4%	1238	40.0%

For both fluids the same simplified plant layout is assumed except for two additional overflow vessels for the operation of PDMS at 425 °C. Development of hydrogen concentration in both systems is considered taking a series of ideal operation days each with 10 hours at maximum operation temperature into account. Aging of the fluids below steady state thermal situation and in parts of the plant below maximum temperature is neglected according to the exponential dependency of reaction rate on temperature. Accordingly, aging is only relevant during the passage through hot headers. In the case of BP/DPO the residence time at maximum temperature is 36% and in the case of PDMS only 32% of the total time. During the night the concentration built up during the day is reduced by back mixing with HTF from the overflow vessels which has the concentration of the previous day. Before the next operation period hydrogen removal is assumed e. g. by venting gas out of the system during the heating up phase or by any other method of hydrogen removal. [13]
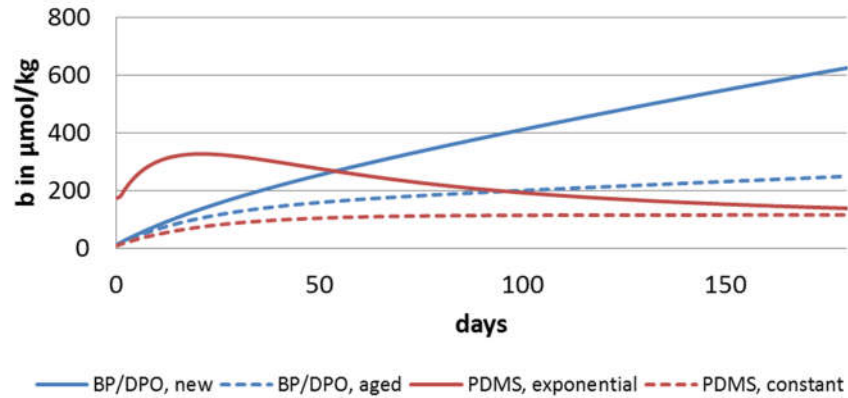
FIGURE 10. Accumulation of hydrogen in parabolic trough model systems operated with BP/DPO at 400 °C (solid line formation according to equation 2, broken line according to Fig. 7) and PDMS at 425 °C at 15% daily hydrogen removal (solid line formation according to equation 9, broken line according to equation 10)

The accumulation of hydrogen in BP/DPO at 400 °C and in PDMS at 425 °C each in the case of 15% daily elimination of hydrogen by some removal measure is shown in Fig. 10. Initial concentration for each fluid is zero. When fresh PDMS is considered (PDMS, exponential) initially higher formation of hydrogen compared to BP/DPO (BP/DPO, new) causes considerably higher concentrations in the first days of operation. After about 95 – 100 days identical concentrations are reached for both fluids. After this time the concentration in PDMS is lower compared to BP/DPO. Final concentration level in PDMS will be more realistically calculated by the constant rate model (PDMS, constant).

CONCLUSION

Controlling the concentration of dissolved hydrogen in the heat transfer fluid within the solar field is important for maintaining the efficiency of heat collecting elements. Enduring high concentration levels cause accelerated exhaustion of getter materials and early depreciation of vacuum insulation. The hydrogen formation of BP/DPO mixtures is steadily increasing as shown by lab experiments of new and field samples of the fluid. Accordingly, the efforts for controlling hydrogen have to be steadily adjusted and increased to maintain a particular hydrogen concentration level. In contrast to BP/DPO, mixtures of polydimethylsiloxanes reveal no tendency of increasing hydrogen formation rate. The initial formation rate is initially higher but decreases rapidly on prolonged operation. Accordingly, only in the start-up phase of PDMS more intense hydrogen removal is required.

After about 60 – 65 days of operation less hydrogen concentration results in the HTF when model systems corresponding approximately to 100 MW parabolic trough plants with 6 hours storage are compared with new BP/DPO at 400 °C and new PDMS at 425 °C field outlet temperature.

ACKNOWLEDGMENTS

NOMENCLATURE

R is the ideal gas constant. In equations 1 – 5, 9 and 10 it is used in kJ/(mol*K).

TABLE 4. List of abbreviations

Parameter	unit	Definition
t	h	Aging time
T	K	Absolute temperature
b_{H2}	µmol/g	Molality of hydrogen in HTF/ hydrogen formed per mass of HTF
Ea	kJ	Pseudo energy of activation*
A		Pseudo pre exponential factor*
n		Pseudo order of reaction*

* 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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