



Development of a liquid chromatographic method for the separation of a liquid organic hydrogen carrier mixture



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ABSTRACT

Liquid organic hydrogen carriers (LOHC) are an interesting option for hydrogen storage and transportation. This concept is based on reversible hydrogenation and dehydrogenation of a carrier compound for uptake and release of hydrogen respectively. Among others, dibenzyltoluene is a potential LOHC due to its reasonable hydrogen storage capacity (6.2 ma-%) and high thermal stability. However, a huge number of stable intermediates with different degrees of hydrogenation are observed in a partially hydrogenated reaction mixture of dibenzyltoluene. For the process development and studies of the dibenzyltoluene reaction mechanism, it is crucial to determine physico-chemical properties of its various partially hydrogenated fractions, which requires their isolation from the reaction mixture. In this work, a reversed-phase high performance liquid chromatography (RP-HPLC) method for the separation and purification of partially hydrogenated mixtures of dibenzyltoluene is presented. The method was developed and validated at analytical scale and successfully scaled up to semi-preparative scale. The mixture was separated into four fractions according to their degree of hydrogenations using phenylhexyl silica stationary phase and a mobile phase consisting of acetone/water (96/4, v/v). Fractions with purity above 98% and yield higher than 90% were obtained in a semi-preparative column with an internal diameter of 50 mm.

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1. Introduction

Liquid organic hydrogen carriers (LOHC) represent a promising approach for hydrogen storage using a chemical reaction. The LOHC concept provides a solution to the problem of low hydrogen density and safe hydrogen transportation in most storage technologies [1]. Thermodynamically, aromatics are the most feasible potential candidates as LOHC systems [2]. A number of chemicals like N-ethylcarbazole, naphthalene, and toluene are under investigation in this regard [1,3–5]. Recently the heat transfer oil, dibenzyltoluene (known under the brand name Marlotherm SH[®]), came into focus of research as a possible material for the LOHC technology due to its reasonable hydrogen storage capacity and thermal stability [6,7].

Dibenzyltoluene (C₂₁H₂₀) is not available as a pure compound, but consists of various structural isomers (6–8 isomers could be identified) [7]. Isomers detected by NMR and GCMS studies in a commercially available dibenzyltoluene mixture are presented in the supporting information (Fig. S1). Reversible hydrogenation and dehydrogenation results in the formation of various stable spe-

cies in the reaction mixture. Number of the stable intermediates are increased due to the fact that dibenzyltoluene is not a pure compound in its fully lean form. Subsequently, more than 24 stable species are observed in a partially hydrogenated reaction mixture. These intermediates can be classified into four main fractions based on the degree of hydrogenation: dibenzyltoluene (C₂₁H₂₀, H₀-DBT), hexahydro-dibenzyltoluene (C₂₁H₂₆, H₆-DBT), dodecahydro-dibenzyltoluene (C₂₁H₃₂, H₁₂-DBT), and perhydro-dibenzyltoluene (C₂₁H₃₈, H₁₈-DBT). A simplified hydrogenation/dehydrogenation reaction mechanism for dibenzyltoluene (for one isomer i.e. 2,6-dibenzyltoluene) is presented in Fig. 1.

In order to implement dibenzyltoluene as LOHC system, these fractions need to be purified not only for the measurement of thermo-physical properties and toxicological analysis but also to study the detailed kinetics of both, hydrogenation and dehydrogenation reactions. Separation by distillation is challenging as the compounds are very low volatile and boiling point of fractions overlap each other (boiling point ranges of DBT fractions at 1 mbar is presented in supporting information, Table S1). Such high and close boiling compounds (b.p. ranges between 360 and 390 °C at atmospheric pressure) require high temperature vacuum distillation making it an energy intensive choice. On the other hand, reversed phase high performance chromatography (RP-HPLC) has

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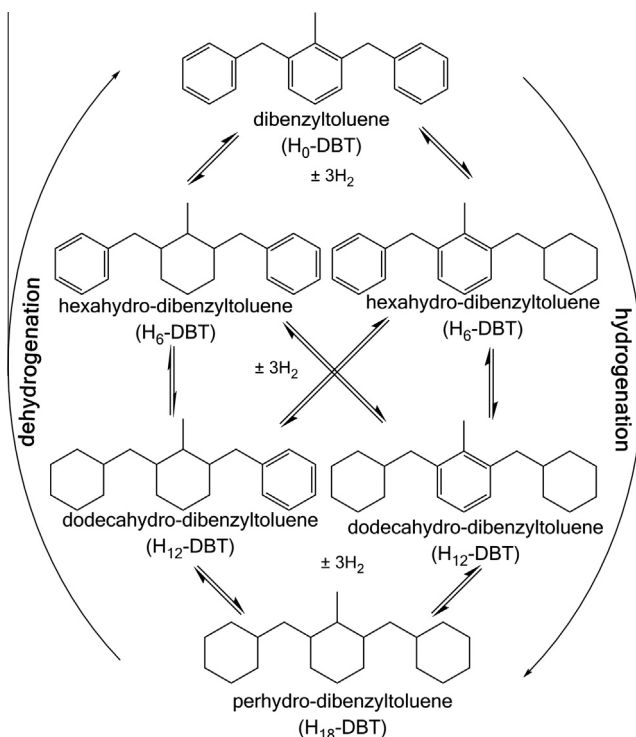


Fig. 1. Simplified (de)hydrogenation reaction mechanism for one isomer of dibenzyltoluene.

already been used to analyze very complex mixture of polyaromatics [8–14] and could be an alternative method for the separation of such complex fractions on a large scale.

In this contribution, a RP-HPLC method is developed at analytical scale for the separation of various partially hydrogenated fractions of dibenzyltoluene and then successfully scaled up to a semi-preparative scale in a 250 mm (L) × 50 mm (I.D.) column.

2. Materials and methods

2.1. Materials

HPLC grade solvents including acetone, acetonitrile, methanol, ethanol and isopropanol were purchased from VWR Germany. The partially hydrogenated reaction mixture of dibenzyltoluene

(DBT-Mix) was prepared in house by partial (de)hydrogenation reaction at the *Institute of Chemical Reaction Engineering at FAU Erlangen-Nürnberg*. The details of reaction conditions can be found in our previous work [15]. For semi-preparative separation, technical grade acetone was provided by CSC-Jäklechemie, Germany. The details of the chemicals used in this work with supplier and purity information are given in Table 1. All chemicals were used without further purification. 18 MΩ water produced by a Milli Q integral-3 system (Merck Millipore, Germany) was used in the experimental work.

2.2. Equipment

2.2.1. Analytical HPLC system

A reversed phase column with phenylhexyl silica stationary phase from Phenomenex (250 mm × 4.6 mm I.D., 15 μm) was used for the separation of various fractions of dibenzyltoluene. For the development of the chromatographic method, an analytical scale Merck/Hitachi LaChrom Elite HPLC system equipped with binary gradient pumps, auto sampler, direct injection module, UV-Vis detector, degasifier (from Knauer, Germany) and Ezochrom Elite control software was used.

2.2.2. Semi-preparative HPLC system

For scale up, a semi-preparative Prochrome[®] DAC (dynamic axial compression) column from Novasep (France) was used. The column was connected to a semi-preparative Knauer pump (K-1800, 250 ml/min), Knauer injection pump (10 ml/min), Knauer UV-detector (K-2501) and was controlled with Eurochrom[®] Preparative version 3.05 control software.

2.3. Methods

2.3.1. Solubility measurement

The solubility of dibenzyltoluene, perhydro-dibenzyltoluene and partially hydrogenated mixture of dibenzyltoluene in various RP-HPLC solvents was measured at 22 ± 1 °C. The solute was added stepwise in a particular solvent until precipitates were formed. The solution was placed in shaking water bath for 24 h at 22 ± 1 °C. Then 1 ml of clear solution was taken and analyzed by GC to measure the solubility.

2.3.2. GC analysis

GC-analysis was performed using an Agilent technology 7890 A system. The system was equipped with an Agilent technology auto

Table 1
Supplier information for chemicals used.

Chemicals	Suppliers	Purity (mass %)	Analysis method
Dibenzyltoluene (Marlotherm [®] SH; H ₀ -DBT)	Sasol	>98	GC-MS ^a
Partially hydrogenated dibenzyltoluene mixture (DBT-Mix)	CRT ^b	–	GC-MS ^a
Perhydro-dibenzyltoluene (H ₁₈ -DBT)	CRT ^b	>99	GC-MS ^a
Acetone (HPLC grade)	VWR	>99	GC ^c
Iso-propanol	VWR	>99	GC ^c
Hexane	VWR	>99	GC ^c
Ethanol	VWR	>99	GC ^c
Methanol	VWR	>99	GC ^c
Ethylacetate	VWR	>99	GC ^c
n-Butanol	VWR	>99	GC ^c
Toluene	VWR	>99	GC ^c
Diethylether	VWR	>99	GC ^c
Dioxane	VWR	>99	GC ^c
Acetonitrile	VWR	>99	GC ^c
Technical grade acetone	CSC-Jäklechemie	>99	GC ^c

^a Gas chromatography mass spectroscopy.

^b Institute of Chemical Reaction Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg.

^c Gas chromatography.

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