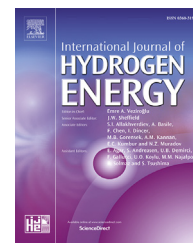




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# Analysis of reaction mixtures of perhydro-dibenzyltoluene using two-dimensional gas chromatography and single quadrupole gas chromatography

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## ABSTRACT

Energy storage via liquid organic hydrogen carrier (LOHC) systems has gained significant attention in recent times. A dibenzyltoluene (DBT) based LOHC offers excellent properties which largely solve today's hydrogen storage challenges. Understanding the course of the dehydrogenation reaction is important for catalyst and process optimization. Therefore, reliable and exact methods to determine the degree of hydrogenation (doh) are important. We here present other possible techniques, namely: comprehensive two-dimensional gas chromatography coupled with time of flight mass spectrometry (2D-GC-TOF-MS) and single quadrupole-mass spectrometry gas chromatogram system (GC-SQ-MS). The 2D-GC-TOF-MS results indicate that isomer fractions lose three molecules of hydrogen, as follows: H18-DBT, H12-DBT, H6-DBT and H0-DBT, and the doh decreases with an increase in dehydrogenation temperature. <sup>1</sup>H NMR and GC-SQ-MS were employed as additional analytical techniques. The GC-SQ-MS was also used to analyse decomposition products that result from thermal cracking of reaction mixture molecules.

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## Introduction

High hydrogen storage densities are difficult to achieve because hydrogen gas has a low gravimetric and volumetric

density [1,2]. Conventional hydrogen storage methods operate under very high pressure, for example, 700 bar compressed hydrogen, or very low temperature (−253 °C) in the case of liquefied hydrogen [3–5]. These methods create risks and require energy-intensive compression and liquefaction

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procedures [6]. Marlotherm SH (a commercially available heat-transfer fluid; Sasol) is an isomeric mixture of dibenzyltoluenes (DBTs) which is used today as an alternative hydrogen storage material [7]. Among other liquid organic hydrogen carriers (LOHCs), the DBT system is highly favoured due to its excellent properties, such as a high boiling point (380 °C), low melting point (−90 °C) and high gravimetric hydrogen storage capacity (6.2 wt%) [8,9]. In this technique, hydrogen is chemically bound in the aromatic rings of DBT through a reversible hydrogenation process [10]. The resulting hydrogen-rich LOHC (H18-DBT) can then be transported under ambient conditions using existing fuel infrastructure, without the demand for high pressures and low temperatures. Chemically bound hydrogen can be released through a catalytic dehydrogenation process and may be used in a hydrogen fuel cell for stationary or mobile power application [11]. It is therefore important to characterize LOHC reaction mixtures in order to determine, and optimize, the performance of both hydrogenation and dehydrogenation systems.

The separation and characterization of isomeric mixtures of DBTs and their corresponding partially or fully hydrogenated intermediates is a difficult analytical challenge. One-dimensional gas chromatography coupled with mass spectrometry (1D-GC-MS), customized for high-boiling-point hydrocarbon liquids is a commonly used technique [11,12]. However, when using 1D-GC-MS for complex mixtures, peaks tend to overlap or broaden, suggesting limited peak capacity of the GC column. It is also reported that such complex mixtures are difficult to separate by 1D-GC, even when highly selective stationary phases and high resolution ‘narrowbore’ columns are used [13,14].

Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (2D-GC-TOF-MS) is a powerful separation and identification technique. In typical 2D-GC-TOF-MS, a primary column is coupled with a secondary column by a special interface modulator. The modulator traps and introduces a fraction of a sample from the main column to the secondary column periodically, at a specific rate that allows the first separation to be preserved [15,16]. Without the modulator interface, fractions may recombine or change elution order in the secondary column. A flame ionization detector (FID) may be included as a primary detector and TOF as a secondary detector. In 2D-GC-TOF-MS, the two types of columns use a different mechanism of separation. The retention times in the first and second dimensions are independent of each other, i.e., the chromatogram is orthogonal [17,18].

In this work, we assess the effect of temperature on the levels of dehydrogenation and distribution of isomer fractions using comprehensive 2D-GC-TOF-MS, complemented with <sup>1</sup>H NMR and single quadrupole-mass spectrometry gas chromatography (GC-SQ-MS) analyses. The GC-SQ-MS is also used to quantify and qualify decomposition products. Quadrupoles of GC-MS are mass analyzers which consist of four rods of which DC and RF voltages are applied [19]. An ion of a specific mass-to-charge ratio (*m/z*) stabilizes and pass through the quadrupole only when a specific DC/RF voltage combination is applied [19]. Therefore, the advantage of a quadrupole is that it filters masses of interest by the so-called selective ion

monitoring (SIM) mode. In this work, chromatograms of masses of interest are isolated separately, hence isomer fractions are identified and quantified separately, unlike in conventional GC with a FID detector.

## Materials and methods

### Chemicals

Sample preparation solvents, chloroform-*d* (99.8%), chloroform and hexane (GC grade, >99.9% pure) were purchased from Sigma Aldrich (Germany) and used without any further purification. Perhydrodibenzyltoluene (95%, certified hydrogenation grade) was supplied by Hydrogenious Technologies GmbH (Germany) and used as a feed for dehydrogenation. All dehydrogenation experiments were carried out using a platinum on alumina support (0.5 wt% Pt loading; Hydrogenious Technologies). Dibenzyltoluene was supplied by Sasol Germany GmbH and used without any further purification. Calibration standards of perhydrogenated compounds were supplied by the Institute of Chemical Reaction Engineering of Erlangen University (Prof. Wasserscheid; Germany). Helium gas (99.999%) was purchased from Afrox (South Africa) and used as a carrier gas for all GC techniques.

### Dehydrogenation experiment

Briefly, our experimental dehydrogenation system consists of a liquid feed loop for hydrogen-rich LOHC, a horizontal plug flow reactor made of quartz glass equipped with an electrical heater and a system control loop (see Fig. 1).

The hydrogen-rich substrate is pumped via a peristaltic pump into a horizontally orientated plug flow reactor made of quartz glass. Heat is supplied by an electrical heating jacket, divided into three heating zones, and a thermocouple, with three stages, centred horizontally in the reactor. Since the catalyst bed is located between two inert zones, the middle stage or reaction zone temperature is used for experiments. The dehydrogenation process is controlled by an electrical switch box in combination with a control system. Since the main reactor is made of glass, the reaction is generally run at ambient pressure. The maximum allowable temperature is 400 °C in the outer part of the heating jacket. A noble metal catalyst, in this case 120 g of 0.5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> is used. The preheating zone consists of inert particles, which allows controlled heating of the liquid before it enters the catalyst bed.

Connected to the outlet of the dehydrogenation reactor is the product separation unit. The dehydrogenated liquid flows downwards through a liquid cooling unit into the product tank and the hydrogen gas flows upwards through a cooling unit. This cooled gas flows through a filtration device and, finally, the hydrogen produced is measured using a mass flow meter. Liquid samples used for analysis were collected before reaching the receiving tank. For all experiments the feed flow rate is kept constant at 4.5 ml/min and 90 min resident time, only temperature is varied.

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