Benzyltoluene/ perhydro benzyltoluene – Pushing the performance limits of pure hydrocarbon liquid organic hydrogen carrier (LOHC) systems

Timo Rüde,[a,b] Stefan Dürr,[b] Patrick Preuster,[a] Moritz Wolf,[a] Peter Wasserscheid[a,b*]

[a] Forschungszentrum Jülich, Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK 11), Cauerstr. 1, 91058 Erlangen, Germany

[b] Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany

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

Supplementary Information (ESI)

Extended discussion on the selection of the DoH range for assessing the productivity:

It can be seen from Figure 4 and Figure 5 that the hydrogenation rate is quite constant up to a DoH of 90% (probably due to mass transfer limitations in the system) so that the error introduced by the DoH evaluation range is less significant than the error introduced by these temperature fluctuations. Note, though, that the productivity values of the hydrogenation cycle are very likely affected by mass transfer limitations that could not be avoided in the experimental setup applied.

Schematic flow diagram:

Figure S1 shows the schematic flow diagram used for the semi continuous experiments for hydrogenation/ dehydrogenation cycling as described in the experimental section.
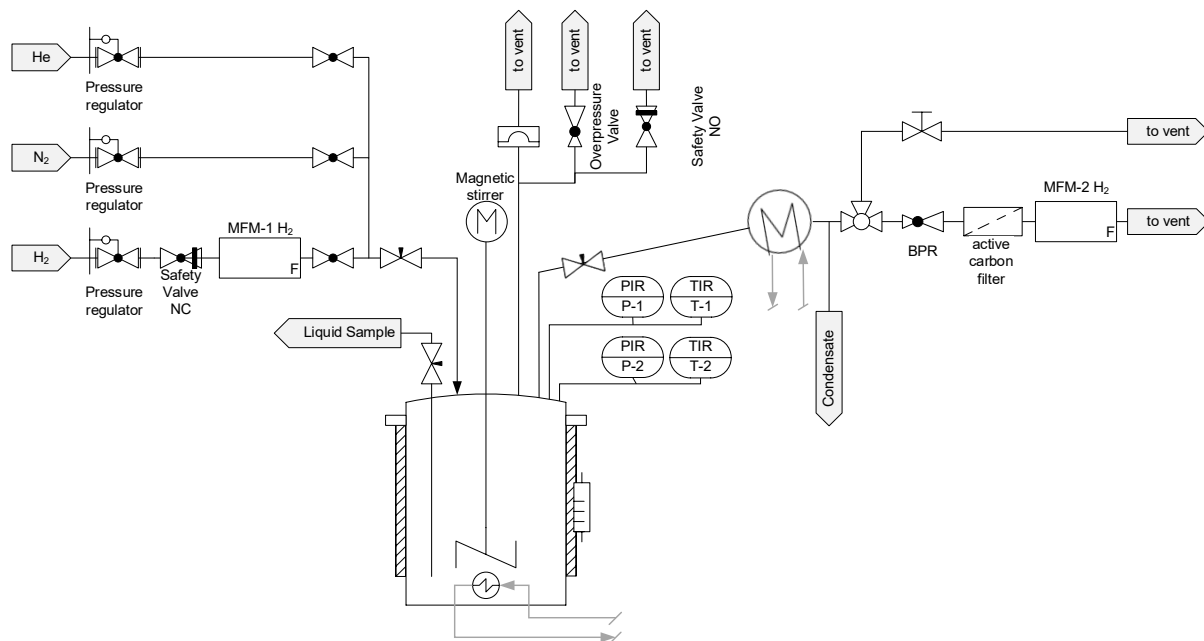

Figure S1: Schematic flow diagram of the plant set-up used in this study.

GC method:

Figure S2 shows the processed chromatogram of a typical Hx-BT reaction mixture with low degree of hydrogenation (DoH). The integration ranges of the major components H12-BT, H6-BT, H0-BT, Methylfluorenes, Anthracenes and further heavy boilers and are indicated by dashed vertical lines.
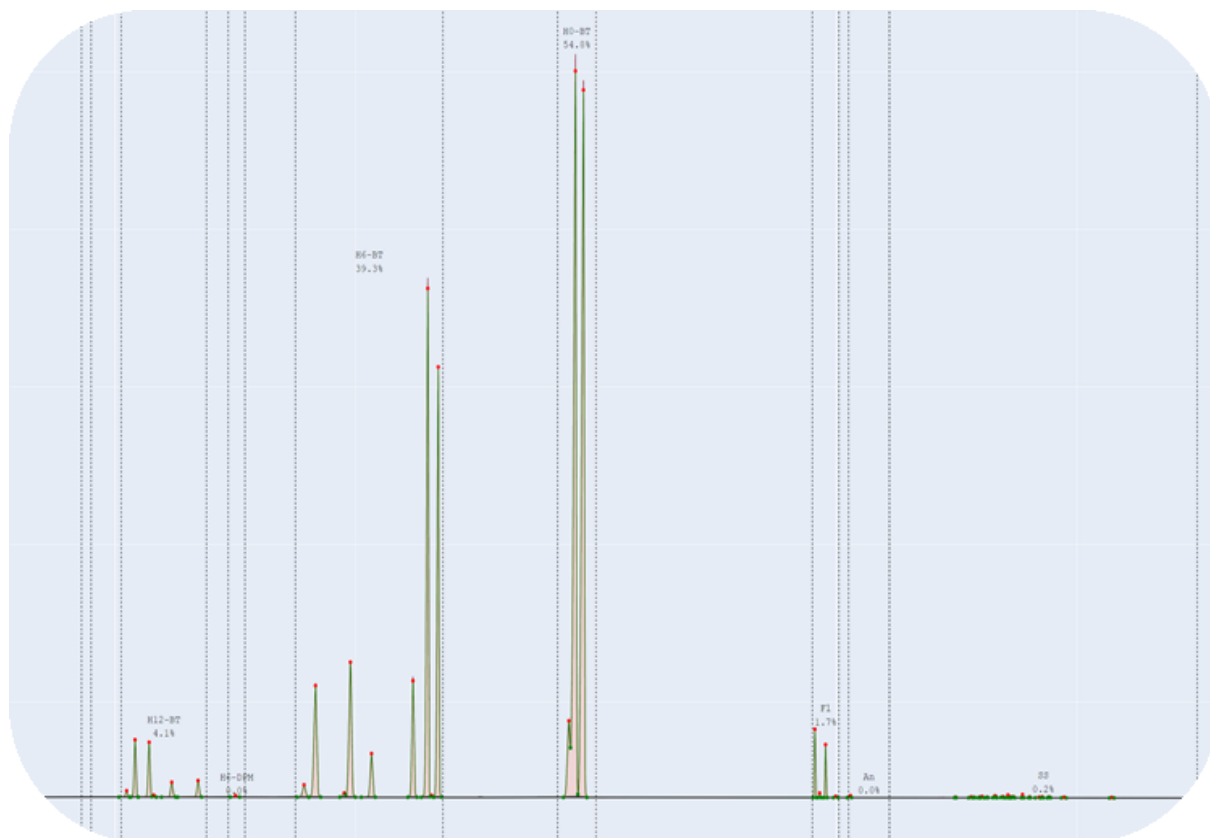

Figure S2: Gaschromatogram showing ranges of H12-BT (with 6 peaks), H6-BT (with 9 peaks), H0-BT (with 3 peaks), and methylfluorenes (with 4 peaks)

Viscosity:

Figure S3 depicts viscosities of fully dehydrogenated and fully hydrogenated LOHC systems of BT and DBT. Values are calculated from the correlation given by Müller et al..[S1] The viscosities are plotted on a logarithmic scale since BT species have viscosities one to two orders of magnitude lower than DBT species.
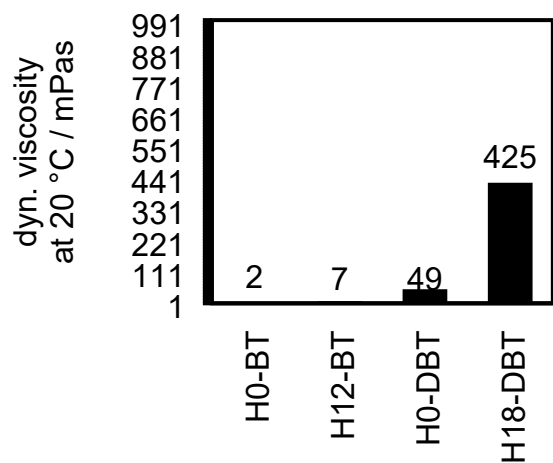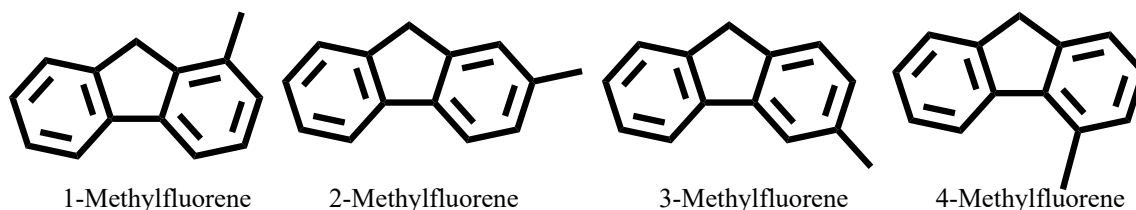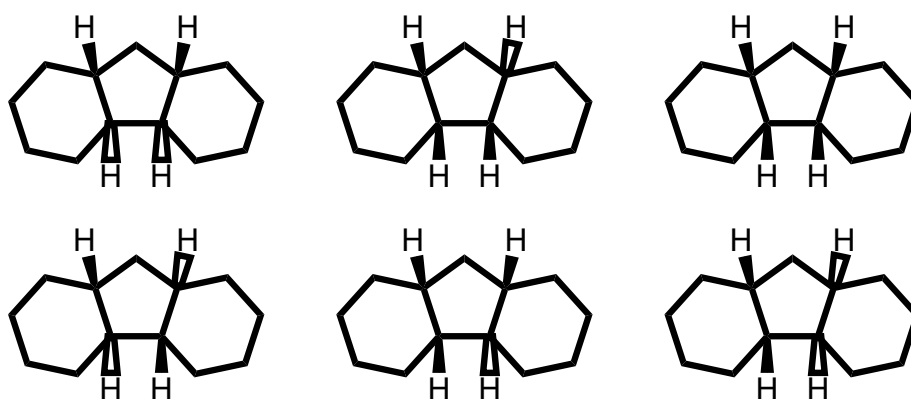

Figure S3: Viscosity of H0-LOHC and perhydro-LOHC

Fluorene derivatives:[S2, S3]

1-,2-,3-,4-methylfluorene
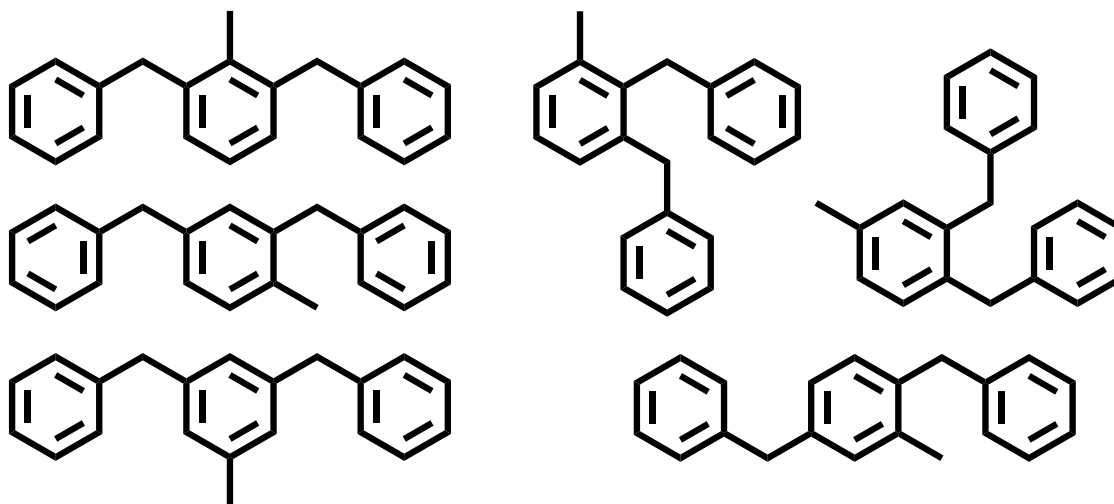

1-Methylfluorene   2-Methylfluorene   3-Methylfluorene   4-Methylfluorene

6 possible perhydrofluorene isomers exemplifying the many
perhydromethylfluorenes that may occur

6 H0-DBT species that can occur

Exemplary intramolecular condensation with DBT depicting
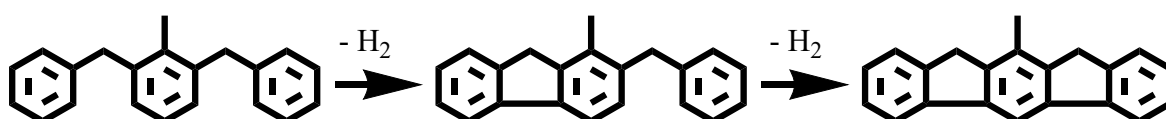path to DBT fluorene derivatives as dehydrocyclization products

Figure S4:Illustration of four methylfluorene isomers, six perhydrofluorene isomers, six

H0-DBT isomers and an exemplary dehydrocyclication pathway for an H0-DBT isomer.

Chemical equilibrium overall sigmoidal fit to data points:

The coefficients b and c from singular fits to every isobaric equilibrium curve were used to determine the pressure dependency of the equilibrium. In line with the good approximation achieved for DBT, a linear function was assumed for coefficient b. A logarithmic relation was chosen for coefficient c. Internal cross validation with leave more out (LMO) technique was conducted. Multiple training sets with each 7 out of 9 temperature ramps and with 2 remaining temperature ramps as test sets were generated. Each of these training sets was fitted and tested separately (see Figure S5 Left and Right). By comparing the mean deviation of the test fits, the final coefficient fit functions were found. The corresponding relations are given in equation (6) and (7).
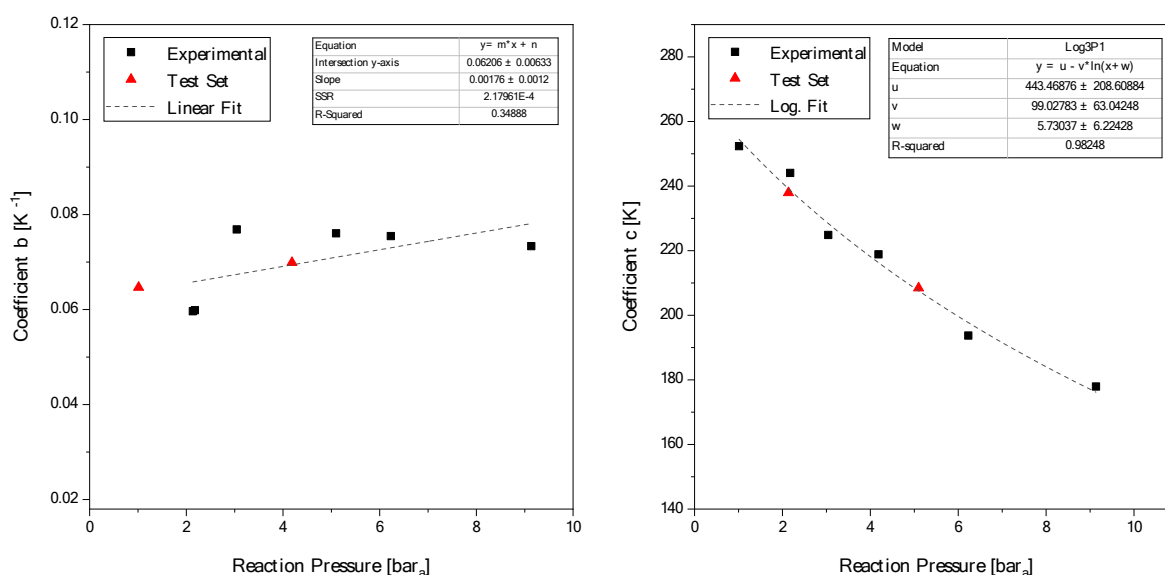

Figure S5 Left: Coefficient b as a function of p_D. Values obtained from single fit of experimental data. Figure S5 Right: Coefficient c as a function of p_D. Values obtained from single fit of experimental data

Literature:

S1   K. Müller, K. Stark, V. N. Emel'yanenko, M. A. Varfolomeev, D. H. Zaitsau, E. Shoifet, C. Schick, Sergey P. Verevkin, W. Arlt, *Ind. Eng. Chem. Res.* 2015, 54, 32, 7967-7976

S2   G. Do, P. Preuster, R. Aslam, A. Bösmann, K. Müller, W. Arlt and P. Wasserscheid, *Reaction Chemistry & Engineering*, 2016, **1**, 313-320.

S3   F. Auer, Dr. Dissertation, Friedrich-Alexander-Universität Erlangen Nürnberg, 2019.