



**HYDROGEN SUPPLY AND TRANSPORTATION USING LIQUID ORGANIC HYDROGEN CARRIERS
(HYSTOC)**

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D5.4

Potential DBT Mixtures Identified

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<i>PRO</i>	Technical/economic progress report (internal work package reports indicating work status)
<i>DEL</i>	Technical reports identified as deliverables in the Description of Work
<i>MoM</i>	Minutes of Meeting
<i>MAN</i>	Procedures and user manuals
<i>WOR</i>	Working document, issued as preparatory documents to a Technical report
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1 Introduction

The following document presents investigations concerning the question if a mixture of benzyltoluene (BT) and dibenzyltoluene (DBT) species could be an interesting alternative LOHC system. One of the drawbacks of DBT is its high viscosity at low temperatures. Especially the hydrogenated form H18-DBT is hard to pump at temperatures below -10°C . First, material properties of BT and DBT were compared. In doing so, a focus was laid on the viscosity and the vapor pressure. After that the kinetics of the dehydrogenation reaction of BT/DBT mixtures were studied.



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2 Motivation

The LOHC system used by Hydrogenious Technologies GmbH is dibenzyltoluene (H0-DBT) / perhydro-dibenzyltoluene (H18-DBT). It is characterized by the following advantageous physical and chemical properties:

- Hardly inflammable, non-explosive
- High boiling point
- Non hazardous good
- High H₂ release rates at temperatures above 290°C

A very similar LOHC-system is benzyltoluene (H0-BT)/perhydro-benzyltoluene (H12-BT) which shares many positive physio-chemical properties with H0-DBT/H18-DBT. As shown by Brückner et al. [1] a faster dehydrogenation of H12-BT compared to H18-DBT was possible at a temperature of 270°C. Due to its lower boiling point and consequently a higher vapor pressure H12-BT cannot be used at reaction temperatures > 300°C. Thus it is not favorable for the state of the art reactor technology with temperatures rising above 300°C. However, a mixture of both carriers could enable high H₂ release rates at moderate temperatures with low vapor pressure and low viscosities at temperatures below room temperature.

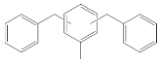
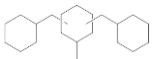

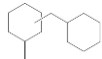


3 Mixtures of DBT and BT as LOHCs

3.1 General Aspects

A comparison of the four different species of (di)benzyltoluene LOHC carrier systems are presented in Table 1.

Table 1 - General Properties of DBT and BT

	H0-DBT	H18-DBT	H0-BT	H12-BT
Structure				
Density (20°C) / kg m ⁻³	1044 [2]	913 [2]	996 [2]	876 [2]
H ₂ capacity / wt. %	6.2		6.2	
Heat of (de)hydrogenation / kJ mol _{H₂} ⁻¹	-65.4 [2]	65.4 [2]	-65.4 [2]	65.4 [2]
Molecular weight / g mol ⁻¹	272.39	290.54	182.27	194.36

3.2 Material Properties

3.2.1 Viscosity

The viscosities of the different species at room temperature are remarkably different between BT and DBT, especially those of the hydrogenated species. This is a point of great interest when it comes to the handling of the LOHC materials.

In general, the viscosity decreases with increasing temperature. Müller et al. [2] presented an equation for the calculation of viscosities (in mPa s) in dependency of the temperature (in K):

$$\ln(\eta(T)) = A + \frac{B}{T} + C \cdot \ln(T)$$

The parameters A, B and C can be found in Table 2. Two temperature ranges are presented for the H18-DBT-specie.



Table 2 - Parameters for the calculation of the temperature dependency of the density of BT and DBT [2]

	H0-DBT (> 293.15 K)	H18-DBT (< 313 K)	H18-DBT (> 313 K)	H0-BT	H12-BT
A	-124.51101	-26.7272214	-231.7406117	-39.3966559	-94.6172747
B	9262.53778	9620.10641	15784.3287	3655.68111	6569.32652
C	17.0230528	0	32.2896344	4.99820468	13.0445002

At CRT the viscosities of several mixtures of hydrogenated carriers (H12-BT and H18-DBT) and dehydrogenated carriers (H0-BT and H0-DBT) have been analyzed for six different temperatures with an *Anton Paar* rheometer (Physica MCR 100). The results are presented in Figure 1 and Figure 2.

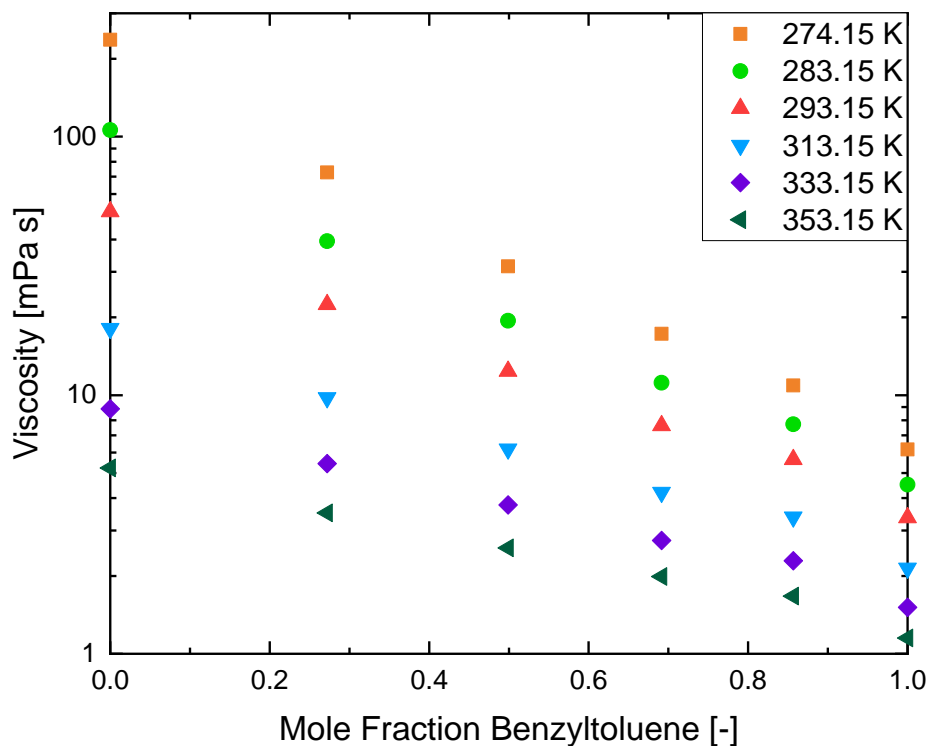


Figure 1 - Viscosity versus the mole fraction of H0-BT in a H0-BT/H0-DBT mixture for six different temperatures

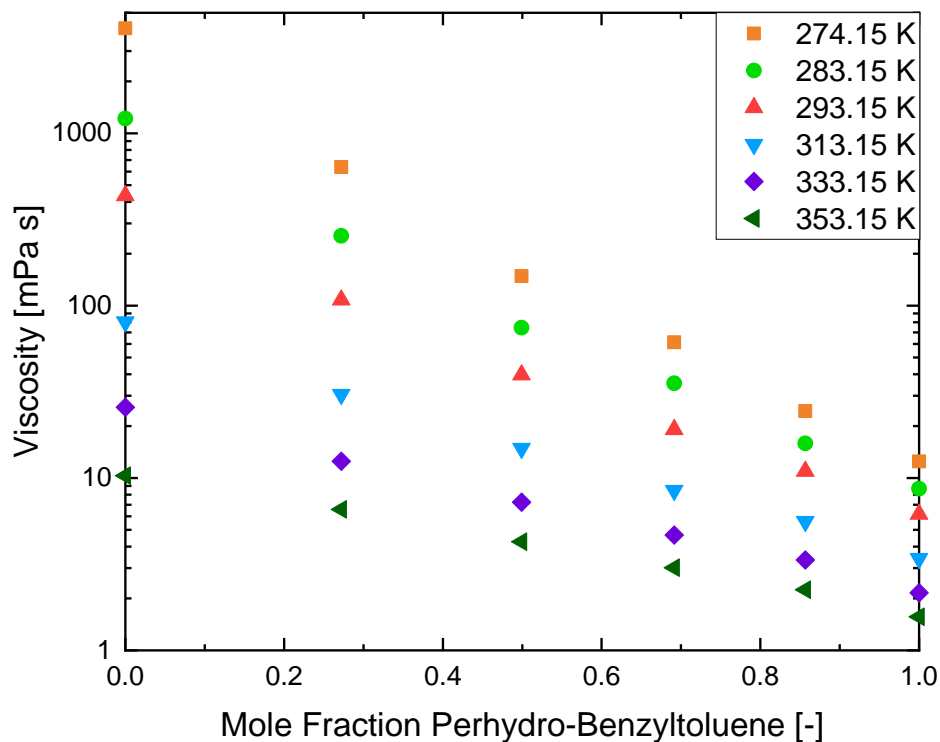


Figure 2 - Viscosity versus the mole fraction of H12-BT in a H12-BT/H18-DBT mixture for six different temperatures

It was found that the viscosity of mixtures of DBT and BT (hydrogenated and dehydrogenated) can be described with the Grunberg-Nissan-Equation by neglecting the linear term:

$$\ln(\eta_{mix}) = x_{BT} \cdot \ln(\eta_{BT}) + x_{DBT} \cdot \ln(\eta_{DBT})$$

3.2.2 Vapor Pressure

As mentioned in Section 2 a lower vapor pressure was one of the reasons DBT was favored over BT as a hydrogen carrier. In this respect, a mixture of DBT and BT could be interesting as it might enable higher hydrogen release rates of BT at lower temperatures and lower vapor pressure compared to pure DBT.

The vapor pressure as a function of the temperature is shown in Figure 3 for different mixtures of hydrogenated DBT and BT. No measurements have been executed for the dehydrogenated species because in general the hydrogenated species have a higher vapor pressure and high temperatures are more crucial during the dehydrogenation reaction.

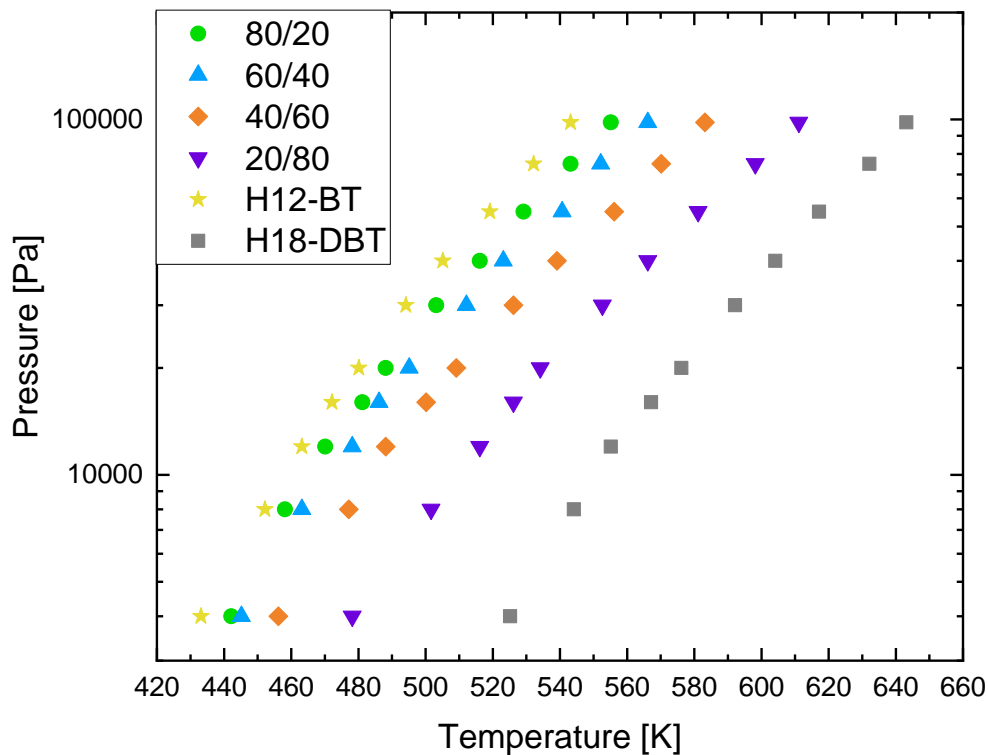


Figure 3 - Vapor pressure versus temperature for H12-BT/H18-DBT mixtures

The vapor pressure of pure hydrogenated BT and DBT and mixtures of hydrogenated BT and DBT can be described with the Antoine-Equation:

$$\log_{10} \left(\frac{p^{LV}}{Pa} \right) = A - \frac{B}{\frac{T}{K} + C}$$

3.3 Kinetic Measurements

In the following section the results of kinetic measurements of the dehydrogenation reaction of different BT/DBT mixtures will be presented and discussed. *Nuclear Magnetic Resonance Spectroscopy (NMR)* has been used to analyze the degree of hydrogenation, i.e. the hydrogen fraction still bound in the carrier.

The reaction temperature was 270°C at 1 bara for 3 hours. As already shown by Brückner et al. [1] at 270°C the dehydrogenation of pure H12-BT is significantly faster than the dehydrogenation of pure H18-DBT. As expected, a positive effect on the dehydrogenation by adding small amounts of BT to DBT can be seen. Surprisingly no further increase of the dehydrogenation rate can be seen at mixtures of BT/DBT > 40/60.



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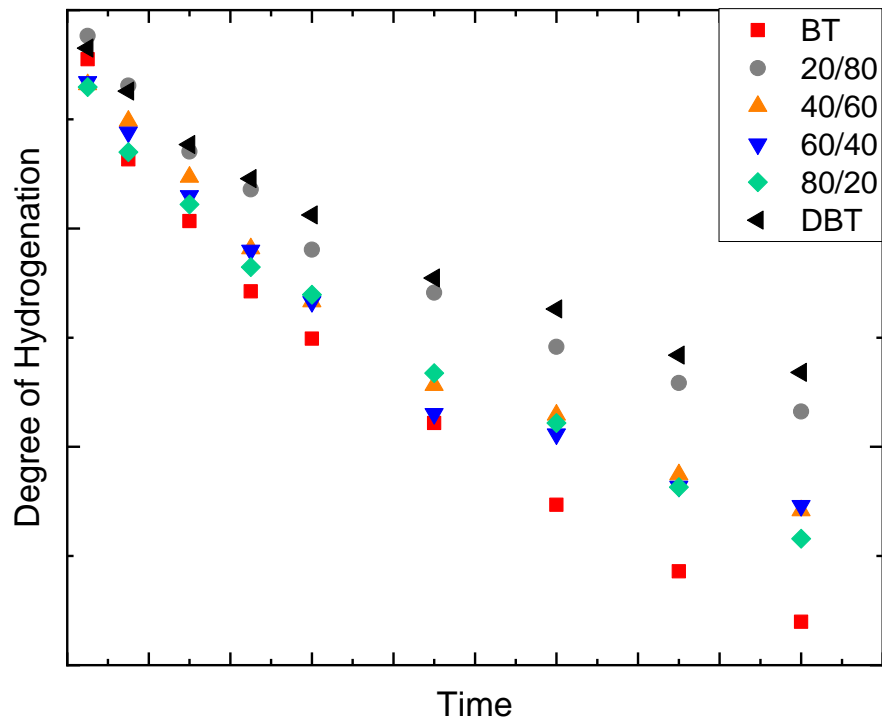


Figure 4 - Degree of Hydrogenation versus time for BT/DBT mixtures during a dehydrogenation reaction at 270°C and 1 bara



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4 Conclusion

The investigations of BT/DBT mixtures as an LOHC system have shown that adding BT to DBT, especially small amounts, might be interesting for the future. We have shown, that the viscosity is significantly lower and the kinetics of the dehydrogenation step is faster in case of using a mixture of BT/DBT compared to pure DBT. Adding too much BT to DBT (ratio > 40/60) no further benefit was visible when it comes to the hydrogen release rate of the dehydrogenation. Attention must be paid to the increased vapor pressure of BT/DBT mixtures compared to pure DBT leading to an increased energy demand.



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5 Literature

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