Highly Efficient, Low-Temperature Hydrogen Release from Perhydro-Benzyltoluene Using Reactive Distillation

**M. Geißelbrecht,[a] S. Mrusek,[a] K. Müller,[b] P. Preuster,[b] A. Bösmann,[a]
P. Wasserscheid[a,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, 91058 Erlangen, Germany

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

Abstract

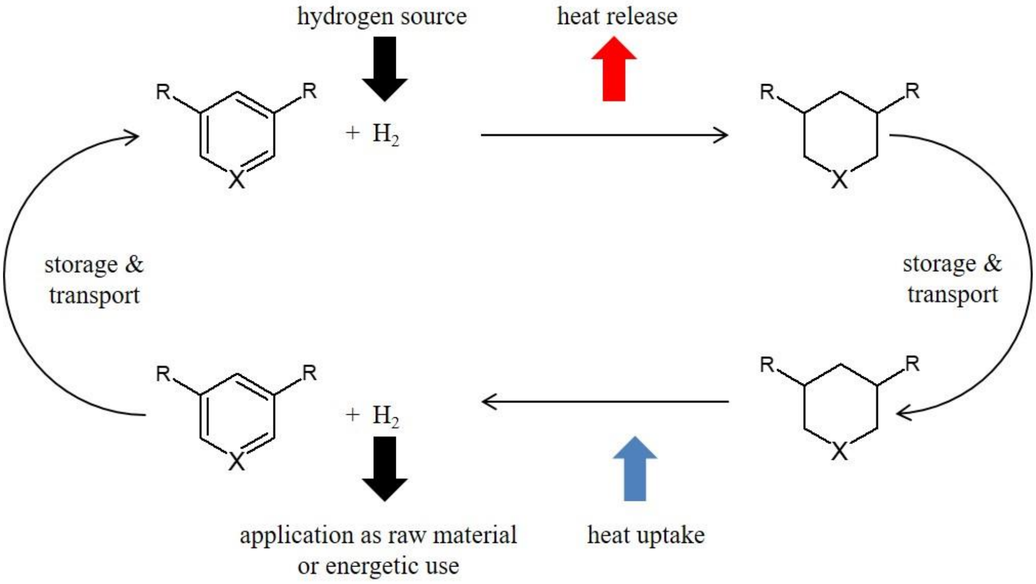
The need to supply significant amounts of heat at the high temperature level required thermodynamically for cycloalkane dehydrogenation has so far been seen as the main hurdle to bring the otherwise highly attractive Liquid Organic Hydrogen Carrier (LOHC) technology to broad technical use. The LOHC technology promises infrastructure-compatible storage and transport of hydrogen in chemically bound form, e.g. for long-term energy storage, global energy logistics and heavy-duty mobility. Our contribution shows that hydrogen release from the hetero-atom free, pure hydrocarbon LOHC compound perhydro-benzyl toluene is possible at temperatures down to 200 °C, if the operation is carried out in a reactive distillation column under reduced pressure. Such low temperature dehydrogenation of hydrocarbon-based LOHC systems facilitates heat integration with waste heat sources and the energetic use of the released hydrogen considerably, and this will greatly enhance the attractiveness of LOHC-based hydrogen storage for many applications.

Key words

LOHC, hydrogen storage, dehydrogenation, reactive distillation, heat integration

Introduction

Liquid organic hydrogen carriers (LOHC) offer an interesting way to store and distribute hydrogen using today's infrastructure for hydrocarbon fuels [1-3]. In particular for long transport distances and extended storage times of large hydrogen quantities, LOHC-based hydrogen logistics has been shown to be the most sustainable, implementable and efficient option [4, 5]. The LOHC storage cycle includes catalytic hydrogenation of the hydrogen-lean LOHC molecule to the corresponding hydrogen-rich LOHC molecule at elevated hydrogen pressure (typically > 20 bar hydrogen partial pressure; ideally the hydrogen pressure provided by the source of hydrogen, e.g. a PEM electrolyser). The hydrogen-rich LOHC molecule can safely be stored over long time periods at ambient conditions without any hydrogen losses. Additionally, hydrogen can be transported in LOHC-bound form at ambient temperature and pressure in common storage or distribution devices for liquid fuels. Hydrogen can be released from the liquid carrier by a catalytic dehydrogenation of the hydrogen-rich LOHC-molecule at ambient or only slightly elevated pressure (typically < 5 bar hydrogen partial pressure). The LOHC molecule is not consumed in the hydrogenation/ dehydrogenation cycle and can be reused over several cycles (Scheme 1).



Scheme 1: Schematic description of the hydrogenation/dehydrogenation cycle in LOHC-based hydrogen storage technologies.

Dibenzyl toluene (H0-DBT)/ perhydro-dibenzyl toluene (H18-DBT) is one of the most promising LOHC-systems due to its reasonable hydrogen storage capacity, great technical availability and excellent compatibility with the hydrocarbon-based energy infrastructures [6-11]. A chemically similar LOHC-system with an almost identical gravimetric hydrogen uptake capacity of 6.2 wt% and also very similar technical characteristics (concerning e.g. availability and compatibility) is benzyl toluene (H0-BT)/ perhydro-benzyl toluene (H12-BT) [6]. The dehydrogenation of H18-DBT and H12-BT is strongly endothermic and requires a comparable high heat of dehydrogenation per mol hydrogen (63.5 kJ $mol_{H_2}^{-1}$ in case of H12-BT, 65.4 kJ $mol_{H_2}^{-1}$ in case of H18-DBT; both at reference conditions) [7]. H12-BT has a lower boiling point (270 °C) compared to H18-DBT (370 °C), which somewhat limits the temperature for its liquid phase dehydrogenation [12]. Additionally, the technical effort for separating LOHC vapours and hydrogen increases for the dehydrogenation of H12-BT due to its higher vapour pressure. On the other hand, H0-BT offers the possibility to be used at boiling conditions at ambient pressure in contrast to H0-DBT, which would undergo significant thermal decomposition at its boiling temperature of 370 °C [13, 14]. Furthermore, the hydrogen charging proceeds faster for H0-BT hydrogenation than for H0-DBT hydrogenation [6]. H6-BT is the only relevant intermediate of the hydrogenation and dehydrogenation processes of the H0-BT/H12-BT system (although present in various regioisomers) making the system structurally less complex compared to H0-DBT/H18-DBT [15]. Another noteworthy fact is that the viscosity of H12-BT is significantly lower than that of H18-DBT, which simplifies the handling of the LOHC, in particular for low temperature storage application, e.g. as energy storage system for winter times [7, 12].

Comparing the hydrogen release rates of H12-BT and H18-DBT at temperatures below 270 °C and ambient pressure, hydrogen release from H12-BT has generally found to be faster in liquid phase dehydrogenation [6, 12]. While liquid phase dehydrogenation at ambient pressure is limited for H12-BT to 270 °C, liquid phase H18-DBT dehydrogenation has been shown to be effective up to 340 °C enabling faster hydrogen release kinetics due to the higher temperature level. This is why, previous research on hydrocarbon LOHC systems has mainly focused on the system H0-DBT/ H18-DBT [3].

Because hydrogen release from any LOHC system is a strongly endothermic reaction, effective heat input into the reactor and effective heat integration with other steps are the key to an overall efficient energy storage process [3, 16]. In the case of H12-BT, the reaction enthalpy required for complete hydrogen release amounts to 26 % of the combustion heat of the released hydrogen at reference conditions. If this heat is supplied by burning a part of the released hydrogen, the energy demand for hydrogen transport by LOHC is higher compared to a hydrogen transport by pipeline [4]. If this heat demand, however, is covered by waste heat, the hydrogen transport via LOHC is the most energy and efficient way of hydrogen storage. Waste heat integration is possible, for example, by combining the endothermal LOHC dehydrogenation with exothermal hydrogen digestion in a solid oxide fuel cell (SOFC) operating at 650 °C [17, 18]. Here, an overall efficiency of ‘LOHC-bound hydrogen to electricity’ of 45 % has been demonstrated. Another option to facilitate heat integration between LOHC dehydrogenation and fuel cell operation is to reduce the dehydrogenation enthalpy (and thus the dehydrogenation temperature) of the hydrogen release by using nitrogen-containing LOHC systems [3]. For such systems, dehydrogenation temperatures as low as 160 °C have been reported [19], but thermal robustness of these molecules is reduced with splitting of N-C bonds being a frequently observed degradation path [19]. Additionally, nitrogen-containing LOHCs lack full materials compatibility with the existing pure hydrocarbon fuel infrastructure and are typically not available in technical quantities. Therefore, it is technically highly interesting to find ways of realising effective hydrogen release from pure hydrocarbon LOHC systems at temperatures below 250 °C.

It is well-known for the dehydrogenation of cyclohexane or methyl cyclohexane - both LOHC molecules of high structural similarity to H12-BT and H18-DBT - that the rate of dehydrogenation is inhibited by the rate of desorption of the formed aromatic product molecule [20-24]. This is why the rate of hydrogen release decreases with increasing degree of dehydrogenation (DoDH), as a high DoDH goes hand in hand with a high concentration of aromatic product in the reaction mixture. The same effect of reducing dehydrogenation rate with increasing DoDH has been found for the dehydrogenation of H18-DBT. It could be demonstrated that partial poisoning of the supported Pt nanoparticles of the applied catalyst helps to facilitate aromatics desorption and this leads to a drastically increased rate of dehydrogenation [8].

Apart from this catalyst design approach, there is another attractive way to reduce catalyst blocking by slow product desorption. This is to separate within the reactor the hydrogen-lean aromatic LOHC molecule from the hydrogen-rich LOHC molecule and to contact only the latter preferentially with the dehydrogenation catalyst. A reactor concept that enables Hx-LOHC dehydrogenation and separation of Hx-LOHC from H0-LOHC at the same time and in the same reaction volume is reactive distillation. Prerequisites for such an innovative concept of boosting the dehydrogenation productivity are i) that the volatilities of the components of the LOHC system under investigation (here: H0-BT, H6-BT and H12-BT) differ to enable separation by distillation, and ii) that the reaction can be effectively carried out at boiling conditions. As the boiling point of H0-BT is higher than that of H12-BT (boiling point of H0-BT is 283-287 °C vs. 270 °C for H12-BT) [12], the hydrogen-rich LOHC material accumulates at the top of the column, where the catalyst should be placed to benefit from the maximised H12-BT concentration, while the dehydrogenated, aromatic LOHC compounds collect at the bottom of the column [14].

We report here the highly beneficial application of such a reactive distillation set-up for the dehydrogenation of hydrogen-charged LOHC compounds. While previous publications have mentioned the term ‘reactive distillation’ in the context of decalin dehydrogenation experiments [25-27], these earlier described experiments applied the catalyst in the liquid phase under refluxing conditions. In contrast, this work uses a separation zone to enrich the hydrogen-charged LOHC compounds at the top of the column where the catalyst is placed while the hydrogen-lean LOHC forms the liquid phase at the bottom where in our set-up no catalyst is present. Thus, the reactive distillation lead to an effective enrichment of hydrogen-charged LOHC at the catalyst. An account of using this principle for the promotion of dehydrogenation reactions has, however, been reported in the past by Xin et al. for the dehydrogenation of isopropanol [28]. The liquid-phase dehydrogenation of isopropanol is strongly inhibited by adsorption of the product acetone to the applied catalyst [29, 30]. Using a reactive distillation process (where acetone as the light boiler was removed from the catalyst bed through evaporation) could significantly improve the hydrogen production compared to the simple liquid-phase dehydrogenation process. Xu et al. modelled the dehydrogenation of isopropanol as a liquid-phase process and as a reactive distillation process and stated that the latter is characterised by a superior energy performance and exergy efficiency [31].

This contribution reports on a drastic enhancement of dehydrogenation efficiency in the hydrogen release from H12-BT by using a reactive distillation process. First, vapour-liquid-equilibrium measurements of H12-BT and H0-BT are reported. The gas phase composition is modelled using modified Raoult’s law and our modelled data are compared with experimental data. Batch dehydrogenation experiments are then conducted to prove product inhibition in the liquid-phase dehydrogenation of H12-BT. We show in subsequent H12-BT dehydrogenation experiments in a reactive distillation apparatus that this new principle is highly efficient to promote H12-BT dehydrogenation under very mild reaction conditions. Finally, the influence of pressure on temperature and hydrogen release rate in the reactive distillation column is examined.

Experimental

Vapour-Liquid-Equilibrium

The experimental setup applied to measure the equilibrium composition of the liquid and vapour phase is shown in Figure 1. It consisted of a three-necked flask equipped with a total condenser and one neck was used for temperature measurements in the vapour and in the liquid phase through two independent thermocouples (Rössel Messtechnik, type K). Moreover, one neck was closed with a septum through which samples of the vapour phase and of the liquid phase could be taken for analysing their composition by gas chromatography (GC-2010 Plus, Shimadzu, column: Rxi-5 Sli ms (L = 30 m, di = 250 µm)) as reported by Leinweber and Müller [15]. The flask was heated with a PILZ laboratory heater (WHG2, Winkler GmbH).

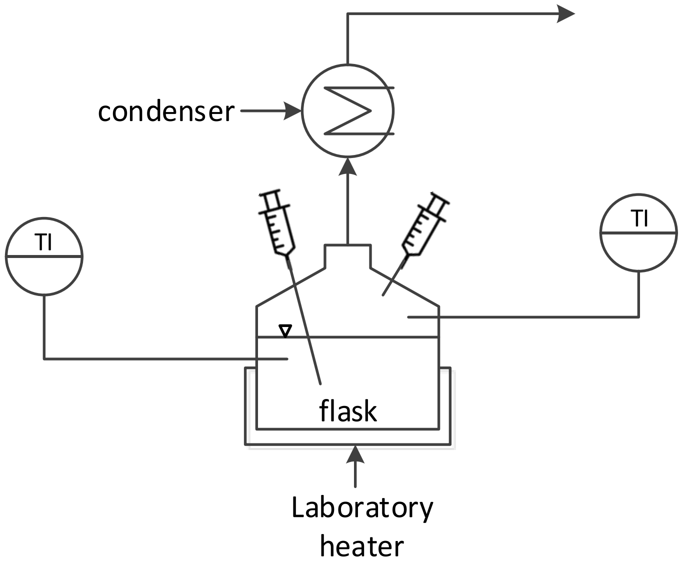


Figure 1: Schematic representation of the experimental setup for the vapour-liquid equilibrium measurements reported in this paper.

At the beginning of the experiment, 30 g of each mixture consisting of H0-BT and H12-BT with a defined composition were added in the flask. Then the setup was purged with argon for 10 min to remove oxygen from the system. Afterwards, the whole flask was heated under total condensation to 260 °C. ~~,~~ A sample of the liquid phase was taken with a syringe out of the liquid bulk after a 10 min period of constant temperature. Additionally, a sample of the vapour phase above the liquid bulk was taken and analysed. After condensing the gas phase, the composition of the two liquid samples was analysed by gas chromatography as reported by Leinweber and Müller [15].

Reactive distillation

The applied batch reactive distillation setup consisted of four zones: an evaporator, a separation zone, a reaction zone and a condenser. A heated three-necked flask with a volume of 250 ml served as evaporator. A PILZ laboratory heater (WHG2, Winkler GmbH) supplied the heat. The temperature of the liquid phase in the flask was measured by a thermocouple. A glass column with a diameter of 30 mm and a length of 450 mm was connected to the top of the flask. This column was divided in a separation and in a reaction zone. The upper part of the flask and the connection to the column was insulated with glass wool to reduce heat losses. The column was heated via a heating jacket, controlled by a microprocessor temperature regulator (HT MC1, Horst GmbH). The separation zone in the lower section of the column was packed with glass Raschig rings (6 x 6 mm) to increase the contact area between vapour and liquid phase. Perhydro-benzyl toluene (H12-BT) was the low-boiling component and therefore enriched in the upper part of the separation zone, while benzyl toluene (H0-BT) accumulated in the lower separation zone. So the reaction zone was placed above the distillation zone to benefit from the higher concentration of H12-BT. The reaction zone contained the commercial dehydrogenation catalyst (Clariant, EleMax-D101). The catalyst consisted of an egg-shell-impregnated spherical alumina support containing 0.3 wt% of platinum loading in form of nanoparticles. A cylindrical wire mesh with a diameter of 10 mm was inserted in the upper part of the column as a gas channel to prevent flooding of the column. A multi-point thermocouple was inserted via the column-head to measure the temperature profile in the column. Since the separation of Hx-BT species and hydrogen is easy, there is no need for a separation zone above the reaction zone. A condenser is installed above the column to condense vaporised Hx-BT while the released hydrogen passes the condenser. The condenser is connected to a Venturi nozzle (Festo VAD-1/8) that generates low pressure in the column by a flow of nitrogen through the nozzle. The resulting vacuum pressure is measured by a digital manometer directly at the Venturi nozzle. Figure 2 shows a scheme of the applied dehydrogenation setup.

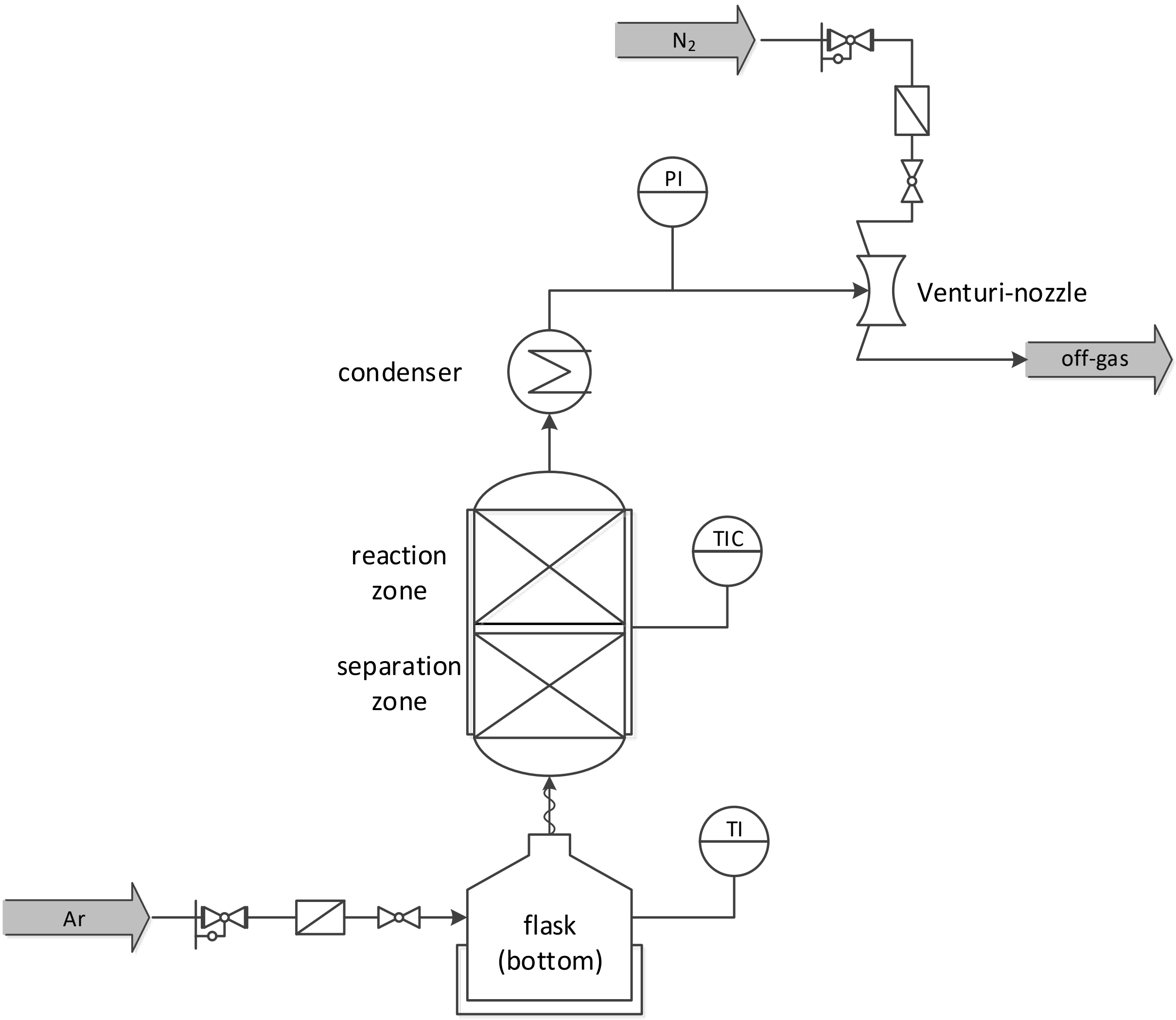


Figure 2: Schematic representation of the used dehydrogenation setup.

For each experiment the column was loaded with approximately 125 g of Raschig rings (6 x 6 mm) and 15 g of the catalyst on top. The three-necked flask was filled with 45 g of H12-BT and connected to the column. Afterwards, the set-up was purged with argon for 10 min to remove oxygen. The temperature of the flask was set around 5 °C above the expected boiling temperature for the given pressure of the experiment to ensure vaporisation of the H12-BT at the bottom. The reaction start was defined as the point in time when the first droplet of H12-BT refluxed from the total condenser into the catalyst bed. To monitor the reaction progress, liquid samples were taken in regular intervals from the bottom. The liquid samples were analysed by gas chromatography as earlier reported by Leinweber and Müller [15]. The degree of dehydrogenation (DoDH) was used as a measure for the amount of hydrogen released. The DoDH is defined as the ratio of hydrogen released from H12-BT to the maximum amount of reversibly releasable hydrogen form H12-BT. The DoDH can be regarded as hydrogen yield and can be calculated via Equation (**1**) based on the molar amount of each isomeric compound class x_i.

$$DoDH = 0.5 \cdot x_{H6-BT} + x_{H0-BT} \tag{1}$$

A DoDH of 1 is thus equivalent to a complete hydrogen release and a DoDH of 0 means that the LOHC is completely saturated with hydrogen. In order to quantitatively compare the hydrogen release rates at different conditions, a term for the productivity $P_{x\text{-}y}$ (t) is introduced. The productivity has been defined as the mass of hydrogen release $\Delta m_{\mathrm{H2,x-y}}$ in a period of time $\Delta t_{\mathrm{x-y}}$ per mass of noble metal of the applied catalyst m_{nm} acoording to Equation **(2)**. M_{H2} represents the molar mass of hydrogen.

$$\mathrm{P_{x-y}}\ (\mathrm{t}) = \frac{\Delta m_{\mathrm{H2,x-y}}}{m_{\mathrm{nm}} \cdot \Delta t_{\mathrm{x-y}}} \tag{2}$$

$$= \frac{n_{\mathrm{i,H2,max}} \cdot (\mathrm{DoDH_{i,y}} - \mathrm{DoDH_{i,x}}) \cdot \mathrm{M_{H2}}}{m_{\mathrm{nm}} \cdot (t_{\mathrm{y}} - t_{\mathrm{x}})}$$

The hydrogen release between a DoDH of 0.1 and 0.3 was considered as an appropriate point of comparison to determine the productivity for each investigated hydrogen pressure.

Results and Discussion

Vapour-liquid equilibrium

The proper design of a distillation process requires knowledge on the composition of the liquid and the vapour phase in vapour-liquid-equilibrium (VLE). In VLE, temperature and pressure of the liquid and vapour phase are equal. Additionally, the fugacity of each substance in the liquid and vapour phase is identical. The deviation of fugacity in the liquid phase from an ideal, pure substance is described by the activity coefficient. For the vapour phase the fugacity coefficient describes deviation from ideal gas behaviour. Equation (**3**) shows the description of the VLE for each component.

$$x_i \cdot \gamma_i \cdot P_{0i}^{LV} \cdot \varphi_{0i}^{LV} \cdot \exp\left(\frac{v_{0i}^{L} \cdot (P - P_{0i}^{LV})}{R \cdot T}\right) = \varphi_i^{V} \cdot y_i \cdot P \tag{3}$$

The ratio of the fugacity coefficient of the phase equilibrium φ_{0i}^{LV} and the fugacity coefficient of the vapour phase φ_i^{V} can be approximated as 1 for a system pressure below 10 bar.

Additionally, the pointing factor exp $\left(\frac{v_{0i}^{L}\cdot(P-P_{0i}^{LV})}{R\cdot T}\right)$ is near 1, if the difference between system pressure and vapour pressure is below 10 bar. So Equation (**3**) can be simplified to the modified Raoult's law, which is described in Equation (**4**).

$$x_i \cdot \gamma_i \cdot P_{0,i}^{LV} = y_i \cdot P \qquad (4)$$

Here x_i is the molar fraction of component i in the liquid phase and y_i the molar fraction in the gas phase, p is the system pressure, $P_{0,i}^{LV}$ the vapour pressure of component i and γ_i the activity coefficient. The activity coefficient can be predicted by the UNIFAC method [32, 33]. The vapour pressure of perhydro-benzyl toluene (H12-BT) can be estimated using Antoine parameters presented by Jorschick et al. [12]. The vapour pressure of benzyl toluene (H0-BT) is taken from the manufacturer data sheet [14]. The measured and predicted vapour-liquid equilibrium data are presented in Figure 3.

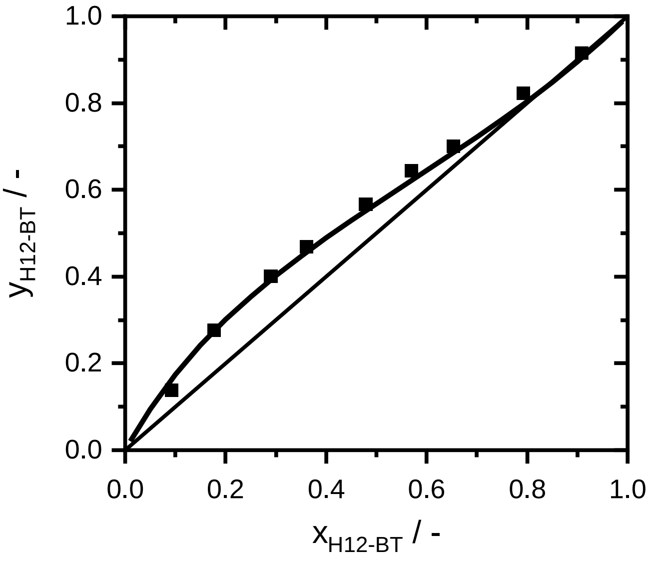


Figure 3: Comparison of the measured and predicted composition in vapour-liquid-equilibrium of H12-BT and H0-BT (T = 260 °C).

The predicted compositions fit the measured compositions quite well (average absolute deviation= 0.015; maximum absolute deviation= 0.026). Hence, it can be concluded that the composition in the VLE can be predicted with sufficient accuracy utilising the UNIFAC model and available vapour pressure data. The predicted data indicate an azeotrope for a molar fraction of H12-BT of around 0.83. Nevertheless, the separation factor is sufficiently high to accumulate H12-BT in the gas phase and thus in the catalyst bed.

Liquid phase dehydrogenation experiments

One key advantage of the reactive distillation concept is the reduction of product inhibition by decreasing the concentration of the aromatic product (H0-BT) at the catalyst. In order to prove this effect, we performed a set of experiments to quantify the rate accelerating effect of a reduced concentration of H0-BT at the applied Pt on alumina catalyst. For this purpose, the dehydrogenation of a premixed blend of 47 mol% H12-BT and 53 mol% H0-BT was compared with the dehydrogenation of a reaction mixture with the same DoDH of 0.53. Note, that this reaction mixture consisted of 23 mol% H12-BT, 48 mol% H6-BT and 29 mol% H0-BT according to the dehydrogenation scheme shown in Figure 4, and thus the amount of H0-BT was almost twice as high in the premixed H12-BT/H0-BT blend compared to the reaction mixture.

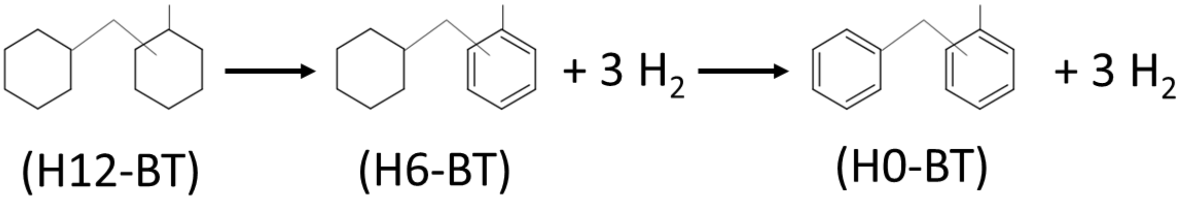


Figure 4: Reaction scheme of the dehydrogenation of perhydro-benzyl toluene (H12-BT) involving H6-BT as intermediate and benzyl toluene (H0-BT) as final product.

The change of DoDH and molar amount of H0-BT in the reaction mixture over time for the dehydrogenation experiments with both LOHC mixtures are compared in Figure 5.

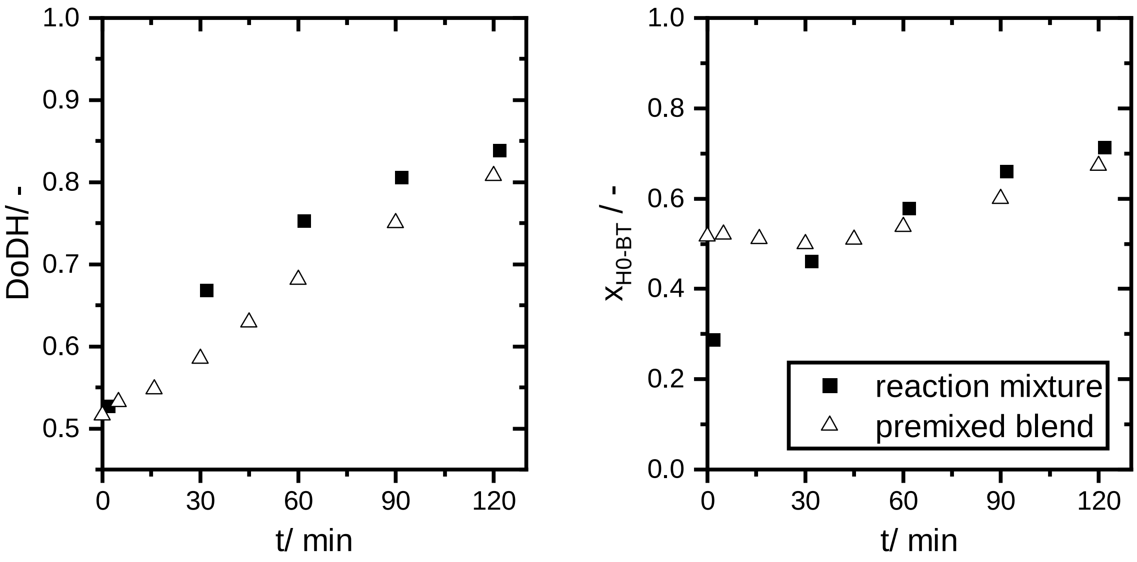


Figure 5: Comparison of the change of DoDH (left) and the molar amount of H0-BT (right) over time for a reaction mixture and a premixed blend of H12-BT and H0-BT of identical DoDH in liquid phase dehydrogenation (T = 270 °C, p = 980 mbar, catalyst 0.3 wt% Pt/Al_2O_3, $m_{catalyst}$ = 4.9 g, $m_{Hx\text{-}BT}$ = 14.65 g, starting amounts of H0-BT: $x_{reaction\ mixture}$ = 0.29, $x_{premixed\ blend}$ = 0.53).

Obviously, the dehydrogenation of the reaction mixture with the lower content of H0-BT proceeds faster at the beginning of the reaction. After 30 min the change in DoDH is 0.14 for the reaction mixture, but only 0.07 for the premixed blend (see Figure 5, left). Therefore, the hydrogen release rate of the reaction mixture is about twice as high as the rate of the premixed system at the start of the reaction. Later on, the difference in the reaction rate becomes negligible as the concentration of H0-BT is almost identical for both mixtures after 30 min reaction time (see Figure 5, right). To understand the development of the amount of H0-BT in the first 30 min reaction time for the case of the premixed blend, we have to take into account transfer hydrogenation that converts H0-BT and H12-BT into H6-BT. This comparison clearly demonstrates that the presence of H0-BT exhibits a deactivating effect on the dehydrogenation process due to the slow desorption of the fully aromatic product from the catalyst surface.

Reactive distillation experiments at atmospheric pressure

Encouraged by these results, we tested in the next step if the product inhibition can be further reduced, if the reaction is performed in the above described reactive distillation setup, that accumulates the light-boiling H12-BT and H6-BT at the top of the column where the catalyst is present, while the heavy-boiling H0-BT collects preferably in the catalyst-free bottom of the column. These reactive distillation experiments where performed in batch mode using again the reaction mixture and the premixed H0-BT/H12-BT blend, both of identical DoDH of 0.53. The comparison is shown in Figure 6.

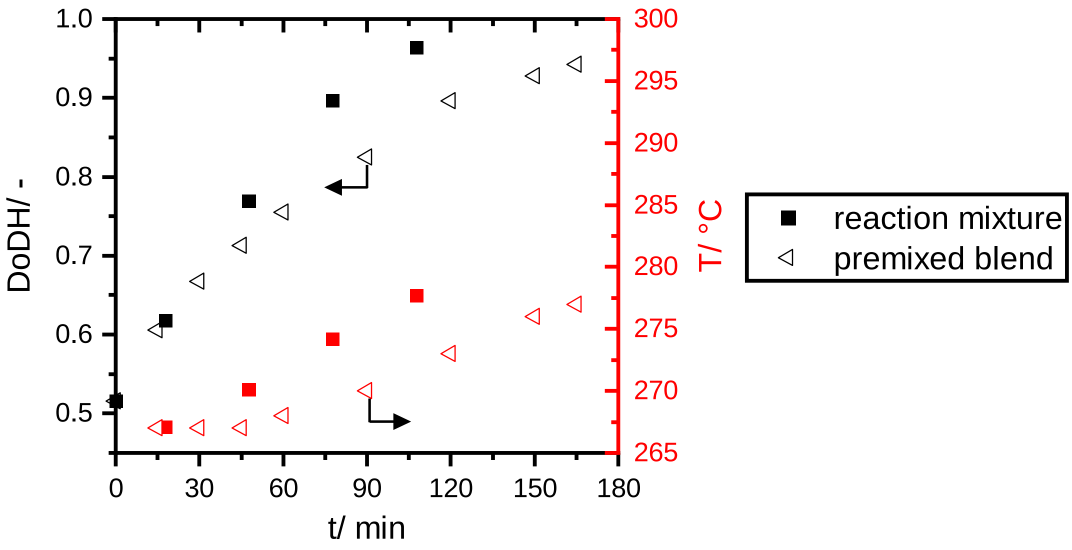


Figure 6: Comparison of the change in DoDH with time and catalyst bed temperature of a reaction mixture and a premixed blend of initial DoDH 0f 0.53 dehydrogenating in a batch-wise operated reactive distillation column (p = 980 mbar, catalyst 0.3 wt% Pt/Al$_2$O$_3$, $m_{catalyst}$ = 15.05 g, $m_{Hx\text{-}BT}$ = 45 g, starting amounts of H0-BT: $x_{reaction\ mixture}$ = 0.29, $x_{premixed\ blend}$ = 0.53).

Note, that in contrast to the liquid phase reaction (Figure 5), the change in the DoDH in the first 30 min (and thus the hydrogen release rate) is nearly identical for the operation in the reactive distillation. Later on, the DoDH increases faster in the dehydrogenation of the reaction mixture. But this is in-line with the higher catalyst bed temperature that results from the atmospheric distillation conditions as a consequence of the different composition of two different mixtures in the column. The very similar hydrogen release rate for the first 30 min (with almost equal catalyst temperatures) indicates, however, that the product inhibition of H0-BT can be largely suppressed in the reactive distillation setup. This is because much less of the aromatic compound is in contact with the catalyst.

The rate accelerating effect resulting from the distillative separation in the column becomes also very obvious from a comparison of the change in DoDH for the premixed blend (containing significant amounts of the aromatic H0-BT) between the liquid phase reaction (Figure 5) and the reaction in the reactive distillation column (Figure 6). Although the temperature in the catalyst bed has been lower than the 270 °C of the liquid phase experiment during the complete first 60 min of the reactive distillation experiment, the DoDH in the reactive distillation was 0.53 (at the reaction start), 0.61 (after 15 min), 0.67 (after 30 min) and 0.75 (after 60 min) in the distillation column compared to 0.53 (at the reaction start), 0.55 (after 15 min), 0.58 (after 30 min) and 0.68 (after 60 min) in the liquid phase reaction. This proves impressively that the reactive distillation mode of operation leads to a significant rate increase, in particular at conversion levels where already a high degree of aromatic products has been formed.

Reactive distillation experiments at reduced pressure levels

A variation of the absolute pressure in the reactive distillation column has a direct influence on the catalyst bed temperature. Because the dehydrogenation is carried out under boiling conditions either temperature or pressure can be chosen freely, the other parameter is coupled. Thus, a decrease in pressure results in a decrease in the catalyst bed temperature according to the Clausius-Clapeyron equation. Figure 7 shows the temperature in the bottom of the reactive distillation column (left) and in the catalyst bed for a dehydrogenation experiment with pure H12-BT as feedstock for different pressure levels.

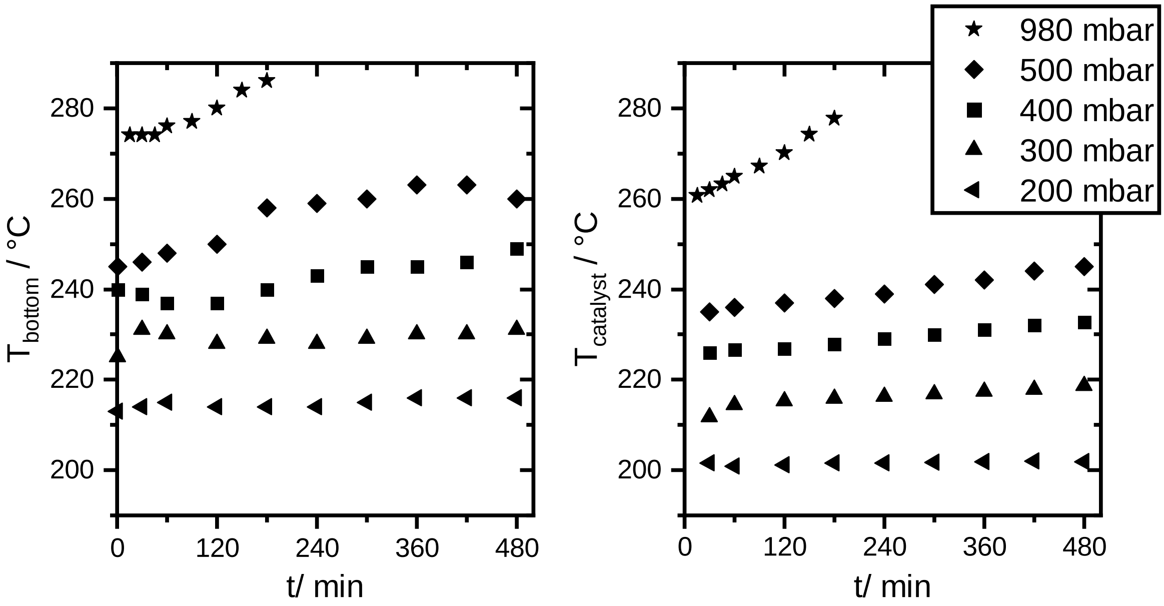


Figure 7: Pressure dependent temperature in the bottom (left) and in the catalyst bed of the reactive distillation of H12-BT under operation conditions (right) (catalyst 0.3 wt% Pt/Al_2O_3, $m_{catalyst}$ = 15.05 g, $m_{H12\text{-}BT}$ = 45 g).

Note, that the temperature in the bottom of the column (where no catalyst is present) is always higher than the temperature in the catalyst bed. This is due to a concentration gradient over the column height with the highest amount of the high-boiling H0-BT in the bottom of the column causing there the highest boiling temperature. Additionally, the temperature is increasing with reaction time as more and more low-boiling H12-BT is converted to the high-boiling H0-BT. In Figure 8, the influence of these pressure and temperature conditions on the hydrogen release rate is shown. For technical reasons, all samples were taken from the bottom of the column, which results in a slight overestimation of the DoDH. Comparison with the whole column composition after cooling down the experiment at the end of the reaction time confirms this effect (see Figure 8, open symbols).

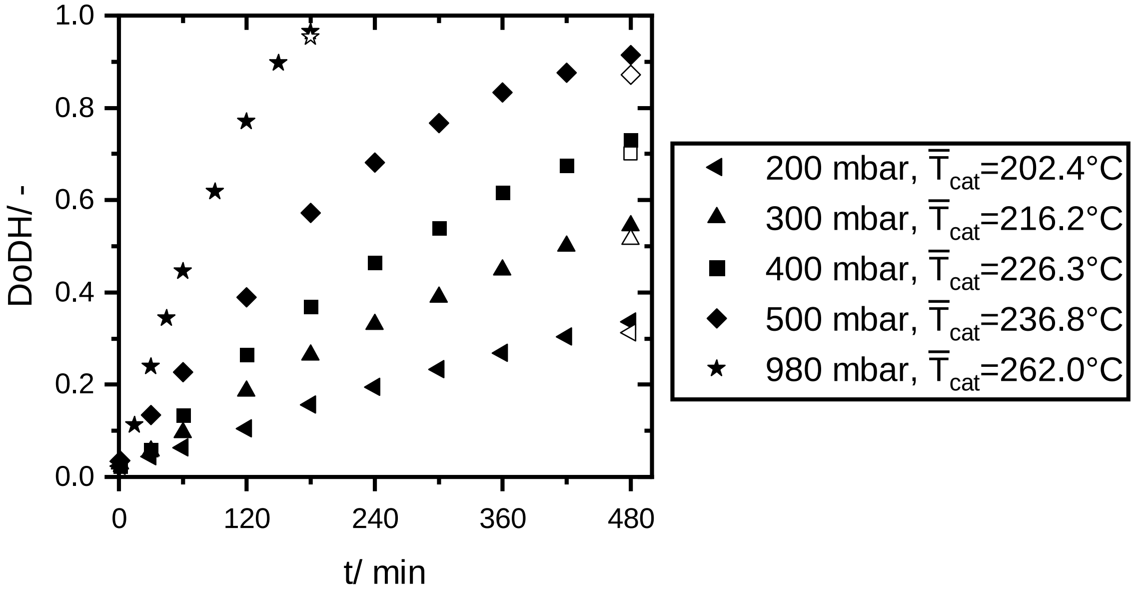


Figure 8: Pressure dependent DoDH over reaction time in reactive distillation dehydrogenation of H12-BT (catalyst 0.3 wt% Pt/Al_2O_3, $m_{catalyst}$ = 15.05 g, $m_{H12\text{-}BT}$ = 45 g); closed symbols indicate results calculated based on the composition of samples taken in the bottom of the reactive distillation column, open symbols show the whole column composition after cooling the experiment after the defined reaction time.

At ambient pressure nearly complete hydrogen release is possible in the reactive distillation column after 180 min reaction time. If the pressure is reduced to 500 mbar the temperature in the catalyst bed goes down to 235 – 245 °C (as shown in Figure 7). Very remarkably, under these very mild reaction conditions almost full hydrogen release was still possible within 480 min. While the reduced total pressure favours dehydrogenation thermodynamically, the low temperature of the catalyst bed causes reduced reaction rates due to the exponential link between rate constant and reaction temperature (Arrhenius law) [12]. Further reduction of the pressure in the reactive distillation column leads to further decrease in the catalyst bed temperature. At 200 mbar pressure, the temperature in the catalyst bed went down to little above 200 °C. Still under these reactive distillation conditions, significant hydrogen evolution was observed reaching 0.35 DoDH after 8 hours and 0.85 DoDH after 24h dehydrogenation time. Note, that for thermodynamic reasons nearly no hydrogen release is possible (< 2%) at temperatures below 210 °C at ambient pressure [12]. This shows clearly that the reduced total pressure enables much lower dehydrogenation temperatures and at the same time the operation mode in form of a reaction distillation results in reasonable dehydrogenation rates at these low temperatures. To the best of our knowledge the lowest temperature reported so far leading to any significant dehydrogenation of non-condensed, purely hydrocarbon LOHC systems was 230 °C, resulting in a DoDH of 0.37 % after 3,5 h reaction time using a Pt/C catalyst [6].

To further prove the rate accelerating effect of the dehydrogenation under reactive distillation we performed a comparison with the liquid phase dehydrogenation of H12-BT. In this latter case the entire catalyst was placed in the liquid H12-BT present in the bottom flask (see Figure 2) and this suspension was heated to 218°C at 300 mbar total pressure. A very similar temperature was also present in the respective reactive distillation experiment at 300 mbar at the catalyst in the distillation column (see Figure 7, right). The comparison shown in Figure 9 illustrates that the reactive distillation mode of operation has a very beneficial effect on the DoDH over time. As expected the positive effect of the reactive distillation on rate increases with increasing DoDH and thus with increasing amounts of aromatic H0-BT in the LOHC mixture.

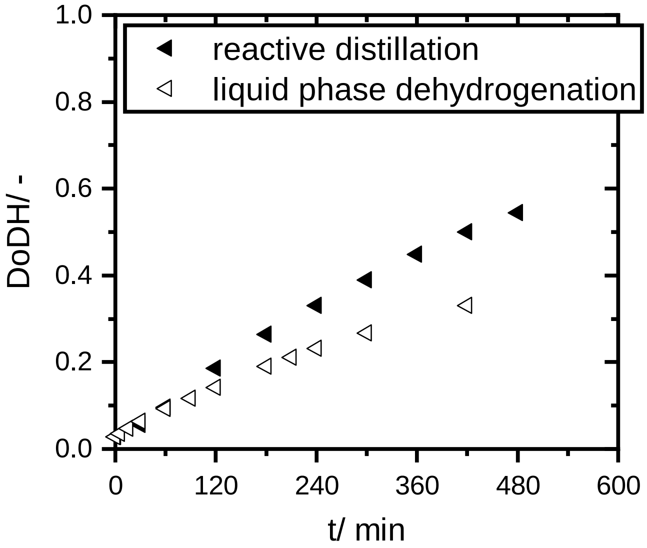


Figure 9: Comparison of the liquid-phase dehydrogenation of H12-BT at boiling conditions and the dehydrogenation of H12-BT in a reactive distillation column at 300 mbar (T at catalyst= 218 °C in both cases, catalyst 0.3 wt% Pt/Al_2O_3, reactive distillation: $m_{catalyst}$ = 15.05 g, $m_{H12\text{-}BT}$ = 45 g; liquid-phase dehydrogenation: $m_{catalyst}$ = 6.51 g, $m_{H12\text{-}BT}$ = 19.43 g).

Figure 10 summarises all results of our pressure variation experiments by showing the dependence of dehydrogenation temperature and hydrogen release productivity $P_{10\text{-}30}$ as described in Equation **(2)** as a function of overall pressure.

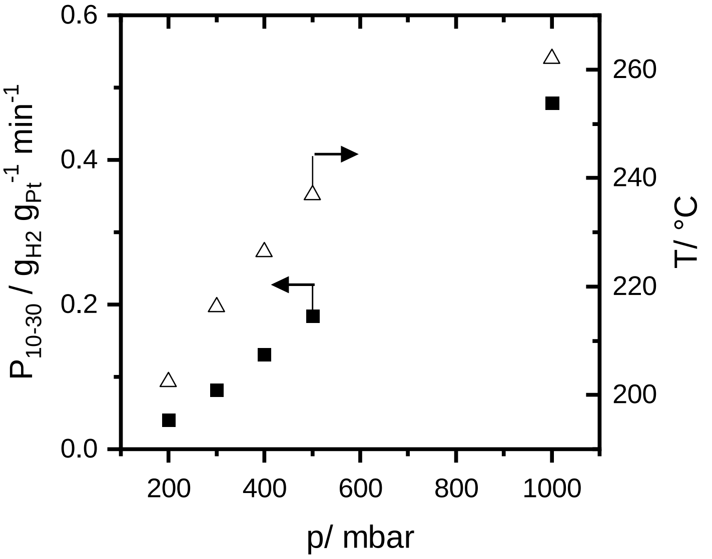


Figure 10: Dependency of the productivity and average catalyst temperature on pressure in the dehydrogenation of H12-BT in a reactive distillation column (catalyst 0.3 wt% Pt/Al_2O_3, $m_{catalyst}$ = 15.05 g, $m_{H12\text{-}BT}$ = 45 g).

As discussed before the average catalyst bed temperature is directly linked under boiling conditions to the overall pressure. Decreasing pressure results in lower temperature in the catalyst bed and lower dehydrogenation rates and productivities. Reduced pressure enables effective dehydrogenation of H12-BT at very low temperatures. Furthermore, our results demonstrate that simple pressure adjustment in the LOHC dehydrogenation reaction operated in a reactive distillation column allows to control catalyst temperature and reactor productivity.

The here-presented way to reduce the dehydrogenation temperature of pure hydrocarbon LOHC systems is practically highly relevant as a lower dehydrogenation temperature facilitates greatly the heat integration between the endothermal hydrogen release reaction and any available heat sources of appropriate temperature level, in particular with heat generated by the typically exothermic utilisation of the released hydrogen. For example, operation of a HT-PEM fuel cell at temperatures up to 230 °C seems to be within reach and such fuel cell could inject its waste heat into a hydrogen release apparatus operated with H12-BT at 200 mbar pressure thereby completely covering the heat of dehydrogenation [34, 35]. But lower dehydrogenation temperatures are also very beneficial if the exothermic hydrogen utilisation proceeds in a device that operates at significantly higher temperature than dehydrogenation. The fully heat integrated combination of LOHC dehydrogenation and SOFC operation has been demonstrated for example [17, 18]. Alternatively, the hot exhaust gas from a hydrogen combustion engine may be applied to drive the endothermal hydrogen release from the LOHC storage systems [3]. In both cases a lower dehydrogenation temperature increases the share of useable heat and results in steeper temperature gradients in the heat exchange units. Both facts reduce the size of the heat transfer units and increase the operational flexibility of the SOFC or engine, respectively. So, from the perspective of practical use the reduced dehydrogenation temperature enabled by reduced pressure operation may largely overcompensate the somewhat reduced rate of dehydrogenation at these lower temperatures. The discovery of better dehydrogenation catalysts may further mitigate this obvious drawback of the low temperature operation.

Conclusion

The efficiency of hydrogen storage in LOHC systems can be significantly increased, if the heat for the endothermal hydrogen release can be provided by waste heat sources or by the energetic use of the released hydrogen. With decreasing dehydrogenation temperature heat integration becomes easier and more effective.

In this paper we have introduced a novel approach to reduce the dehydrogenation temperature for hydrogen release from LOHC systems and we have exemplified this technology for the dehydrogenation of H12-BT. We propose to operate the catalytic dehydrogenation in a reactive distillation column under boiling conditions. With this innovative concept we achieve four very significant conceptual advantages compared to classical slurry phase (catalyst suspension in liquid LOHC) or gas phase (catalyst fixed bed contacted with gaseous LOHC):

- The boiling H12-BT reduces the hydrogen partial pressure in the gas phase, a fact that results in an **increase of thermodynamic driving force** for the hydrogen release reaction. This remarkable effect has been demonstrated by achieving 85% dehydrogenation of H12-BT at 210 °C and 200 mbar over 24 h, while the same reaction at ambient pressure shows negligible hydrogen release.
- The endothermal reaction in the catalyst bed leads to cooling in the catalyst bed where – as a consequence – H12-BT vapour condenses within the catalyst bed. This condensation process makes most effective use of the heat that was previously required to evaporate the H12-BT and represents a **very effective way to provide the dehydrogenation heat** directly at the location of the catalytic hydrogen release reaction.
- The reactive distillation leads to an enrichment of the light boiling H12-BT at the top of the column (where the catalyst is placed), while H0-BT collects preferably at the bottom; this leads to a significant **increase in rate of dehydrogenation**. In this contribution, we have demonstrated, for example, that H12-BT dehydrogenation in reactive distillation

mode led to a more than 50% increase in the overall hydrogen release compared to the same reaction under otherwise identical temperature and pressure conditions ($T_{catalyst}$= 218 °C; p= 300 mbar) carried out as liquid slurry phase reaction.

- The reactive distillation mode of operation effectively separates the fully aromatic H0-BT product from the catalyst fixed bed at the top of the column. This reduces the probability of undesired consecutive reactions of the aromatic product at the catalyst, such as transfer hydrogenation and Pt-induced condensation reactions. The reduced concentration of H0-BT at the catalyst does not only lead to an **enhanced recyclability of the LOHC system** applied. It results, in addition, in enhanced **catalyst lifetime** as these avoidable condensation products play a critical role in deactivation pathways leading to catalyst coking.

These advantages could be observed in our experiments, although it is difficult to disentangle all effects to describe quantitatively their individual contribution to the observed boost in dehydrogenation performance. In any case, the interplay of these four advantages led to an effective hydrogen release from H12-BT at temperatures as low as 200 °C at a total pressure of 200 mbar in the reactive distillation column, which represents – to the best of our knowledge - a world record for the low temperature dehydrogenation of heteroatom-free, non-condensed hydrocarbon LOHC systems. Note that hydrogen pressures of 200 mbar can directly be used in PEM fuel cells without loss in fuel cell performance as typical PEM fuel cells are limited in their performance on the cathode side where oxygen is reduced to oxide ions and react with protons to water.

Our paper describes the vapour-liquid-equilibrium of H0-BT/H12-BT mixtures and proves the negative effect of aromatic product inhibition on dehydrogenation kinetics by comparing the dehydrogenation of LOHC reaction mixtures and premixed LOHC blends with identical DoDH but very different content of H0-BT. From all our results we conclude that LOHC dehydrogenation at reduced pressure in a reactive distillation column represents a highly attractive mode of operation, if heat at a temperature level of 230 – 250°C is available from waste heat sources or from the energetic use of the released hydrogen.

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