**Experimental Determination of the Hydrogenation/Dehydrogenation - Equilibrium of the LOHC System H0/H18-Dibenzyltoluene**

**S. Dürra, S. Zilma, M. Geißelbrechta,b, Karsten Müllerc, P. Preusterb, A. Bösmanna, P. Wasserscheida,b\***

a Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, D‑91058 Erlangen, Germany

b Forschungszentrum Jülich, Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK 11), Egerlandstr. 3, D-91058 Erlangen, Germany

c University of Rostock, Institute of Technical Thermodynamics, Albert‑Einstein‑Str. 2, D‑18059 Rostock, Germany

(\*Corresponding Author’s E-mail: [p.wasserscheid@fz-juelich.de](mailto:p.wasserscheid@fz-juelich.de))

**Abstract**

Liquid organic hydrogen carrier (LOHC) systems store hydrogen through a catalyst-promoted exothermal hydrogenation reaction and release hydrogen through an endothermal catalytic dehydrogenation reaction. At a given pressure and temperature the amount of releasable hydrogen depends on the reaction equilibrium of the hydrogenation/dehydrogenation reaction. Thus, the equilibrium composition of a given LOHC system is one of the key parameters for the reactor and process design of hydrogen storage and release units. Currently, LOHC equilibrium data are calculated on the basis of calorimetric data of selected, pure hydrogen-lean and hydrogen-rich LOHC compounds. Yet, real reaction systems comprise a variety of isomers, their respective partially hydrogenated species as well as by-products formed during multiple hydrogenation / dehydrogenation cycles. Therefore, our study focuses on an empirical approach to describe the temperature and pressure dependency of the hydrogenation equilibrium of the LOHC system H0/H18-DBT under real life experimental conditions. Because reliable measurements of the degree of hydrogenation (DoH) play a vital role in this context, we describe in this contribution two novel methods of DoH determination for LOHC systems based on 13C-NMR and GC-FID measurements.

# Introduction

In recent years, liquid organic hydrogen carriers (LOHC) have been increasingly discussed as an attractive option for the safe, cost-effective and efficient storage of hydrogen and energy. In LOHC systems, hydrogen is bound to an organic carrier molecule by catalytic hydrogenation to form a fuel-like, hydrogen-rich storage liquid. The latter can be handled and shipped at ambient conditions using the existing infrastructure for fuels. At the time and at the location of energy or hydrogen demand, a catalytic dehydrogenation reaction is then applied for on-demand hydrogen release.

A LOHC system that has attracted particular attention is dibenzyl toluene (H0-DBT)/perhydro-dibenzyl toluene (H18-DBT). In both, its hydrogen-lean (H0-DBT) and hydrogen-rich form (HX-DBT), the substance is composed of several regioisomers. Since the 1960s, this mixture is widely used as heat transfer fluid.[1-5] The LOHC system H0-DBT/H18-DBT offers a hydrogen capacity of up to 6.2 wt%, corresponding to a volumetric hydrogen content of 56 gH2/L.[6] To illustrate the potential of LOHC-based hydrogen transport for a future global trading of renewable energy in form of chemically bound hydrogen, we can consider a tankship of the class Suezmax full of H18-DBT. Its 150,000 metric tons of liquid load would then contain 9,300 metric tons of hydrogen, i.e. 309.9 GWh of energy based on the Lower Heating Value (LHV) of the chemically bound hydrogen. This shows, that LOHC-based, transcontinental hydrogen trading from wind- or sun-rich areas to industrialized countries with currently a high share of imported energy, such as e.g. Germany [7], is a realistic option for the future.

With the advent of global emission pricing [8] and rising electricity prices (in Germany due to the shutdown of nuclear and coal-fired power plants and increasing electricity demand, e.g. for battery vehicle mobility), the import of LOHC-bound hydrogen will become attractive already at the short to medium time scale. [4, 9, 10] Runge et al. analyzed the mobility costs for different renewable fuels which are produced at sweet spots and consecutively transported to Germany. They concluded that hydrogen distributed via LOHC is the cheapest option in many scenarios for importing renewable fuels. [9]

The present study deals with the experimental determination of the hydrogenation/dehydrogenation equilibrium of the H0-DBT/H18-DBT system. Detailed knowledge of equilibrium data is highly relevant for the proper design, modeling, and engineering of the reversible hydrogenation/dehydrogenation processes. Note, that earlier published data on the reaction enthalpy of the H0-DBT/H18-DBT system have been calculated from experimentally derived enthalpies of combustion and enthalpies of vaporization [11, 12]. The enthalpy data are known with a good accuracy.[13] However, calculation of the equilibrium constant additionally requires the entropy of reaction. Knowledge about the entropy data of the H18/H0‑DBT system is still limited. Furthermore, it should be kept in mind that dehydrogenation of H18‑DBT is a reaction in a two-phase system. Hence, the reaction equilibrium is superimposed by a vapor-liquid-equilibrium (VLE). This superimposed VLE not only requires further substance property data (vapor pressures), but also leads to a problem of different reference experiments.

Calculations of reaction equilibria are based on the assumption that the total system is in equilibrium. This includes the VLE. The reference experiment for the equilibrium calculation of a dehydrogenation would be a reaction setup in which the hydrogen that is released inflates a gas balloon, which is kept isothermal and isobaric. However, lab-scale setups as well as technical dehydrogenation apparatuses are both equipped with a condensation unit. As a consequence, most of the hydrogen, which would contain saturated HX‑DBT vapor in the gas balloon reference experiment, is nearly free of vapor. Instead the HX‑DBT vapor returns to the liquid phase. Thus, the assumption of the VLE is disturbed. There is still a situation similar to the VLE in immediate proximity to the liquid phase, but this does not hold for the complete system. Since superimposed phase equilibria can have a tremendous effect on the reaction equilibrium, the calculated equilibrium conversion does not necessarily fit exactly to the experimental observations. Nevertheless, the reaction is still limited by the reaction equilibrium and suited reference data are needed.

Another important aspect is the fact that by‑products are formed under the process conditions of multiple cyclic hydrogenation and dehydrogenation [11, 12, 14, 15]. The reactive system becomes more complex as it is no longer limited to hydrogen and the original LOHC components. Particularly light‑boiling by‑products are important in this regard. Their accumulation in the gas lowers the partial pressure of hydrogen. This can lead to a shift of the dehydrogenation equilibrium towards the products. [16] However, taking into account the multitude of possible by-products in modelling and calculating the two-phasic equilibrium system is challenging as their share on the total system varies over cycle number. Consequently, a more empirical approach towards description of the reaction equilibrium might be advantageous for the design of H0-DBT/H18-DBT-based hydrogen storage processes.

The hydrogenation of H0‑DBT is a step-wise consecutive reaction [17]. The first step is the hydrogenation of one outer benzyl ring to form H6‑DBT, followed by the hydrogenation of the second outer benzyl ring to form H12‑DBT. In the final and rate limiting hydrogenation step the middle ring is hydrogenated to form H18‑DBT. As H0‑DBT is a mixture of several regioisomers, the corresponding H6‑DBT, H12‑DBT and H18‑DBT fractions comprise of the corresponding regioisomers (Figure 1) [9]. Note, that for the dehydrogenation process the sequence of the ring dehydrogenation is less clear. Previous studies have not revealed any distinct preference for the dehydrogenation of either the central or the outer rings [9].

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| Catalyst  Catalyst  Catalyst |
| Figure 1: Proposed reaction scheme for hydrogenation of H0‑DBT, respectively dehydrogenation of H18‑DBT. |

Our contribution introduces a new method to determine the degree of hydrogenation (DoH) in the H0-DBT/H18-DBT LOHC system by 13C-NMR spectroscopy. The new method is very robust against temperature fluctuations and side-product/impurity influences and is therefore proposed as a valuable addition to the well-established 1H-NMR techniques [9], density measurements, and refractive index measurements.[18] This method is used to experimentally determine the equilibrium compositions in the H0-/Hx-/H18-DBT LOHC system at various, process-relevant conditions.

# Experimental and Analytics

All hydrogenation / dehydrogenation experiments were conducted in a high pressure, high temperature autoclave (VL,max = 0.6 L) manufactured by Parr (Moline, USA). Figure 2 shows the applied setup schematically. The same 0.3 wt-% - Pt/AlOx catalyst (Clariant, Heufeld, Germany, LOT D2016002) was used in both the hydrogenation and the dehydrogenation reaction. The catalyst pellets were ground using a ball mill. A molar Pt to LOHC ratio of 1:3125 (0.032 mol-% Pt) was used in the experiments. The temperature range of our investigations was from 220 °C to 360 °C. Temperatures in this range are relevant for the practical application of the H0-DBT/H18-DBT LOHC system and have been deployed in the past for reversible hydrogen storage experiments using the same catalyst for hydrogenation and dehydrogenation at varying hydrogen pressures.[11] To fully establish the thermodynamic equilibrium at each set of condition parameters, constant conditions were held for 15 hours (see Supporting Information). The desired reaction pressure during the dehydrogenation experiments was set using a back pressure valve in front of the mass flow meter in the H2 off gas. All mass flow meters were acquired from Bronkhorst, Almelo, NL (MFM1: FG-111B; 15 lN/min H2, MFM2: F-201DV; 100 mlN/min NH3, calibrated to H2). In order to prevent low boiling components from leaving the reactor and from contaminating the downstream flow meter, a two stage cooler (T < 5 °C) was applied. As the first stage of the cooler (HE-1) is mounted directly above the reactor, condensate flows back into the reactor. During the experiments, almost no condensate reached the second stage of the cooler (HE‑2).

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| Figure 2: Simplified scheme of the reactor setup used for the equilibrium experiments. |

At the beginning of each equilibrium experiment, the dehydrogenation pressure was set and the initial amount of N2-stripped H0-DBT was pumped into the reactor using P-1, a high accuracy HPLC pump (Knauer, Berlin, Germany). The reactor was heated to hydrogenation temperature (TH= 260 °C). Subsequently hydrogen was fed to the reactor until reaction pressure (pH= 31 bara) was reached, then flow measurements were started. Hydrogenation was completed after 5 h and a sample was taken to determine the initial DoH as a starting point for the subsequent dehydrogenation experiment. Sample weights were recorded to account for the reduction in Hx-DBT mass due to sampling. During the dehydrogenation experiment, temperatures were adjusted automatically according to a defined 11-step temperature profile with keeping each temperature for 15 h. After that, a final sample was taken and the reactor was allowed to cool down.

For the determination of the DoH by carbon nuclear magnetic resonance spectroscopy (13C‑NMR), an ECX 400 from JEOL (Akishima, Japan) was applied. First, 0.5 ml of the solvent chloroform-d was mixed with 17.5 mg of the relaxation agent Tris(acetylacetonato)iron(III) (Acros Organics, Geel Belgium). The relaxation agent reduces the relaxation time and a quantitative spectrum can be recorded in reduced measuring time.[19] Afterwards, 0.2 ml of the Hx‑DBT sample was added. The acquisition time is 2.5 s and 160 scans were collected in order to obtain a spectrum.

A GC-3900 gas chromatograph (Varian/Agilent) equipped with a capillary column (Rtx-225, Restek GmbH) was used to analyze the samples. The applied method features split injection (1:50 split, He at 1.4 ml/min constant column flow) at 210 °C injector temperature and an oven temperature program (Table 1) dedicated to enable efficient separation of the various Hx-DBT isomers.

Table 1: Temperature program of the chromatographic method used to separate Hx-DBTs by gas chromatography. Flow conditions: 1:50 split injection, 1.4 ml/min helium at constant column flow at 210 °C injector temperature.

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| --- | --- | --- | --- |
| Step | Heating rate (°C/min) | Temperature (°C) | Step time (min) |
| 1 |  | 90.00 | 3.65 |
| 2 | 10.50 | 130.00 | 3.50 |
| 3 | 10.70 | 170.00 | 3.45 |
| 4 | 7.40 | 210.00 | 60.00 |

Determination of the sample composition is based on pre-defined peak areas (more information concerning peak determination is given in the discussion), using the software Varian star chromatography workstation, version 6. These results are exported to the automated calculation of DoHs and by-product contents.

# Results and discussions

## Determination of Degree of Hydrogenation (DoH)

In its hydrogen-lean form, dibenzyl toluene (H0-DBT) consists of 3 aliphatic and 18 aromatic carbon atoms. By reaction with hydrogen, aromatic carbon atoms are converted into aliphatic carbon atoms with the total number of carbon atoms remaining constant. Thus, the amount of aliphatic carbon atoms increases linearly with increasing degree of hydrogenation. In contrast to 1H-NMR, the 13C-NMR spectra representing the hydrogenation process are independent on the reaction pathway. In case of complete hydrogenation all carbon atoms are aliphatic. We define the DoH in this context as shown in Equation 1.

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|  |  | (1) |

In 13C‑NMR, carbon atoms show a chemical shift that depends on the functionalization and the surrounding of the carbon atom. Aromatic carbon atoms show a chemical shift below 50 ppm and aliphatic carbon atoms above 100 ppm. Therefore, the distinction between aromatic and aliphatic carbon atoms is possible with 13C‑NMR. Given there is sufficient time for full relaxation, the signal intensity of the peaks of all aromatic, respectively aliphatic carbon atoms is proportional to the concentration in Hx‑DBT. [19] So, no calibration is needed for the determination of the DoH. As the amount of aromatic carbon atoms decreases linearly with increasing DoH, the DoH can be determined by Equation (2). The parameter z is defined as the ratio of the peak area of all aromatic carbon atoms to the peak area of all Hx‑DBT carbon atoms.

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|  |  | (2) |

Samples of Hx‑DBT with a defined DoH are required for the validation of the DoH determination by 13C‑NMR. As the reaction pathway for the hydrogenation of fresh H0‑DBT is known, the DoH can be determined by 1H‑NMR according to the literature. [17] Figure 3 shows the comparison of the DoH determined by 13C‑NMR and 1H‑NMR.

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| Figure 3: Comparison of DoH-measurements by 13C-NMR and 1H-NMR. |

The absolute deviation between the DoH determined by 13C‑NMR and 1H‑NMR during hydrogenation experiments is below 3.4 % absolute. For the dehydrogenation of H18-DBT, the determination by 1H-NMR is intrinsically less reliable as the exact reaction path of dehydrogenation, i.e. the sequence of ring dehydrogenation (central vs. side ring dehydrogenation) is unclear and probably depends on the applied reaction conditions and catalyst material. Figure 3 illustrates the higher reliability of DoH determination by 13C‑ vs. 1H‑NMR spectroscopy in H18-DBT dehydrogenation for the specific example of a DoH value of 0.74. While the absolute error for the DoH determined by 1H-NMR spectroscopy is 6.5 %, it is only 1.2 % for the determination by 13C‑NMR spectroscopy.

In addition to the non-path-dependent 13C-NMR-based DoH determination method, it was desired to further establish a DoH determination methodology based on gas chromatography for process control. The reason is that NMR equipment is expensive and the NMR sample preparation does not easily allow for a high degree of automation. Gas chromatography, however, is an established analytical method for industrial process analytics as it features high versatility, easy sample preparation, accuracies down to ppm contents, straight forward automation and moderate cost.

Here, the path-independent, 13C-NMR-based analytic data were used to develop and validate an improved GC‑based analysis of Hx-DBT mixtures. The focus of the developed GC method was both on efficient separation of the Hx-DBT isomers and on the determination of typical by-products of the hydrogenation/dehydrogenation processes in the H0‑DBT/H18‑DBT LOHC system, such as toluene, mono-benzyltoluene or oxygen-containing aromatic impurities. The developed GC methods allows for categorizing the analyzed mixture into Hx-DBT compounds as well as low- and high-boiling substances relative to the boiling points of Hx-DBT. Figure 4 shows a typical chromatogram obtained from GC-measurement.

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| Figure 4: Full sized chromatogram of a Hx-DBT measurement. |

As can be seen in the enlarged Hx-DBT region of the chromatogram (see Figure 5), the resolution is limited. This is due to the complex nature of the mixture: partly hydrogenated Hx‑DBT-samples contain molecules of H0-, H6-, H12- and H18-dibenzyltoluene and their respective regioisomers, which even 2-D chromatography methods are not able to fully separate. [20]

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| Figure 5: Enlarged view of the Hx-DBT area in the chromatograms of four samples of different degrees of hydrogenation (DoH). |

In order to assign peaks in the Hx-DBT-area of the chromatogram to the four relevant hydrogenation levels (H0-DBT, H6-DBT, H12-DBT and H18-DBT, see also Figure 1) preliminary batch hydrogenation and dehydrogenation experiments were conducted. Samples were taken at different reaction times, and thus different hydrogenation levels. For peak identification, the samples were analyzed using 13C-NMR as well as both the GC-method given in this study and a similar method using a GC (SCION SQ/451-GC) equipped with a mass spectrometry detector (EI, quadrupole detector) and the same column type (Rtx-225). Classification of the different hydrogenation levels and knowledge of their relative composition enables calculation of the degree of hydrogenation. The amount of stored hydrogen can be calculated according to Equations 3 and 4:

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|  |  | (3) |
|  |  | (4) |

Whereas the maximum capacity is specified by the total amount of Hx-DBT species in the reaction system.

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|  |  | (5) |
|  |  | (6) |

The degree of hydrogenation (DoH) therefore can be written as given in Equation (7)

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|  |  | (7) |

In order to use the flame ionization detector (FID) signal for DoH estimation, the detected areas need to be correlated with the amounts of substance of the different Hx-DBT species. This usually requires the response factor (RRF) of each of the substances or an accurate estimation thereof.[21, 22] Clearly, the number of C atoms is one decisive factor contributing to the RRF of a substance, however, the number of hydrogen atoms and the number of benzene rings needs to be considered, as well. Consequently, the isomers of each Hx-DBT species are supposed to feature about the same RRF. It thus can be written and simplified accordingly.

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|  |  | (8) |
|  |  | (9) |
|  |  | (10) |

Since overlapping peaks of isomers of different hydrogenation levels could not be completely avoided, correlation factors are introduced. As the response factors are constants, they can be included in the respective correlation factor:

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|  |  | (11) |

In order to identify the correlation factors, samples from 27 hydrogenation and dehydrogenation experiments were analyzed both by the 13C-NMR and the GC-FID method. Using randomized numbers, 6 different combinations of test (6 data points) and training sets were formed. The coefficients k1 to k4 were calculated using a least square fitting method for each combination. Comparing the mean quadratic derivation of the test sets, the best overall fit was determined (see Table 2 for the corresponding coefficients).

Table 2: Correlation coefficients for DoH estimation from GC-FID measurements obtained by least squares fitting method.

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| --- | --- | --- | --- | --- |
| Coefficient | k1 | k2 | k3 | k4 |
| Value [-] | 122.49 | 60.77 | 101.62 | 81.20 |

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| Figure 6: Comparison of DoH determined by GC-FID analysis and 13C-NMR for samples from both hydrogenation and dehydrogenation experiments. |

As can be seen in Figure 6, accordance between 13C-NMR and GC-FID DoH-values is well within 3.5 % absolute error and the mean absolute deviation is 1.7 %. Only two value exceed an absolute error of 3.5 % DoH. Since other methods used for DoH determination are either path dependent (1H-NMR, see [17]), suffer from errors induced through by-product formation (density, refractive index) or require expensive equipment (13C‑NMR), GC-FID measurements with proper correlation coefficients as presented here represent a useful way of process analytics for DoH determination in LOHC systems.

## Equilibrium experiments

Sampling during the experiments is a significant source of error. Therefore, we tried to avoid this as much as possible. Consequently, the stored or released hydrogen was measured by the mass flow meters, V̇H2,MFM1 and V̇H2,MFM2, respectively. The maximum hydrogen capacity can be calculated from the amount of H0-DBT provided for the initial hydrogenation, mH0-DBT,0. According to equation (1), the DoH as a function of time is

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|  |  | (12) |
|  |  | (13) |

In order to begin dehydrogenation from a fixed starting point, a single sample was taken after the initial hydrogenation step. DoHH,end was determined using the GC-FID method. For one specific experiment the DoH-values obtained by sampling and by monitoring the hydrogen flow rates were compared. For this purpose, several samples were taken at different stages of the dehydrogenation run and were analyzed by GC. Their DoH was compared to the DoH obtained from the MFM measurements. Three out of four DoHs obtained from MFM measurement were found to be within a 1.8 abs-% deviation from sample results. A maximum error of 5.4 abs-% was observed for the remaining sample. Thus, instead of taking multiple samples during the experiments, DoH determination from MFM measurements proved adequate to describe the conversion of H18-DBT to H0‑DBT in a quantitative manner.

## Single experiment fitting and global equilibrium relation

As the aim of this study was to determine the equilibrium conversion of H18-DBT to Hx‑DBT as a function of temperature and pressure, a sigmoid-like function-based model was chosen. In this work, the specific subtype of logistic functions was used to describe the equilibrium data. Similar models are commonly applied to describe both time- and temperature resolved kinetics. A key feature of these models is their versatility and the possibility to include heat and mass transport effects in addition to the chemical reaction itself. [23]

The general equation for a logistic function is given in Equation (14) and can be adjusted to the stepwise dehydrogenation of H18‑DBT.

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|  |  | (14) |

Setting x equal to the difference of the reaction temperature and a fixed maximum temperature Tmax (i.e. 750 K), the curve changes its shape from strictly increasing to strictly descending.

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|  |  | (15) |

Coefficient *a* can be seen as the maximum amplitude, which is the highest possible degree of hydrogenation – *DoHmax*= 100 %. However, both other coefficients, *b* and *c,* are pressure dependent values whose pressure related functionalities are to be determined by fitting of the experimental data. While *b* is a measure for the maximum steepness of the curve, *c* includes information about the position of the area of the steepest descent of the applied logistic curve.

Figure 7 shows the resulting equilibrium data from a full set of experiments in the range of 1.0 bara to 9.9 bara mean reaction pressure. In general, the experimental data as a function of temperature lies well within the expected sigmoidal curve shape. As expected, experiments at higher reaction pressures show a significantly higher equilibrium DoH for a given temperature. Concerning the fitted logistic curves, quite good reproduction of the experimental data was achieved especially at medium pressures. One reason for higher deviations between fitted and experimental data at lower temperatures is the boundary condition DoH (T = 290 K) = 1.0. Due to the already quite low DoH at the lower end of the observed temperatures, no data points are available to accomplish a better fit towards DoH = 1.0. Furthermore, vapor pressure of the substances contained in the liquid reaction mixture reduces the partial pressures of hydrogen in the gas phase, as only the overall reaction pressure can be controlled by the applied back pressure valve. The applied commercially available DBT-mixture already contains small amounts of low boiling substances. Also, small amounts (< 2 area% according to GC‑FID) of low boiling side products can be formed (preferably at higher temperatures) during hydrogenation, which are condensed and fed back to the reactor during the experiment. Thus, accumulation of low boilers could lead to diminished partial pressure of hydrogen and lower equilibrium DoH at a given temperature. This effect is more relevant for experiments with lower absolute pressures.

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| Figure 7: Experimental equilibrium DoHs (e) covering the pressure range between pD = 1.0 bara to pD = 9.9 bara for temperatures between 490 K and 635 K and corresponding fit curves (f). Error bars account for mass flow and temperature measurements. |

A similar explanation can be given for the non-asymptotic curvature in the area close to DoH = 0. Here, high temperatures are applied for several hours and the probability for side product formation is higher. The content of low boiling substances at the end of the experiments was measured to be up to 6.1 area-% for the experiments. Common low-boiling by-products are aromatic compounds of smaller size, such as e.g. monobenzyl toluene, diphenylmethane, or toluene. These can be removed from the hydrogen product gas by condensation or adsorption filters, such as activated carbon filters. More sophisticated separation techniques, e.g. pressure swing adsorption, may be required for very high hydrogen purities, i.e. for hydrogen provision in hydrogen refueling stations. Please note, that most of the low boiling by-products offer the possibility of reversible hydrogenation/dehydrogenation cycles and thus hydrogen storage. While effects of low-boiling by-products on vapor pressure, dehydrogenation kinetics and equilibrium states are obvious, the hydrogen capacity of the LOHC system under investigation is not strongly affected by these low-boiling by-products.

Table 3: Experimental pressure data (including sensor measurement errors) and values of the fit coefficients as seen Figure 7.

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| --- | --- | --- | --- |
| Mean Pressure  [bara] | Pressure range  [bara] | Coefficient b  [K-1] | Coefficient c  [K] |
| 1.0 | 0.986 – 1.073 | 0,055 | 212.529 |
| 2.2 | 2.112 – 2.304 | 0.059 | 198.819 |
| 3.2 | 3.128 – 3.320 | 0.065 | 189.841 |
| 4.3 | 4.169 – 4.439 | 0.065 | 176.753 |
| 5.5 | 5.435 – 5.575 | 0.058 | 171.854 |
| 6.4 | 6.307 – 6.580 | 0.062 | 164.456 |
| 9.9 | 9.626 – 10.060 | 0.054 | 155.007 |

In order to describe the equilibrium DoH values in a simple manner as a function of pressure, the pressure dependency of both coefficients *b* and *c* is plotted in Figure 8 and Figure 9, respectively.

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| Figure 8: Coefficient *b* as a function of pD. Values obtained from single fit of experimental data. | Figure 9: Coefficient *c* as a function of pD. Values obtained from single fit of experimental data. |

As already seen from Figure 7, the steepness of the equilibrium curves is quite similar, a fact that is represented by an almost constant value of *b* over the applied pressure range (see Figure 8). The coefficient *b* scatters closely around a value of 0.06 K –1. Fitting of the pressure dependent data was performed by using the method of the so called LMO cross-validation: Multiple training sets of 14 experiments were randomly chosen from the 17 experiments conducted during our studies. Each of these sets was used in order to approximate the pressure dependency of *b* by a linear relationship. The resulting linear equation was subsequently tested via the corresponding test set of the remaining 3 experiment results. Comparing the deviations of the calculated values from the experimental values, the best fit was assigned to the linear relation given in Equation 16.

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| --- | --- | --- | --- |
|  |  |  | (16) |

Coefficient *c*, however, shows a significant pressure dependency (see Figure 9), as values start at 211.6 K to 213.6 K for pD = 1.0 bara and continuously decrease to a minimum of 142.8 K at pD = 9.9 bara. The function type describing this behavior best was determined to be a logarithmic function. As for the determination of the linear pressure dependency of coefficient *b*, multiple training and test sets were used in order to find the best approximation of the pressure dependency of coefficient *c.*

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|  |  | (17) |

Consequently, an overall expression to describe the degree of hydrogenation of Hx-DBT as a function of reaction pressure and temperature is obtained by using equation (16) and equation  (17) in equation (15). This results in Equation 18.

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|  | (18) |

This overall expression was used to generate curves for each experiment. Figure 10 shows three experiments from both the test and the training set with their respective single experiment fits and a curve generated by the overall fitting relation.

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| Figure 10: Comparison of experimental DoH data and both single fitted curve (marked as fit(e)) and curves obtained from the overall fit using equation Fehler! Verweisquelle konnte nicht gefunden werden. (marked as fit(g)). Experiments from both training (pD= 2.2 bara and 5.5 bara) and test sets (pD' = 4.3 bara) |

Given the examples from the training set, experimental data is approximated well for the experiment at 2.2 bara. Experimental data and the curve generated from the overall equation for pD = 5.5 bara differ significantly. Yet, as discussed above, the same is true for the respective experimental data in comparison to the other experimental datasets. Concerning the experiment at 4.3 bara mean reaction pressure, which is part of the test set, very good approximation could be achieved. Overall, for the training set an overall mean absolute deviation from experimental data of 3.49 % DoH was obtained. The training set of three experiments can be approximated with 5.8 % mean absolute error. The observed maximum error of 10.8 % DoH occurred as a single outlier.

For a better representation of the determined experimental equilibrium DoHs as a function of reaction pressure and reaction temperature, a map can be calculated that is shown in Figure 11.

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| Figure 11: Experimental equilibrium DoH values calculated from Equation Fehler! Verweisquelle konnte nicht gefunden werden.. |

# Conclusion

An affordable, practicable and path independent method for DoH measurement was developed, using standard GC-FID equipment. Calibration was carried out using 13C-NMR. Overall deviations between GC-FID and 13C-NMR are within 3.5 % absolute error, in general a mean deviation of 1.7 % is achieved.

Long-term, stepwise dehydrogenation experiments were conducted in order to approximate hydrogenation/dehydrogenation equilibrium data of the dibenzyl toluene/perhydro dibenzyl toluene (H0‑/Hx‑/H18-DBT) LOHC-system. A correlation equation for the reaction equilibrium as a function of pressure and temperature could be derived through fitting to multiple experimental data. Deviations from the calculated equilibrium DoHs and experimental data are within 5.8 % absolute error. Hence, the relationship can be considered as accurate enough for reactor and process design studies. It is noteworthy, however, that there is a complex interplay of the reaction equilibrium, the vapor pressure of the various substances in the reaction mixture (including light and high boilers formed in small amounts as by-products) and the experimental setup.

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