

Evaluation of perhydrodibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production

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SOLEMN DECLARATION

I, Phillimon Mokanne Modisha, declare that the thesis entitled: "*Evaluation of perhydrodibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production*", submitted in fulfilment of the requirements for the degree Doctor of Philosophy in Engineering with Chemical Engineering, is my own research work unless otherwise stated, it has been text edited as required, and has not been previously submitted for a degree at any tertiary institution.

Signature:  _____

Date: 28/04/2021

Signed at: Potchefstroom

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“For we live by faith, not by sight.”

2 Corinthians 5:7

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PREFACE

I, Phillimon Mokanne Modisha, have chosen to submit my thesis in article format as permitted by the North West University under the General Academic Rules (A-rules) designated for post-graduate curricula. The tables, figures, and general outline of the thesis were adapted and formatted to ensure uniformity throughout the thesis, with the technical content of the published articles remaining the same. Therefore, the manuscripts format may appear in a slightly different to what is presented in this thesis. All co-authors have granted their permission for the articles to be used in this thesis, and the author consent forms are attached in Appendix C.

Peer reviewed articles related to this study are listed below:

- Modisha, P., Jordaan, J. H., Bösmann, A., Wasserscheid, P., & Bessarabov, D. (2018). Analysis of reaction mixtures of perhydro-dibenzyltoluene using two-dimensional gas chromatography and single quadrupole gas chromatography. *International journal of hydrogen energy*, 43(11), 5620–5636.
- Modisha, P., Ouma, C. N., Garidzirai, R., Wasserscheid, P., & Bessarabov, D. (2019). The prospect of hydrogen storage using liquid organic hydrogen carriers. *Energy & fuels*, 33(4), 2778–2796.
- Modisha, P., Gqogqa, P., Garidzirai, R., Ouma, C. N., & Bessarabov, D. (2019). Evaluation of catalyst activity for release of hydrogen from liquid organic hydrogen carriers. *International Journal of Hydrogen Energy*, 44(39), 21926–21935.
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Conference presentations related to this thesis are listed below:

- Poster presentation: Nov 2016, “Unlocking fundamentals of dehydrogenation of LOHC for hydrogen production” CATSA, Drakensberg
- Oral presentation: Nov 2017, “First in Africa LOHC hydrogenation plant: A field study” CATSA, Pilanesburg
- Oral presentation: March 2018, “Analysis of reaction mixtures of LOHCs using 2D-GC-TOF-MS and GC-SQ-MS”, European Hydrogen Energy Conference, Malaga, Spain
- Poster presentation: May 2020, “Hydrogen charging and discharging cycles for liquid organic hydrogen carriers” HYPOTHESIS XV, Cape-Town

ABSTRACT

Hydrogen storage using liquid organic hydrogen carrier (LOHC) technology offers numerous advantages over conventional hydrogen storage systems. LOHCs are organic compounds that can store and release hydrogen through catalytic hydrogenation and dehydrogenation reactions. Globally, there are a few key-industry players involved in this technology. In South Africa, there are identified opportunities for the future application of LOHC technology. Probably the most widely used LOHC material for commercial applications is dibenzyltoluene. However, dibenzyltoluene (technical grade) (H0-DBT) consists of various structural isomers that are difficult to analyse by conventional gas chromatography. Products of reaction mixtures of H0-DBT contain numerous isomeric compounds (>20). This results in overlapping of peaks in conventional gas chromatography. Further challenging topics, associated with the use of H0-DBT as a LOHC, include the following: development and optimization of suitable catalytic materials for the dehydrogenation reaction, durability of the H0-DBT molecule, and the unknown number of hydrogenation and dehydrogenation cycles that a H0-DBT molecule can withstand. Investigations into these and other areas in this field are of a great importance.

Specific topics to be addressed here included the following: determination of a suitable chromatographic method and optimum conditions for the separation, identification and quantitative analysis of isomeric reaction mixtures of H0-DBT-based LOHC; evaluation and characterization of monometallic catalysts (Pt/Al₂O₃ and Pd/Al₂O₃) and their bimetallic counterparts (Pt-Pd/Al₂O₃) for the dehydrogenation of perhydrodibenzyltoluene (H18-DBT); optimization of the catalyst metal loading and reaction temperature for the reaction, towards achieving a reasonably high degree of dehydrogenation (dod), coupled with high-purity hydrogen; and determination of the durability of H0-DBT-based LOHCs.

Suitable analytical methods were successfully developed for the analysis of isomeric mixtures of H0-DBT using the state-of-the-art techniques: two-dimensional gas chromatography coupled with time of flight mass spectrometry and single quadrupole-mass spectrometry gas chromatography. Results of chromatography data were confirmed by spectrometry techniques (direct analysis in real time mass spectrometry and proton nuclear magnetic resonance spectrometry). Furthermore, good use was made of a refractometer to obtain measurements regarding the dod. This analytical technique enables us to obtain rapid measurements of the degree of hydrogenation (i.e., amount of hydrogen available in the molecule) or the dod (i.e., amount of hydrogen released from the molecule.)

Results of chromatographic analyses revealed that at higher dehydrogenation temperatures fewer partially dehydrogenated products were formed (hexahydro-dibenzyltoluene and dodecahydro-dibenzyltoluene isomers) but higher amounts of H0-DBT were formed; hence, a higher

dod value is obtained. On the other hand, at lower dehydrogenation temperatures a higher amount of partially dehydrogenated products formed but a lower amount of H0-DBT; hence, a lower dod value is obtained.

Regarding the catalysts for the reaction, both experimental and density functional theory calculations revealed that Pd- and Pt–Pd-based catalysts are not preferred for the dehydrogenation of H18-DBT. On the other hand, a Pt based catalyst gave good results. When using 1 wt % Pt loading, dehydrogenation of H18-DBT at 300 °C was found to be optimum: the hydrogen purity was 99.99% as confirmed by gas chromatography and reasonable values for the hydrogen flow and dod were recorded, 10 NL/h and 60%, respectively. Moreover, the turnover frequency (TOF) based activity, as shown in Chapter 4, also indicated that an increase in Pt metal loading is effective for 0.5 and 1 wt %, further increase to 2 wt % resulted in low TOF values. Productivity based on the metallic surface area (determined by chemisorption measurements), remained the same for 1 and 2 wt % loading.

The number of hydrogenation/dehydrogenation cycles depends on the type and amount of by-products produced during the reaction and this is linked to the nature of a catalyst and operational conditions. If toxic compounds are produced in large quantities, the number cycles will be limited. In the absence of any form of by-products, usage of the H0-DBT molecule could be unlimited. Accelerated stress tests revealed that H0-DBT did not fully decompose at extremely high temperature (355 °C); 7.4% of by-products were predicted to be obtained after 89 h of normal stress operation at 300 °C. Indications are therefore that the H0-DBT molecule can endure many years of cycling, provided that the side reactions are minimized, by modification of the catalyst, and the by-products produced are non-toxic.

Keywords: hydrogen storage; degree of dehydrogenation; accelerated stress test; liquid organic hydrogen carriers; hydrogen purity; density functional theory; two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (2D-GC-TOF-MS); single quadrupole-mass spectrometry gas chromatography (GC-SQ-MS)

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LIST OF ABBREVIATIONS

1D-GC-MS	One-dimensional gas chromatography coupled with mass spectrometry
2D-GC-TOF-MS	Two-dimensional gas chromatography coupled with time of flight-mass spectrometry
AC	Activated carbon
ACC	Activated carbon cloth
AHEAD	Advanced Hydrogen Energy Chain Association for Technology Development
AST	Accelerated stress test
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CSTR	Continuous stirred reactor
DART-MS	Direct analysis in real time mass spectrometry
DFT	Density functional theory
DMR	Department of Mineral Resources
dod	Degree of dehydrogenation
doh	Degree of hydrogenation
EJ	Exajoule
FBR	Fixed bed reactor
GC-SQ-MS	Single quadrupole-mass spectrometry gas chromatography
H0-DBT	Dibenzyltoluene
H0-NEC	N-ethylcarbazole
H12-NEC	Perhydro-N-ethylcarbazole
H18-DBT	Perhydro-dibenzyltoluene
HPR	Hydrogen production rate
LHD	Load haul dump
LHV	Lower heating value
LOHC	Liquid organic hydrogen carrier
MBT	Monobenzyltoluene
MR	Microchannel reactor
PEMFC	Proton exchange membrane fuel cell
PFR	Plug flow reactor
PMR	Palladium membrane reactor

RI	Refractive index
SC-CNT	Stacked cone carbon nanotubes
SEBM	Selective electron beam melting
SIM	Selective ion monitoring
SOFC	Solid oxide fuel cell
SPR	Spray pulsed reactor
TOF	Turnover frequency
TPR	Temperature-programmed reduction
TWh	Terawatt hour
UHG	United Hydrogen Group
XLP	Extra low profile

LIST OF SYMBOLS

A_F	acceleration factor	R_t	retention time
P	productivity, gH ₂ .gPt ⁻¹ .min ⁻¹	R	ideal gas constant, J.mol ⁻¹ .K
m_{H_2}	mass of hydrogen, g	T	temperature, K
m_{Pt}	mass of platinum, g	T_{use}	normal operating temperature, K
v_m	molar volume of hydrogen, L.mol ⁻¹	T_{stress}	Stress temperature, K
v_{H_2}	volume of hydrogen, L	t_{opt}	time of operation, h
E_a	activation energy, kJ.mol ⁻¹	t_{test}	test period, h
k_A	apparent rate constant	C_f	final concentration, mol.L ⁻¹
A	pre-exponential constant	C_o	initial concentration, mol.L ⁻¹
E_{S+A}	total energy of surface and adsorbate	t	time, min or h
F_{feed}	feed flow, ml min ⁻¹		
F_{H_2}	hydrogen flow		
E_{RXN}	reaction energy, eV		
E_A	adsorption energy		
E_{ADS}	total energy of adsorbate		

CHAPTER 1: INTRODUCTION

1.1 Background

This research work was motivated by the requirement for a cost-effective, safe and efficient method of storing renewable hydrogen. A competitive hydrogen storage technology could render the so-called ‘hydrogen economy’ more sustainable and feasible across various sectors. Such sectors include chemicals, food, glass manufacturing, electricity, hydrogen logistics and mobility (e.g., hydrogen-powered fuel cell vehicles). Figure 1.1 illustrates the integration of various sectors that make use of hydrogen produced from renewable sources [1–3]. The use of clean hydrogen in these sectors fulfils the global mandate of moving away from fossil-based fuels. By 2017, the annual consumption of hydrogen globally was estimated at 7.7 EJ (2140 TWh), half of which is utilized in ammonia production, while one third is used in oil refining [4]. The production of methanol accounts for 11% of hydrogen consumption, while only a small share is consumed in the production of other chemicals and the manufacturing of steel and glass. As increasingly more people and industries adopt new hydrogen-based technologies, the demand is expected to increase significantly; by 2050, hydrogen utilization is projected to be 78 EJ [4]. Other applications of hydrogen include its use in the cooling of power generators and the blending of natural gas with hydrogen for heating buildings. Employing the liquid organic hydrogen carrier (LOHC) technology for the storage and distribution of hydrogen is an alternative hydrogen storage method, to curb challenges associated with conventional hydrogen storage methods.

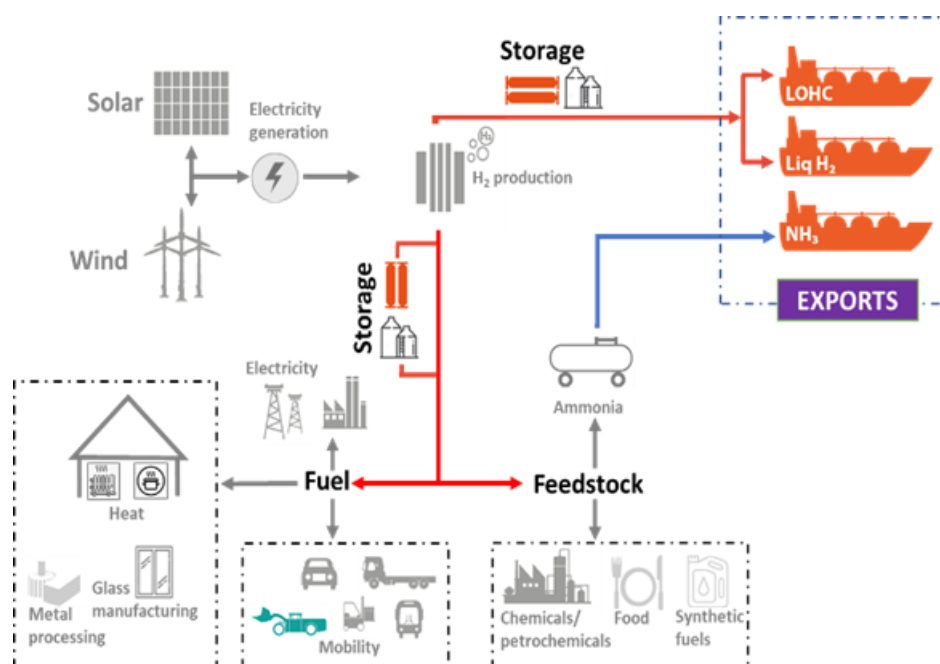


Figure 1.1: Sectoral integration by renewable hydrogen.

LOHCs are organic compounds that can store and release hydrogen through catalytic hydrogenation and dehydrogenation reactions. Hydrogen is chemically bound to the LOHC (e.g., aromatic or heteroaromatic hydrocarbons). Challenges otherwise associated with the handling of high-pressure gas cylinders and cryogenic liquid systems are thereby eliminated. Prominent LOHC compounds have excellent hydrogen storage properties. For example, the possibility to store a hydrogen-charged LOHC at ambient conditions for a long period of time, without self-discharge, using existing infrastructure for fuels.

Table 1.1 provides a comparison of hydrogen storage targets set by the U.S. DOE and the hydrogen storage properties of LOHC compounds (2017 data) [5]. It is evident from this data that the hydrogen storage by LOHCs exceeds the ultimate U.S. DOE targets—hence proving that the LOHC technology is competitive.

Table 1.1: Liquid organic hydrogen carrier storage vs. U.S. DOE hydrogen storage targets [5]

U.S. DOE storage parameter targets	2020	2025	Ultimate	LOHC
Gravimetric capacity (wt %)	4.5	5.5	6.5	4.9–7.2
Volumetric capacity (gH ₂ /L)	30	40	50	45–72
System fill time (5 kg H ₂ , min)	3–5	3–5	3–5	Est 2.0
Fuel purity (%)	99.99	99.99	99.99	99.99+
Boil-off loss target (%)	10	10	10	0

LOHC technology for the storage and release of hydrogen always involves a pair of molecules: hydrogen lean (LOHC-) and hydrogen rich (LOHC+) molecules. Hydrogen is stored by converting a LOHC- compound into a LOHC+ compound under a catalytic hydrogenation reaction, and hydrogen is released by converting a LOHC+ into a LOHC- under a catalytic dehydrogenation reaction. In this context, the LOHC- molecules could be aromatic or heteroaromatic hydrocarbons that are hydrogenated at pressures in the range 10–70 bar and temperatures >140 °C, in the presence of a catalyst; see Figure 1.2 [6–8]. Hydrogen is then released from the LOHC+ molecule (aliphatic hydrocarbon) by a catalytic dehydrogenation process at temperatures >250 °C and pressures in the range 1–5 bar [6–8]. During these catalytic processes, the LOHC molecules are not consumed—only hydrogen is released or loaded. Hence, a LOHC molecule must be sufficiently stable to allow many cycles of hydrogen loading and unloading. Figure 1.2 illustrates the concept of hydrogen storage and release using LOHCs.

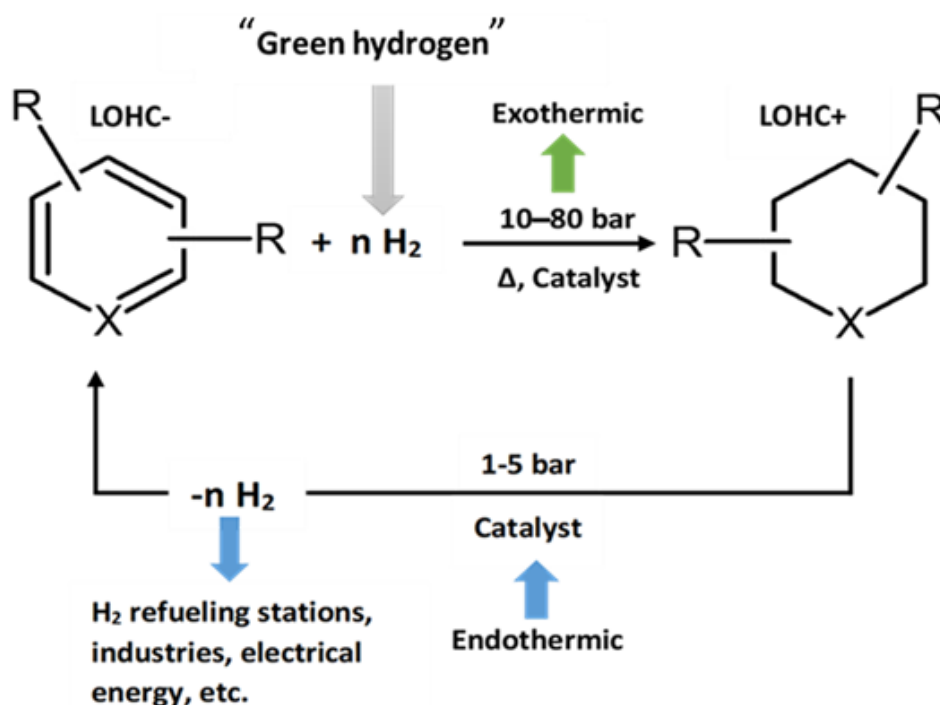


Figure 1.2: Reversible hydrogenation of aromatic compounds. PGM: Platinum group metal, X: heteroatom, R: alkyl (e.g. ethyl, methyl) or aryl (e.g. phenyl).

1.2 Problem statement and motivation

The broad problem statement applicable to the research addressed in this study can be summarized as follows. Several gaps in existing LOHC technology have been identified; for example, there are challenges pertaining to the analysis of isomeric mixtures of the most prominent LOHC molecule dibenzyltoluene (H0-DBT), optimizing the most suitable catalytic materials for the catalytic hydrogenation and dehydrogenation reactions, assessing the durability of a H0-DBT molecule, and then determining the number of hydrogenation and dehydrogenation cycles that H0-DBT can withstand.

One of the specific key motivations for this study was to establish expertise in the field of LOHC technology in South Africa under the framework of Hydrogen South Africa (HySA), i.e., the establishment of expertise and development of capabilities there, for the first time in South Africa. The long-term vision of HySA includes the development of cost-effective hydrogen storage technologies based on LOHC technology. Related to this, this study was to include a review of wider technical developments in the field of LOHCs to date, a description of various suitable molecular LOHC systems and the relevant catalyst developments, and modelling, with consideration of the types of reactors used for the dehydrogenation of specific LOHC molecules.

It is within the HySA North West University mandate to develop hydrogen production systems, as well as hydrogen storage and distribution technologies in South Africa. Hence, the existing opportunities within South African hydrogen market will be explored.

One of the catalyst aspirational targets set by the European Union funded project SHERLOHCK is to reduce the thermal energy required for dehydrogenation to <6 kWh/kg- H_2 and to increase the catalyst productivity to >3 g H_2 /g catalyst/min, whilst maintaining high conversion ($>90\%$) and selectivity ($>99.8\%$) [9].

In this study, hydrogen is stored by converting H0-DBT into H18-DBT (perhydrodibenzyltoluene) in a catalytic hydrogenation reaction and hydrogen is released by converting H18-DBT into H0-DBT in a catalytic dehydrogenation reaction. Both isomeric H0-DBT and H18-DBT can also be partially hydrogenated and dehydrogenated, respectively. Hence, the resulting product (a mixture of isomer fractions of reactants, stable intermediates and products) is referred to as the reaction mixture. Figure 1.3 shows structural isomers detected in a technical H0-DBT mixture [10]. The reaction mixture could contain >20 compounds.

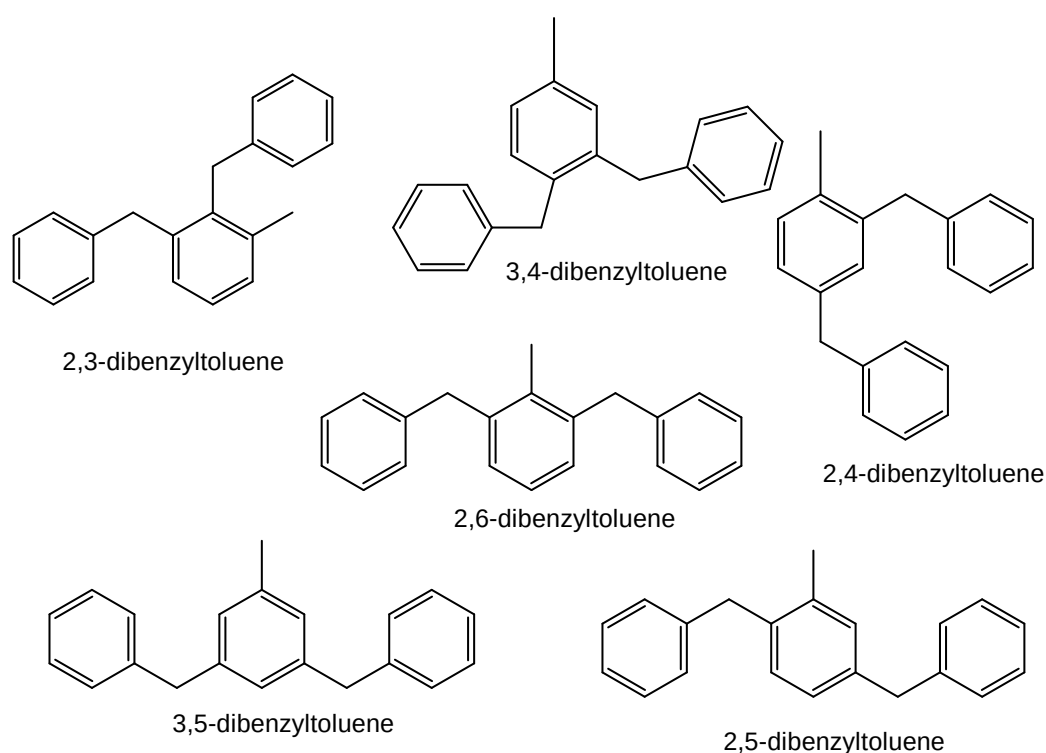


Figure 1.3. Structural isomers of technical dibenzyltoluene. Adapted from ref. [10], with permission from Elsevier.

The separation and the characterization of isomeric mixtures of H0-DBT, and the corresponding reaction mixtures, presents a challenging analytical task. One-dimensional gas chromatography coupled with mass spectrometry, customized for high-boiling-point hydrocarbon liquids, is a commonly used technique. However, peaks often overlap due to the very close boiling points of the various isomeric compounds. This then leads to inaccurate quantification data and difficulties

associated with the identification of isomers due to limited peak capacity or low separation power of the technique.

Having successfully established suitable analytical methods and protocols in this regard, Pt- and Pd-based catalysts were then evaluated, both experimentally and theoretically, by density functional theory (DFT) calculations, for the dehydrogenation of H18-DBT. This was done in an effort to ultimately select a catalyst with high catalytic activity and low by-product formation at optimum reaction conditions.

An LOHC molecule, if it is not durable or recyclable, has direct costs arising from its replacement/disposal. Therefore, it is important to know the number of hydrogenation/dehydrogenation cycles that a LOHC molecule can withstand. This was investigated by utilizing separate hydrogenation and dehydrogenation systems to determine the amount of by-products produced per cycle. Furthermore, the stress tolerance of the molecule was assessed by analysing the by-products produced due to disintegration or decomposition of the molecule at high temperature. The dehydrogenation of H18-DBT under extreme temperatures conditions—as in the case of a possible accidental increase in temperature during system operations—provides information on the stability of the molecule.

The findings that were made, and now presented in this document, should offer a valuable contribution to the good use and recyclability of a LOHC carrier, H0-DBT, which is of great importance in the economics of hydrogen storage.

1.3 Aims and objectives

The overall aim of this study was to obtain valuable information pertaining to the utilization of LOHCs for hydrogen storage, specifically, as related to the use of H0-DBT as a LOHC molecule. In this regard, the following tasks were envisaged: optimization of suitable catalytic materials for the hydrogenation/dehydrogenation reactions, assessing of the durability of H0-DBT-based LOHCs, and then determining the number of hydrogenation and dehydrogenation cycles that a H0-DBT molecule can withstand. This was to be approached by, first, investigating the most suitable characterization methods for the analysis of isomeric LOHC mixtures; second, determining the catalysts' activity in the hydrogenation/dehydrogenation reactions; and then, finally, determining the durability of the LOHC molecule, by performing hydrogenation/dehydrogenation cycles and accelerated stress tests (ASTs).

The following six specific objectives were identified.

- I. To determine existing gaps in the LOHC technology, by reviewing the following, for example: (a) hydrogen storage properties of common aromatic and heteroaromatic LOHC molecules, (b) suitable catalytic materials for the hydrogenation/dehydrogenation

reactions (noble and non-noble metal catalysts supported on metal oxides and perovskites), and (c) various reactor configurations, including the heating options used for dehydrogenation reactions. An underlying goal, throughout, was also to ascertain the maturity of LOHC technology, overall, and subsequently identify application scenarios and opportunities available within the South African hydrogen market—this falls within HySA North-West University mandate to develop hydrogen production systems as well as hydrogen storage and distribution technologies in South Africa.

- II. To develop a suitable chromatographic method for the separation, identification, and then quantitative analysis of isomeric reaction mixtures of dibenzyltoluene-based LOHCs, and to determine the effect of reaction temperature on the distribution of isomer fractions and the degree of hydrogenation (doh).
- III. To reduce the turnaround time required for obtaining dehydrogenation results for the degree of dehydrogenation (dod) when using chromatographic methods.
- IV. To evaluate (both experimentally and theoretically, by DFT calculations) Pt- and Pd-based catalysts, and then characterize monometallic catalysts Pt/Al₂O₃ and Pd/Al₂O₃, as well as the bimetallic counterparts (Pt-Pd/Al₂O₃), for the dehydrogenation of H18-DBT.
- V. To optimize the catalyst metal loading and reaction temperature, towards achieving a reasonably high dod, with a minimum amount of by-products and a high purity of hydrogen.
- VI. To determine the durability of dibenzyltoluene-based LOHCs, by performing an increasing number of hydrogenation and dehydrogenation cycles, and then carrying out ASTs.

1.4 Research methodology

The research approach to this study included the use of experimental data, theoretical DFT calculations, and the development and application of suitable characterization tools, and associated experimental conditions, to address the dehydrogenation of H18-DBT for hydrogen production. Further investigations included determining the durability of the molecule and, finally, the number of hydrogenation/dehydrogenation cycles that can be achieved (depending on the type and amount of by-products produced in the reaction).

It was therefore vitally important to develop accurate analytical methods to characterize reaction mixtures of LOHCs and, furthermore, to ultimately better understand the effect of different reaction parameters and catalysts on the dod and the stability of the LOHCs.

Two-dimensional gas chromatography coupled with time of flight-mass spectrometry (2D-GC-TOF-MS) was identified as a promising analytical tool. It was employed in this study, for the first time, due to its capability to separate complex molecules using the primary and secondary dimension columns of different selectivities. Single quadrupole-mass spectrometry

gas chromatography (GC-SQ-MS) was also to be used for the separation and identification of isomer fractions by filtering/separating chromatograms of masses of interest using the selective ion monitoring. Proton nuclear magnetic resonance spectrometry (^1H -NMR) and direct analysis in real time mass spectrometry (DART-MS) were later also utilized, as complementary techniques.

The sophisticated analytical equipment mentioned above was later applied to calibrate the less expensive and handy refractometer instrument. A calibrated refractometer provides measurements regarding the doh (i.e., available amount of hydrogen in the molecule) or the dod (i.e., the amount of hydrogen released from the molecule), at a fast turn-around time than above-mentioned equipment. This is possible because the reaction mixture samples of dibenzyltoluene based LOHC obtained at various reaction temperatures have different refractive indices and doh values. Therefore, the refractive index values can be correlated with the respective doh values to generate a calibration curve. Moreover, the use of a refractometer is less complex, and it can form an integral part of a LOHC plant, particularly in remote areas—to effectively monitor the efficiency of a plant.

In a 2D-GC-TOF-MS, a primary column (where separation is based on the boiling point of a molecular species) is coupled with a secondary column (aromatic selective) by a special interface cryogenic modulator. This 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. In GC-SQ-MS, chromatograms of masses of interest are gathered by the SIM mode of the quadrupole. This method only responds to compounds that possess the selected mass fragments. The GC separation columns are selected based on the properties of the LOHC molecules (e.g., boiling point, type of isomers, and polarity). Thereafter, with several iterations of operating parameters (e.g., injection temperature, oven temperature program, split ratio), a suitable chromatographic method can be created.

To assess the methods, H18-DBT was dehydrogenated using a Pt/Al₂O₃-loaded horizontal plug flow reactor at temperatures ranging from 270 to 300 °C, to intentionally produce reaction mixtures that have different dod values. Samples of the obtained reaction mixtures were analysed to determine the effect of temperature on the distribution of isomers and the dod. The peak areas of chromatograms were used for quantification. The molecular ion peaks and the software library (NIST) were used to predict the identity of the molecules. Moreover, the refractive index of known LOHC samples was collected and a calibration of refractive index vs. the doh plotted. A compact refractometer provides results within 30 sec, which is much faster than what can be achieved with the state-of-the-art equipment mentioned earlier. ^1H -NMR and DART-MS data confirmed the results obtained using the chromatography techniques.

Evaluation of the catalytic activity of monometallic ($\text{Pt}/\text{Al}_2\text{O}_3$, $\text{Pd}/\text{Al}_2\text{O}_3$) and bimetallic ($\text{Pt-Pd}/\text{Al}_2\text{O}_3$) catalysts for the dehydrogenation of H18-DBT was performed using a batch reactor. The best performing catalyst was then used to further investigate the effect of metal loading (0.5, 1 and 2 wt %) on the dehydrogenation of H18-DBT. The optimum metal loading was selected, followed by an investigation into the effect of temperature on the dehydrogenation of H18-DBT, the formation of by-products (if any), and ultimately the purity of the hydrogen produced. A gas chromatograph equipped with a thermal conductivity detector was used for the analysis of hydrogen purity.

The reusability of the catalyst was also determined, by performing several runs of H18-DBT dehydrogenation. In a further step, ab initio density functional theory (DFT) calculations were used to investigate the dehydrogenation of H18-DBT on Pt, Pd and bimetallic Pt-Pd catalyst surfaces. Using the surface favoured for H18-DBT adsorption, i.e., the 110 surface, the reaction for hydrogen removal/abstraction was calculated using a dispersion-corrected DFT method, as implemented in the plane-wave code Quantum ESPRESSO.

Information on the catalysts' chemical and textural properties was obtained using various characterization techniques: temperature programmed reduction, CO pulse chemisorption, Brunauer–Emmett–Teller (BET) surface area analysis, inductively coupled plasma atomic emission spectroscopy, and transmission electron microscopy.

Hydrogenation and dehydrogenation reactions were performed repeatedly, to recycle a specific volume of a H0-DBT-based LOHC, and then determine the rate of by-product formation per cycle. A by-product formation equation can be used to determine the number of cycles that the molecule can tolerate. This is based on the lower and upper limits of the permissible amount of by-products.

Finally, in an effort to predict the time-to-failure of the LOHC molecule H18-DBT under standard operating conditions, ASTs were performed for the dehydrogenation of H18-DBT at extremely high temperatures. Tests were performed using a Ni-packed fixed bed reactor (downflow option) system for hydrogenation and a batch reactor system loaded with $\text{Pt}/\text{Al}_2\text{O}_3$ for dehydrogenation.

1.5 Thesis outline

This thesis comprises six chapters. The chapters 2 to 5 describe work that has already been published, in peer-reviewed journals. In this thesis document, these chapters (and the references) are presented in the format as required by the respective journals. The first chapter provides an overall introduction to the subject field, motivation for the study and the envisaged objectives. In the final chapter, conclusions are presented, and recommendations made for future research.

Chapter 1: This chapter presents an overall introduction to the entire study/document—although each of the middle chapters (the 'experimental' chapters) has its own specific introduction section

to the specific area of the work addressed in the respective chapters. Chapter 1 includes the following subsections: a background to the study, the research problem and purpose of the study, the overall aim and six specific objectives, the applied research methodology and, finally, an explanation of the layout/presentation of this thesis.

Chapter 2: This chapter provides a detailed literature review on dehydrogenation catalysts, dehydrogenation reaction conditions, and the types of reactors used for the dehydrogenation of specific LOHC molecules. A market survey was performed to identify active industry players in the hydrogen generation market, globally, and to determine the most recent developments pertaining to LOHC technology. Furthermore, opportunities within the South African hydrogen market were identified. The content of Chapter 2 is as published (together with other authors) in the journal *Energy & Fuels*: 2019, 33, 2778–2796.

Chapter 3: This chapter describes the development of suitable analytical GC/MS methods, required for obtaining insight into the effects of the dehydrogenation temperature on the distribution of isomer fractions in a H18-DBT reaction mixture and on the doh. Specifically, the following techniques were developed and applied: 2D-GC-TOF-MS and GC-SQ-MS. ^1H -NMR and DART-MS analyses were also used, as complimentary techniques. The content of Chapter 3 is as published (together with other authors) in the journal *International Journal of Hydrogen Energy*: 2018, 43(11), 5620–5636.

Chapter 4: This chapter describes an experimental evaluation of monometallic ($\text{Pt}/\text{Al}_2\text{O}_3$) and bimetallic ($\text{Pt-Pd}/\text{Al}_2\text{O}_3$) catalysts for the dehydrogenation of H18-DBT, using a batch reactor set-up, and then determining the effects of the catalyst loading and reaction temperature. This was followed up with theoretical DFT calculations, to evaluate the Pt- and Pt–Pd-based catalysts, for the dehydrogenation of H18-DBT. In this regard, furthermore, the catalysts' particle size, metal dispersion, metallic surface area, BET surface area and pore volume were determined. The purity of released hydrogen was quantified, and the reaction mixture obtained from the dehydrogenation reaction analysed for the presence of by-products. The content of Chapter 4 is as published (together with other authors) in the journal *International Journal of Hydrogen Energy*: 2019, 44(39), 21926–21935.

Chapter 5: The work described in this chapter addresses, first, the use of a fixed bed reactor system packed with Ni-based catalyst and its optimization for the hydrogenation of pure H0-DBT. Thereafter, the number of hydrogenation and dehydrogenation cycles achieved was estimated. Accelerated stress testing was utilized to predict the time to failure, and the extent of failure of the LOHC molecule. The content of Chapter 5 is as published (together with other authors) in the journal *Sustainable Energy & Fuels*: 2020, 4(9), 4662–4670.

Chapter 6: This, the final chapter, first refers back to Chapter 1—more specifically, to the objectives of the project in its entirety, as stated (Section 1.3). I present the conclusions, based on my findings throughout this study, and highlight the importance of various findings of the study. Then, the chapter is closed with a few/selected recommendations for future work in this field.

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CHAPTER 2: THE PROSPECT OF HYDROGEN STORAGE USING LIQUID ORGANIC HYDROGEN CARRIERS

This chapter is a version of the article published in *Energy & Fuels*, 33(4), 2778–2796. <https://doi.org/10.1021/acs.energyfuels.9b00296>, and adapted for the thesis style, as well as permission was granted in both print and electronic format.

OVERVIEW

Technical developments in the field of LOHCs are reviewed and the focus is on discussing, LOHC technology concept, properties of different LOHC molecule systems, development of catalytic materials including by application of density functional theory (DFT) modelling, different reactor configurations and heat integration options. Furthermore, the main market characteristics and opportunities for the LOHC technology are discussed as well. The process of hydrogen storage and release can take place by utilising 1) separate hydrogenation and dehydrogenation systems 2) the two-in-one reactor system. Dibenzyltoluene is found to be the most preferred LOHC molecule due to its unique hydrogen storage properties. For better gas and liquid separation, a horizontal fixed bed reactor packed with egg-shell type of a catalyst ($\text{Pt}/\text{Al}_2\text{O}_3$) is preferred for dehydrogenation of perhydrodibenzyltoluene. From a thermodynamic point of view, hydrogen storage in LOHC systems requires an exothermic hydrogenation step and an endothermic dehydrogenation step. However, a stable and durable LOHC molecule is required to withstand many charging/discharging cycles. Catalytic materials need to be further developed towards highly efficient dehydrogenation reaction with minimum by-products formation. Hence, DFT techniques are also used to determine adsorption energies and to identify rate-determining steps in the LOHC conversion processes. Other areas of development include optimisation of reaction conditions and modification of catalyst and support material e.g., metal loading, chemical and textural properties. Furthermore, Industrial implementation of the LOHC technology has commenced but it is still in the early stages. Related to this, we have identified promising application scenarios for the South African energy market.

2.1 Introduction

Renewable energy sources such as wind and solar are seen as alternatives to fossil-based fuels. However, wind and solar are not stable, they fluctuate, hence there is a need for energy storage systems that can assist in stabilizing such fluctuations. There are various types of energy storage systems. These can be classified as electrochemical (batteries) [1], chemical (hydrogen systems: metal hydrides, metal organic frameworks, ammonia, etc.) [2], potential (pumped storage hydropower) [3], kinetic (flywheels) [4], magnetic (superconductors) [5] and latent heat thermal

energy storage (molten salt) [6] (see Figure 2.1). These energy storage systems (under listed categories) generally have their own limitations. Battery technology is mature and has been widely used for stationary and mobile power applications. However, the relatively short life cycle of batteries could lead to high replacement costs and the requirement for recycling processes. Moreover, redox flow batteries use toxic electrolytes that could impose severe health hazards, coupled with a large carbon footprint and low power density [7,8]. Chemical-based storage systems (e.g., metal hydrides, metal organic frameworks, etc.) have low gravimetric and volumetric storage densities. Pumped storage hydropower is also a mature technology; however, it is limited to specific locations and its lead time is long (~10 years for new plants). The high self-discharge associated with flywheels and low energy density associated with superconductors limit their intended purpose of supplying energy.

Amongst other energy sources, such as fossil-based fuels, hydrogen is regarded as a clean energy carrier for a variety of fuel cell applications, such as stationary, mobile, and portable power applications, which can be utilized without greenhouse gas emissions [9–11]. In this regard, a future “hydrogen economy” is an alternative scenario to the steadily expanding utilization of carbon-based fuels [12]. One of the factors delaying rapid transition to the hydrogen economy is the lack of suitable hydrogen storage systems [13]. Despite hydrogen being a clean energy carrier, its low volumetric density (0.08988 g/L at 1 atm) makes it challenging to store [14]. The storage of hydrogen and the refuelling infrastructure it requires can be an impediment to its fast adoption as an alternative fuel.

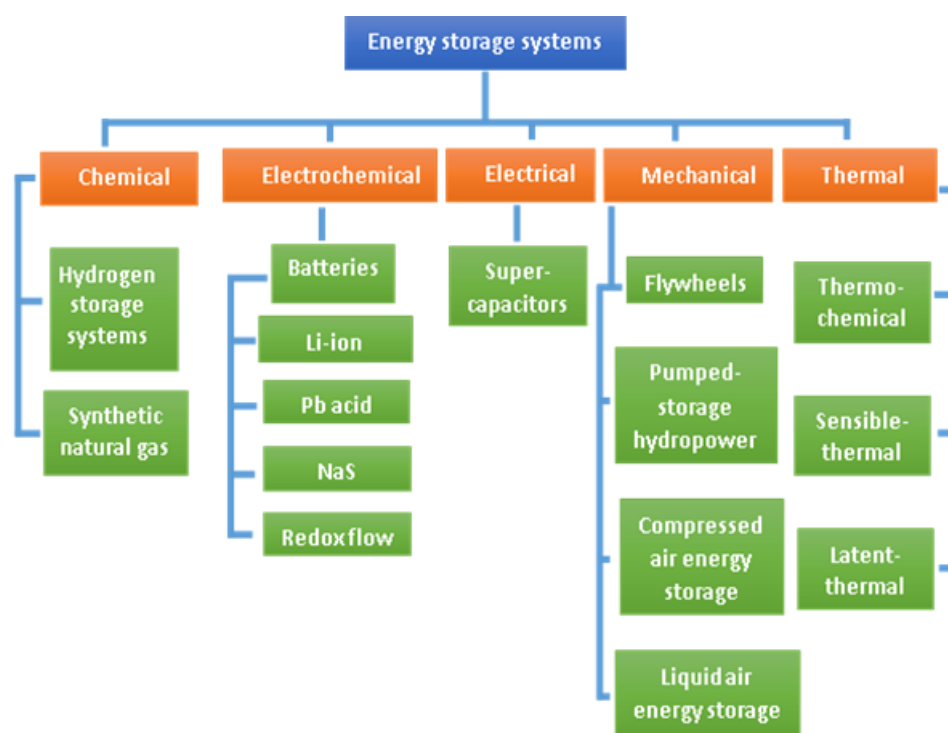


Figure 2.1: Classification of energy storage systems [15].

The challenges associated with conventional hydrogen storage, such as compression and liquefaction technologies, include safety concerns, low storage density, transportation, boil-off losses and relatively high costs [16]–[20]. An alternative option that has gained interest for the storage and transportation of hydrogen in a way that counters the abovementioned challenges is the use of liquid organic hydrogen carrier (LOHC) systems [21].

A LOHC system consists of a pair of one hydrogen-lean organic compound (LOHC–) and one hydrogen-rich organic compound (LOHC+). Hydrogen is stored by converting LOHC– into LOHC+ in a catalytic hydrogenation reaction. Hydrogen is released by converting LOHC+ into LOHC– in a catalytic dehydrogenation reaction [22,23]. An example of how an LOHC system can be integrated into an existing energy infrastructure is shown in Figure 2.2, where a renewable energy source is used to produce hydrogen through electrolysis, followed by the storage of the produced hydrogen using LOHC technology. In an LOHC+ compound, hydrogen can be stored for a very long time without self-discharge, thus favouring seasonal energy storage and transportation to remote areas where dehydrogenation can be performed [24]. This process is reversible and allows rapid hydrogenation and dehydrogenation without consumption of the compounds forming the LOHC system—only hydrogen is released [25–27].

To date, the most studied aromatic and heteroaromatic LOHC based compounds (both hydrogenated and unhydrogenated) include, but are not limited to, benzene and cyclohexane (CHE) [28,29], toluene and methylcyclohexane (MCH) [30–32], naphthalene and decalin [33,34], N-ethylcarbazole and perhydro-N-ethylcarbazole (H0-NEC and H12-NEC) [35,36], dibenzyltoluene and perhydrodibenzyltoluene (H0-DBT and H18-DBT) [37,38].

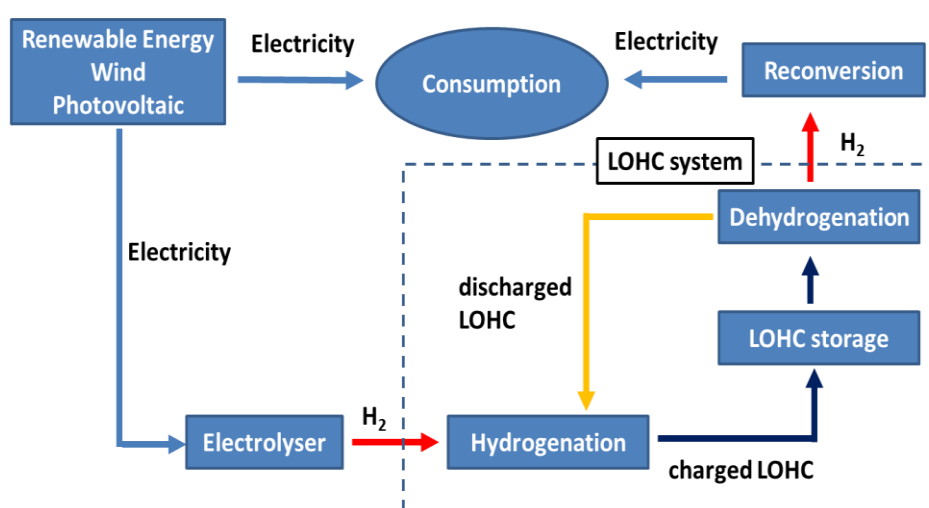


Figure 2.2: Renewable energy storage concept using LOHC technology [39].

This review provides important information about LOHC properties, including the relevant catalytic reactions, catalysts and support materials, and catalyst efficiencies expressed in terms of hydrogen productivity or the degree of dehydrogenation (dod). It expands on earlier reviews

published on the same topic [27,40,41] by presenting practical application examples of the LOHC technology. Moreover, new theoretical approaches, for example, the use of *ab initio* calculations to investigate physico-chemical properties of LOHC systems, and catalysts involved in LOHC hydrogenation and dehydrogenation, are reported. Furthermore, since some understanding of the hydrogen markets can assist in identifying areas where the LOHC technology can be implemented, we describe potential applications in South Africa in the mining and hydrogen logistics industries, and for energy supply at remote areas or rural communities.

2.2 Characteristic properties of known LOHC systems

The following guidelines apply for the choice of suitable LOHC compounds, catalysts, and reaction conditions. This information is based on the reports of several research groups who have introduced the most well-known LOHC systems to the literature.

A good LOHC system should be characterized by as many of the following properties as possible:

- Low melting point ($< -30\text{ }^{\circ}\text{C}$) of all compounds involved [42], and high boiling point ($> 300\text{ }^{\circ}\text{C}$) for simple hydrogen purification by LOHC condensation [42];
- High hydrogen storage capacity ($> 56\text{ kg/m}^3$ or $> 6\text{ wt } \%$)
- Low heat of desorption ($42\text{--}54\text{ kJ/mol-H}_2$) to enable low dehydrogenation temperatures, against 1 bar hydrogen pressure (e.g., $< 200\text{ }^{\circ}\text{C}$) [42];
- Ability to undergo very selective hydrogenation and dehydrogenation for long life cycles of charging and discharging;
- Compatibility with today's infrastructure for fuels;
- Low production costs and technical availability;
- Toxicological and eco-toxicological safety [43] during transportation and use (i.e., not classified as "dangerous goods").

In the case of volatile LOHCs that may induce impurities into the hydrogen released, purification methods such as pressure swing adsorption technology equipped with hydrocarbon condensers could be integrated into the system to provide high purity hydrogen. It is fair to state that none of the known LOHC systems now discussed below are able to fulfil all of these desirable properties completely.

2.2.1 Cyclohexane – Benzene

Figure 2.3 shows the hydrogenation reaction of benzene and the dehydrogenation of cyclohexane (CHE) to establish a LOHC system.

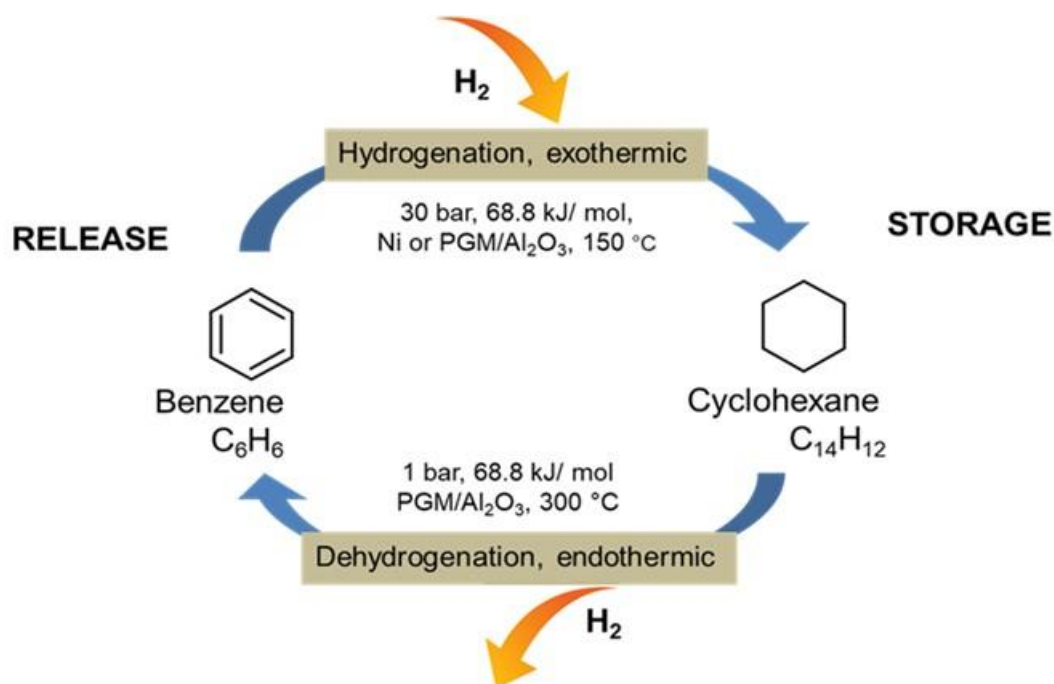


Figure 2.3: Schematic representation of the LOHC system benzene/cyclohexane.

The LOHC compound CHE has a hydrogen storage capacity of ± 7.19 wt % and it is a liquid at room temperature (mp 6.47 °C) [44,45]. However, CHE is flammable and its low boiling point (81 °C) makes its practical use for the release of high-quality hydrogen challenging. Moreover, the reaction product benzene is highly toxic. Nonetheless, a significant amount of work has been carried out to evaluate the dehydrogenation of CHE, in particular with respect to the applied catalyst.

Biniwale et al. used Ni supported on activated carbon cloth (ACC) (20 wt % Ni/ACC) as a catalyst for the dehydrogenation of CHE in a spray-pulsed reactor (SPR) at 300 °C [46]. Their 20 wt % Ni/ACC catalyst was compared with other catalysts, 0.5 wt % Pt/ACC and also a Pt-promoted Ni catalyst (20 wt % Ni/ACC + 0.5 wt % Pt). Results indicated that bimetallic Ni/Pt activity (12.75 mmol/g_{cat}/min) was 60 times higher than monometallic Pt/ACC activity (0.21 mmol/g_{cat}/min) and 1.5 times higher than that of 20 wt % Ni/ACC (8.5 mmol/g_{cat}/min). Furthermore, when bimetallic Ni/Pt was used, the hydrogen selectivity improved from 98.8% to 99.7%. Other examples of the enhanced efficiency of bimetallic catalysts in CHE dehydrogenation have been reported for the use of Ag-based catalysts. For example, Biniwale et al. made progress in improving CHE dehydrogenation activity with 10 wt % Ag supported on ACC, using the same reactor and reaction temperature as mentioned above [46]. The 10 wt % Ag/ACC catalyst was improved by adding noble metals (1 wt % Pt, Pd, Rh). According to Biniwale and co-workers, improved catalyst performance was also obtained when other noble metal catalysts were added [47]. When using the Pt-promoted catalyst 10 wt % Ag/ACC + 1 wt % Pt (14.2 mmol/g_{met}/min), double the hydrogen production rate (HPR) was obtained, compared with the rate achieved with the 10 wt % Ag (6.8 mmol/g_{met}/min) catalyst.

Xia et al. [48] carried out further investigations with bimetallic catalysts, such as using Ni-Cu/SiO₂ catalyst (17.3 mol % Ni, 3.6 mol % Cu) for CHE dehydrogenation. Here, a plug flow reactor (PFR) system was used at 250 °C. At this temperature, a HPR of 58 mmol/h/g_{cat} was obtained. CHE conversion and benzene selectivity were 95.0% and 99.4%, respectively. Furthermore, when the temperature was increased to 350 °C, the HPR decreased to 54 mmol/h/g_{cat}, CHE conversion decreased to 87.8% and benzene selectivity increased to 99.9%. The HPR for CHE dehydrogenation was also improved when the catalyst Ni-Cu/SBA-15 (4.9 wt % Ni, 3.5 wt % Cu) was used in a PFR system at 325 °C. A HPR of 61 mmol/h/g_{cat} and CHE conversion of 99.7% was realized with a benzene selectivity of 99% [49]. Kariya et al. carried out their CHE dehydrogenation experiments in a batch-type reactor at 300 °C [50]. The 2 wt % Pt/activated carbon (AC) and 3.82 wt % Pt/Al₂O₃ catalysts gave 910 mmol/g_{met}/min and 1800 mmol/g_{met}/min, respectively. These results indicated that an increase in metal loading, the application of bimetallic catalysts, and the use of noble metals as catalysts and promoters can lead to improved hydrogen productivity.

2.2.2 Methylcyclohexane – Toluene

Figure 2.4 shows the hydrogenation reaction of toluene and the dehydrogenation of methylcyclohexane (MCH) to establish a LOHC system.

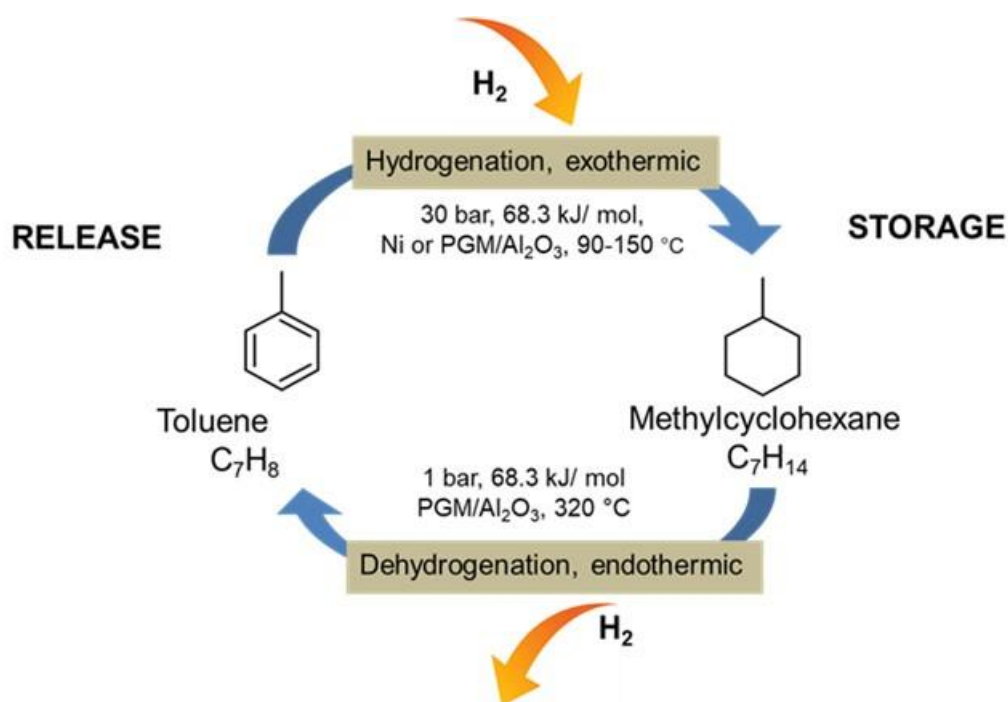


Figure 2.4: Schematic representation of the toluene/methylcyclohexane LOHC system.

The LOHC compound MCH has a hydrogen storage capacity of 6.2 wt % and it is a liquid at ambient conditions. Figure 2.5 gives some important insight to the thermodynamics of the toluene/MCH LOHC system, showing the equilibrium conversion of MCH as a function of

temperature for various pressures. The here presented picture is architypical for many pure hydrocarbon LOHC systems. The lower the pressure, the lower the temperature that allows full conversions of MCH to toluene. Thus, from a thermodynamic point of view, the lowest possible system pressure is to be chosen for dehydrogenation. However, this is not always beneficial for the catalyst and can favour side reactions and catalyst deactivation.

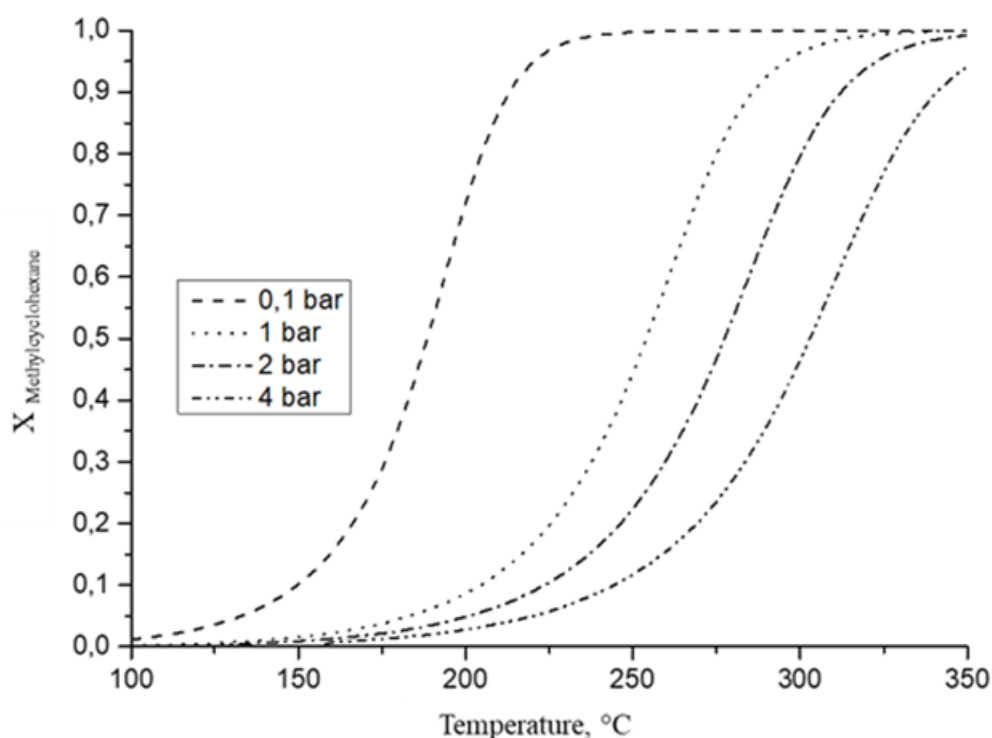


Figure 2.5: Equilibrium conversion as a function of system temperature for various system pressures in the dehydrogenation of MCH to toluene, calculated with AspenTech AspenPlus 7.2, UNIQUAC model.

Taking into consideration the temperatures typically required for dehydrogenation, the dehydrogenation of MCH (bp 100.9 °C) is a gas-phase reaction. MCH is nonetheless an attractive LOHC compound, as is evident from the development activities of the Japanese company Chiyoda Corporation. Chiyoda coined the name SPERA Hydrogen® Technology for their LOHC activities and has commissioned a demonstration plant. Chiyoda has also published details on their dehydrogenation catalyst and its manufacturing process. Okada et al. employed a pH swing method to control the pore distribution of their alumina supports in efforts to obtain the best catalyst for this process [51]. They claimed that pore-control improves the dispersion of the applied Pt precious metal. The Chiyoda demonstration plant has been reported to dehydrogenate MCH with a production rate of 50 Nm³/h (140 kW, based on the lower heating value (LHV) of the released hydrogen) at a MCH conversion >95% and a toluene selectivity >99% [52]. Other researchers, such as Zhu et al., applied mixtures of different support materials to effectively increase the catalyst performance [53]. They used Ni on a Al₂O₃-TiO₂ hybrid composite and

compared the catalyst performance with that of Ni on Al_2O_3 alone. They found that $\text{Ni}/\text{Al}_2\text{O}_3\text{-TiO}_2$ exhibited better performance; MCH conversion was 99.9% at 400 °C, whereas it was 16.5% with $\text{Ni}/\text{Al}_2\text{O}_3$, under the same conditions.

Several other catalyst supports have also been evaluated and show promise. Shukla et al. evaluated metal oxides La_2O_3 , ZrO_2 , TiO_2 , CeO_2 , Fe_2O_3 , Al_2O_3 , MnO_2 and perovskite ($\text{La}_{0.7}\text{Y}_{0.3}\text{NiO}_3$) catalyst supports for MCH dehydrogenation [54]. Their findings revealed that Pt supported on $\text{La}_{0.7}\text{Y}_{0.3}\text{NiO}_3$ exhibited high activity and 100% selectivity for the dehydrogenation of MCH. The productivity increased from 21.1 mmol/g_{met}/min (with Pt/ La_2O_3) to 45 mmol/g_{met}/min (with Pt/ $\text{La}_{0.7}\text{Y}_{0.3}\text{NiO}_3$). This evaluation of catalyst supports was carried out using a SPR at 350 °C. They also compared the use of Pt/ V_2O_5 and Pt/ Y_2O_3 in the dehydrogenation of MCH using the above-mentioned reactor at 350 °C [55]. The Pt/ Y_2O_3 yielded 98% toluene because Y_2O_3 can also be used as a dehydrogenation catalyst. Zhang et al. used pyrolysis char from scrap tyres as catalyst support for platinum, 1 wt % Pt/carbon black (CB) and claimed >95% MCH conversion and almost 100% selectivity towards toluene in a fixed bed reactor (FBR) at 300 °C [56]. The Pt/CB catalyst had a HPR of 342 mmol/g_{met}/min, which is higher than the results reported earlier by Shukla et al. (45.76 mmol/g_{met}/min for 1 wt % Pt/ $\text{La}_{0.7}\text{Y}_{0.3}\text{NiO}_3$).

Boufaden et al. evaluated bimetallic Pt/Mo- SiO_2 catalysts with a constant Pt loading of 5 wt % and a Mo loading varying from 4.1 to 12.7 wt % for the dehydrogenation of MCH [57]. The performances of the Pt/Mo(x)- SiO_2 catalysts were determined in a downflow FBR at 400 °C and 2.2 MPa. The catalyst with a Mo loading of 8.0 wt % was the most active and gave >80% selectivity towards toluene. This catalyst performance was attributed to the high dispersion of the Pt on the MoO_2 phase.

A palladium membrane reactor (PMR) is known to be dual functional—it acts as a reactor and as a hydrogen purification system. Gora et al. used a PMR for the dehydrogenation of MCH at 225 °C, using 1 wt % Pt/ Al_2O_3 as a catalyst [58]. Conversion of 70% was achieved at 225 °C, whereas about 245 °C was required to obtain the same conversion when the palladium membrane was not employed. Therefore, continuous and selective removal of hydrogen by using a PMR promotes high conversion of the reactant at lower dehydrogenation temperature compared to the conventional FBR. Instead of a palladium membrane, porous alumina coated with enamel was used to stop gas permeation. Wang et al. performed the dehydrogenation of CHE and MCH at 315 °C using a FBR [59]. They claimed that Pt supported on stacked-cone carbon nanotubes (1 wt % Pt/SC-CNT and 0.25 wt % Pt/SC-CNT) had similar activity to 1 wt % Pt/ Al_2O_3 ; all gave >90% conversion and 100% selectivity. These studies indicated that catalyst activity can be enhanced in various ways, including using a mixture of different supports, which is in fact a combination of different textural properties. Related to this, some bimetallic catalysts have been found to outperform their monometallic counterparts, of course with screening to obtain the best metals and proper stoichiometric ratios of bimetals [47, 48]. Therefore, a catalyst made of bimetals and a

mixture different supports could effectively improve both the catalytic activity and selectivity. The catalyst supports $\text{La}_{0.7}\text{Y}_{0.3}\text{NiO}_3$ and Y_2O_3 are more effective than most well-known metal oxide supports [54]. Interestingly, catalysts supported on carbon-based materials are even more effective than $\text{La}_{0.7}\text{Y}_{0.3}\text{NiO}_3$ and Y_2O_3 as already indicated.

2.2.3 Decalin – Naphthalene

Figure 2.6 shows the hydrogenation of naphthalene and the dehydrogenation of decalin to establish a LOHC system.

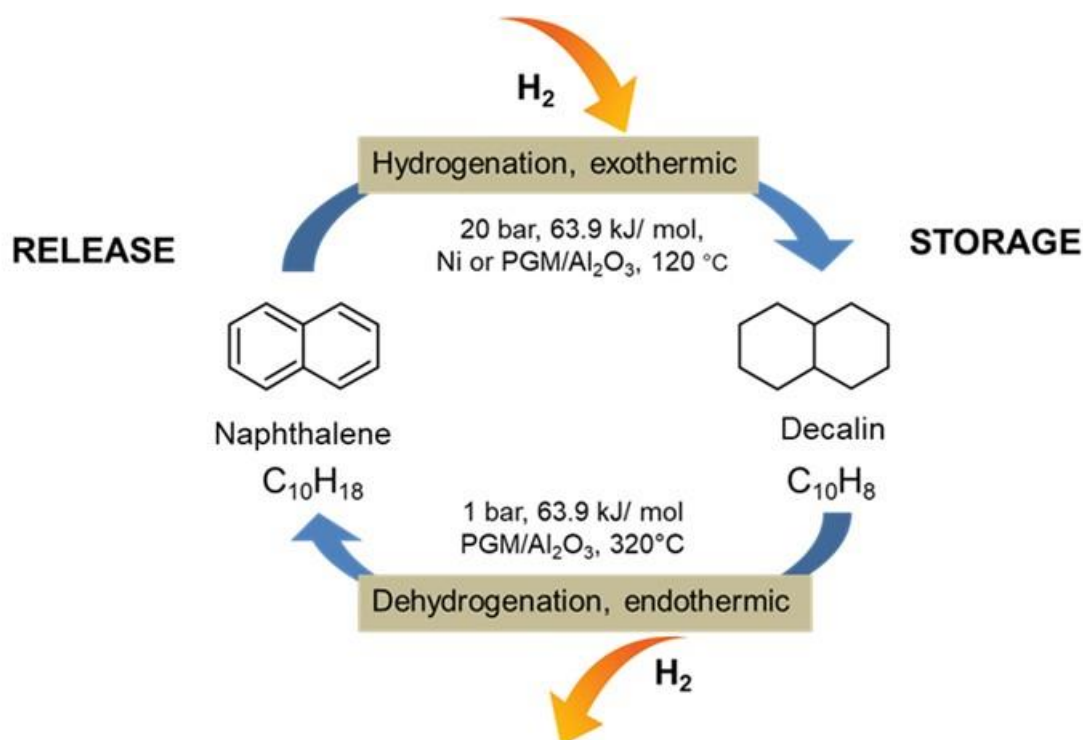


Figure 2.6: Schematic representation of the naphthalene/decalin LOHC system.

The hydrogen storage capacity of decalin is 7.3 wt % ($64.8 \text{ kg-H}_2/\text{m}^3$) [60]. However, here the challenge lies in the fact that the melting point of the hydrogen-lean dehydrogenation product (naphthalene) is high (80°C). Naphthalene is a solid at ambient conditions. On the other hand, the dehydrogenation reaction of decalin to naphthalene is known to be irreversible [61]. The irreversibility of the dehydrogenation step has negative effects on the LOHC cycling and, for this reason, a new batch of material is required for each cycle. Other than the advantage of high hydrogen storage density, the challenges mentioned makes the molecule unsuitable for hydrogen storage and transportation. Research continues, nonetheless, to try to solve these challenges.

In efforts to develop an appropriate catalyst and optimize the process of decalin dehydrogenation, Suttisawat et al. compared microwave and electrical heating mechanisms, at 320°C , using a FBR [62]. The catalyst 1 wt % Pt on active carbon was used in both instances. Decalin conversion decreased from 85% to 10% (electrical heating) and to 13% (microwave heating). The catalyst contact time for high and low conversions was 30 and 260 min, respectively.

They reported the loss in activity at long catalyst contact time to be due to Pt sintering at high temperature. Therefore, high initial conversions could be due to less sintered particles at short contact times (30 min). To avoid this problem, Sn was used as a catalytic promoter for Pt/AC. Decalin conversion for both heating mechanisms then stabilized at 74%, and selectivity towards naphthalene was 90%. This clearly indicated that neither the electrical nor the microwave method improved the reaction activity. Sn modifies Pt electronically by donating electrons to the holes of the 5d band of a Pt atom [62]. Due to this electronic effect, C–C bond cleavage does not occur on the catalyst surface. This reduces carbon deposition and improves adsorption and desorption of reactants and products [62]. Moreover, the geometric effect of Sn prevents sintering and agglomeration of Pt. In this case, Sn plays a major role in improving the selectivity and activity of Pt.

Catalysts can be prepared in many ways, where the method of preparation influences the catalyst performance. Lee et al. compared catalysts prepared by conventional (precipitation and impregnation) and advanced (ion exchange and polyol) methods for the dehydrogenation of decalin [63]. The catalyst used for these tests was 3 wt % Pt supported on carbon. Performance evaluation was carried out using a batch-type dehydrogenation reactor under reflux conditions. Table 2.1 shows that the catalysts prepared by advanced methods (ion exchange and polyol) contain highly dispersed Pt particles, which improved the hydrogen productivity. The higher the Pt dispersion is the higher is the metallic surface area for the reaction to take place.

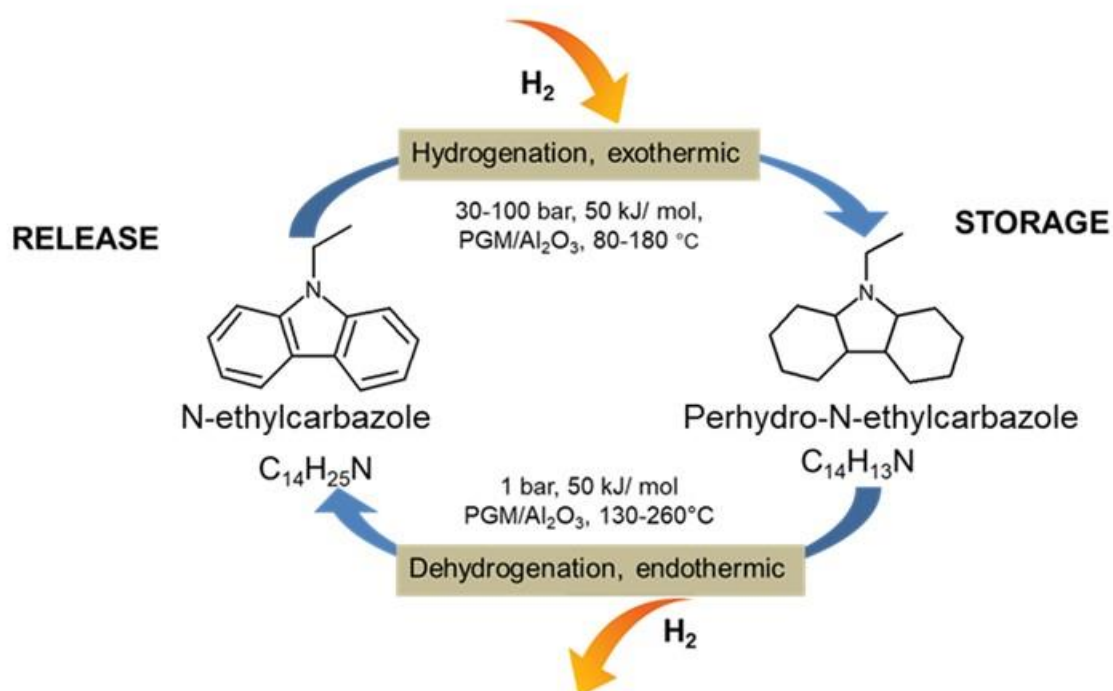
Moreover, Sebastián et al. proved that Pt supported on ordered mesoporous carbon has higher initial catalytic activity (220 mmol/gPt/min) for decalin dehydrogenation, compared with Pt supported on carbon nanofibers, carbon black, carbon xerogel and AC [64]. This high catalyst activity is relative to the high surface area (930 m²/g) of ordered mesoporous carbon. However, at prolonged operation times, catalyst deactivation occurs due to the blockage of active sites. The catalyst supports used are characterized by narrow pores, hence the pores become blocked by naphthalene and tetralin since they are bulkier. A support with wider pores, such as carbon black (9.6 nm), showed consistency in terms of activity at prolonged operation times, regardless of the low initial activity (100–140 mmol g/Pt/min). These experiments were performed using a batch reactor at 260 °C. The catalyst support can be optimized depending on the size of the reactant molecule. For example, bulkier molecules would require a support material with wider pore diameter for the molecules to be readily to enter the pores, so that the reaction can take place.

Table 2.1: Catalyst performance evaluation based on method of preparation

Preparation method	Pt dispersion %	Productivity mmol/g _{Pt} .min
Polyol	14	42.5
Ion-exchange	19.6	45.4
Precipitation	10	38.2
Impregnation	5.4	27.3

2.2.4 Perhydro-N-Ethylcarbazole – N-Ethylcarbazole

Figure 2.7 shows the hydrogenation of N-ethylcarbazole (H0-NEC) and the dehydrogenation of perhydro-N-ethylcarbazole (H12-NEC) to establish the corresponding LOHC system.

**Figure 2.7: Schematic representation of the H0-NEC/H12-NEC LOHC system.**

A patent by Pez et al. (Air Products) discusses the screening of a wide range of heteroaromatic compounds as LOHC systems [65]. According to their evaluation, the most interesting compound was H12-NEC, due to the low energy required for dehydrogenation (50 kJ/mol) and its relatively high hydrogen storage capacity (5.8 wt %). To store hydrogen, H0-NEC is hydrogenated to form hydrogen-rich H12-NEC. Unfortunately, H0-NEC is a solid (mp 68 °C). Hence, the use of other N-alkylcarbazole derivatives with lower melting points but similar hydrogen storage densities has also been proposed [66]. Another drawback of carbazole-derived

LOHC systems is the chemical lability of the N-alkyl bond, leading to decomposition reactions at temperatures $>270\text{ }^{\circ}\text{C}$ [67]. Von Wild et al. improved the H12-NEC dehydrogenation efficiency obtained in packed bed reactors by using a microchannel reactor (MR) [68]. This was possible because small transport distances in the MR enhance internal and external mass and heat transfer without causing additional pressure drop in the reactor. In this way, productivity was improved from $0.2\text{ gH}_2/(\text{gPt min})$ in the packed bed reactor to $1.5\text{ gH}_2/(\text{gPt min})$ in the MR, at a comparable H12-NEC conversion of 90% [68].

Yet another development to improve mass and heat transport in a LOHC dehydrogenation reactor has been reported by Peters et al. [69]. They applied selective electron beam melting (SEBM) technology to produce structured reactors for the dehydrogenation of H12-NEC. A metallic structure optimized for a high surface and low-pressure drop was coated with a $\text{Pt}/\text{Al}_2\text{O}_3$ washcoat by either a spray or dip coating method. The high heat conductivity of the metal core provided excellent heat transport from the wall of the reactor to the active catalytic sites placed in the thin and porous coating layer on the metal struts. The concept was tested using single reactor structures and a 10-fold parallel reactor setup. The highest achievable performance (productivity) from a single monolith reactor was $1.27\text{ gH}_2/(\text{gPt min})$ at a feed flow of 4 ml/min and reaction temperature of $260\text{ }^{\circ}\text{C}$. The 10-fold parallel reactor prototype gave a hydrogen flow of $9.8\text{ NL H}_2/\text{min}$ at a feed flow of 30 ml/min and reaction temperature of $250\text{ }^{\circ}\text{C}$. The power densities of a single reactor and ten reactors were 4.32 kW/L and 3.84 kW/L , respectively [69]. Figure 2.8 shows the hydrogen release unit prototype, with ten parallel and vertical reactors for the dehydrogenation of H12-NEC [69].

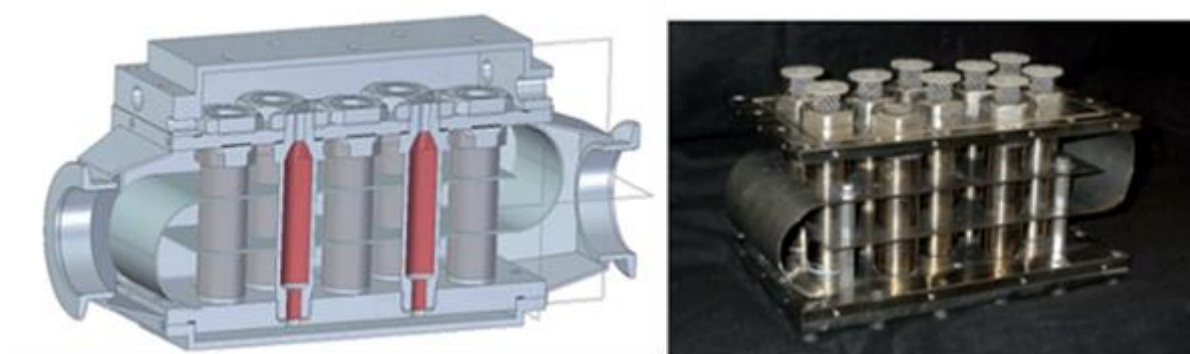


Figure 2.8: Hydrogen release unit prototype showing 10 parallel and vertical reactors for dehydrogenation of perhydro-N-ethylcarbazole. Left: Virtual 3D, showing passage of hot air for heating the reactors. Adapted from ref. [69], with permission from The Royal Society of Chemistry.

Peters et al. also investigated the influence of pore diffusion on the dehydrogenation rate. For this purpose, they prepared eggshell-based catalyst systems with different thicknesses ($22\text{--}88\text{ }\mu\text{m}$) of active Pt-containing shells on a spherical Al_2O_3 support [70]. A downflow tubular reactor was used. They found that an eggshell catalyst (Pt on alumina) with a shell thickness of $33\text{ }\mu\text{m}$

performed better than catalysts with other shell thicknesses, at 260 °C. Under these optimized conditions, the observed hydrogen productivity was 10.9 gH₂/gPt/min at partial hydrogen release (the product still contained 79.1% hydrogen loading). Nevertheless, this hydrogen release rate is impressive as it relates to 21.7 kW power/g (Pt) based on the lower heat value of the released hydrogen. Moreover, it was found that even at very thin catalyst layers (24 μm), the kinetic regime was limited to <235 °C. Above this temperature, pore diffusion effects clearly limited the achievable rate of dehydrogenation.

Optimization of the metal catalyst for the dehydrogenation of H12-NEC was also addressed by Yang et al. [71]. Alumina-supported metals such as Pt, Pd, Rh and Ru with equal loading (~5 wt %) were evaluated for H12-NEC dehydrogenation at 180 °C using a batch reactor system. At this temperature, catalyst performance was found to be in the order Pd>Pt>Ru>Rh. Sotoodeh and Smith [72] used 5 wt % Pd/SiO₂ and obtained 100% conversion of H12-NEC and 60% hydrogen yield (with formation of the intermediates H8-NEC and H4-NEC) at 170 °C. Indications were therefore that Pd was the best catalyst for H12-NEC dehydrogenation at temperatures <200 °C. Above this temperature, Pt is the best catalyst; however, at higher temperatures H12-NEC is prone to dealkylation.

2.2.5 Perhydrodibenzyltoluene – Dibenzyltoluene

The LOHC system established by hydrogenation of dibenzyltoluene (H0-DBT) and by dehydrogenation of perhydro-dibenzyltoluene (H18-DBT) is shown in Figure 2.9.

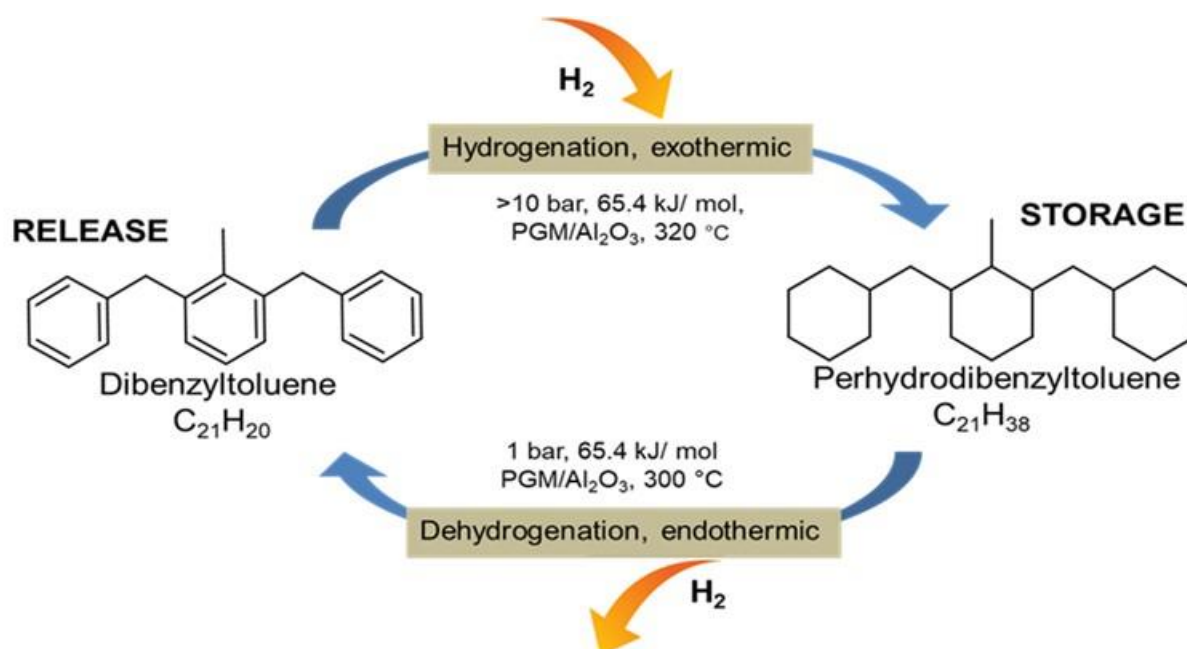


Figure 2.9: Schematic representation of the H0-DBT/H18-DBT LOHC system.

Dibenzyltoluene is a commercial heat transfer oil that is produced on a multi-thousand-ton scale (since the late 1960s). For example, the isomeric mixture of dibenzyltoluenes that is

commercialized by Sasol has the well-known trade name “Marlotherm SH”. This product has found a wide range of industrial applications, including the indirect heating of reactors, distillation columns, polymerization vessels, and heat exchangers [73]. H0-DBT has been reported to exhibit excellent thermal properties and high hydrogen storage capacity of 6.2 wt % (equivalent to 57 kg-H₂/m³ H18-DBT or 2.06 kWh/kg H18-DBT) [73,74]. It is noteworthy that, due to the higher density of H18-DBT vs. MCH (0.91 g/ml vs. 0.77 g/ml), H18-DBT has a significantly higher volumetric hydrogen storage density than MCH, while the gravimetric storage densities are similar.

Dibenzyltoluene is characterized by a low melting point (mp –39 to –32 °C) and high boiling point (bp 390 °C). It is non-flammable, nontoxic, and is not classified as dangerous goods [76], [77]. Moreover, it is important to note that the low vapour pressure of H0-DBT enables easy hydrogen/LOHC separation and the production of very pure hydrogen gas by simple LOHC condensation [77], [78]. The low melting point permits the transportation and storage of hydrogen in liquid form at sub-zero temperatures without transition to solid phase. The H0-DBT/H18-DBT LOHC system has diesel-like properties, with excellent ecological benefits. Its hydrocarbon character allows handling of this LOHC system in the existing infrastructure for fuels. From H18-DBT, hydrogen can be released on demand by catalytic dehydrogenation with an appropriate catalyst (e.g. Pt-based) at temperatures >250 °C [78]. A wide range of stationary power applications, such as grid support and energy self-supply for off-grid applications, can be sustained by Hx-DBT-based LOHCs. As a pure hydrocarbon LOHC system, the reaction enthalpy of H18-DBT is 65.4 kJ/mol-H₂ [79].

Interestingly, the charging of H0-DBT with hydrogen is not only possible with pure hydrogen but also with hydrogen-containing gas mixtures. A prerequisite is that the reaction with the hydrogen-lean carrier is selective and the applied catalyst is not degraded by presence of the other components in the applied gas mixture. Economically, using hydrogen containing gas mixtures for loading LOHC systems is highly attractive as such mixtures are readily available from various processes, such as reforming, gasification, or cracking reactions. Moreover, the economic value of hydrogen in these mixtures is typically very low because costly separation and purification units would be required to purify it.

A first example of LOHC hydrogenation using gas mixtures was published by Dürr et al. [80]. Herein, a mixture of methane and hydrogen, originating from methane decomposition into solid carbon and H₂/CH₄ mixture (catalytic methane decomposition), was successfully applied to hydrogenate H0-DBT. It was found that the presence of methane even had a mildly accelerating effect on the hydrogenation rate, based on a comparison at identical hydrogen partial pressures. This is probably because methane dissolution into the LOHC reduces liquid viscosity and improves hydrogen mass transport.

Jorschick et al. recently described the charging of H0-DBT with hydrogen/CO₂ mixtures; they found that the choice of catalyst is critical, as methanation and reduction of CO₂ to CO are relevant

side-reactions [81]. They identified Pd/Al₂O₃ and Rh/Al₂O₃ as suitable catalysts. The degree of hydrogenation reached ~0.8 for both Rh/Al₂O₃ and Pd/Al₂O₃ at 210 °C and 270 °C, respectively. The CH₄/CO₂ ratio obtained for Pd was <0.1 at temperatures in the range 120–270 °C and for Rh also <0.1 from 120–150 °C. Furthermore, a semi-continuous hydrogenation was performed using 5 wt % Rh/ Al₂O₃ (see Figure 2.10). Other catalysts such as Pt and Ru were not selective towards the hydrogenation of H0-DBT in the presence of CO₂. While Pt is quickly poisoned by traces of CO formed by CO₂ reduction, Ru produces significant amounts of methane.

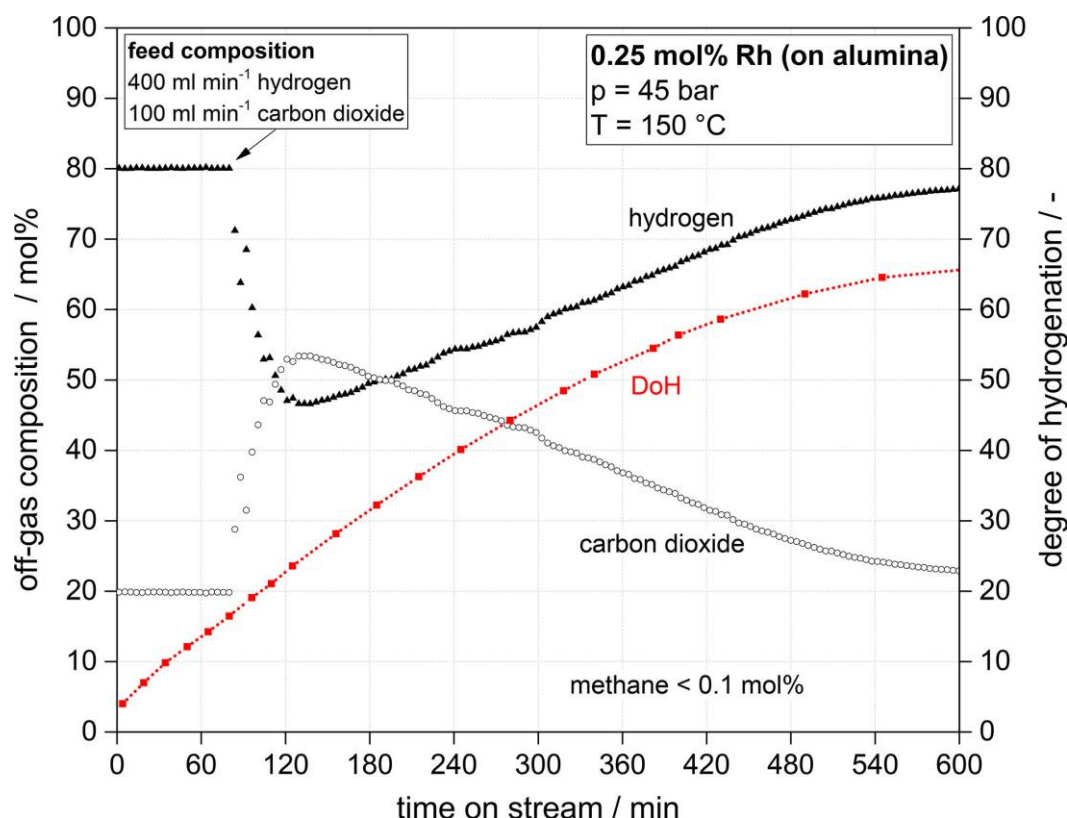


Figure 2.10: Semi-continuous hydrogenation experiment with a H₂/CO₂ using H0-DBT and 0.25 mol % Rh applied as 5.0 wt % Rh/Al₂O₃. Adapted from ref. [81], with permission from Wiley.

Hydrogenious Technologies GmbH (Erlangen, Germany; www.hydrogenious.net) has adopted the LOHC system H0-DBT/H18-DBT as their main workhorse for hydrogen storage [82]. Hydrogenious Technologies is the main European pioneer of LOHC technology. It is a spin-off of the Friedrich-Alexander University Erlangen-Nuremberg (Germany) where much of the basic LOHC research has been undertaken. Brückner et al. were the first to report on the dehydrogenation of H18-DBT for hydrogen production [83]. A batch-type reactor was used and the effects of temperature, catalyst loading, and metal type were investigated. At first, the catalyst screening indicated that Pt/C is a suitable catalyst for the dehydrogenation of H18-DBT. The dod for H18-DBT at 270 °C was 96% when 1 wt % Pt/C was used. In contrast, with 0.5 wt % Pt/Al₂O₃ as catalyst, the dod was only 40%. The performance of metal-based catalysts with lower metal loading (1 wt % Pt/C) was higher than that of 5 wt % Pt/C, with respect to the applied metal. Pd

is certainly not a metal of choice for the dehydrogenation of H18-DBT. In this paper, the catalyst support preference for H18-DBT dehydrogenation is in the order $C > Al_2O_3 > SiO_2$.

Fikrt et al. used a FBR loaded with 0.5 wt % Pt/ Al_2O_3 to evaluate a H18-DBT-based LOHC for dynamic power supply [84]. The hydrogen supply response time from a LOHC system is fastest if the pressure level of the release unit is adjusted. Changes in flow rate and temperature result in relatively long response times, allowing for adjustments of the power demand on a minute scale. The two-in-one reactor proposed by Jorschick et al. has the advantage of performing both hydrogenation and dehydrogenation, hence saving on catalyst and equipment costs, e.g., for stationary energy storage applications in remote areas [85]. By simply changing the pressure between 1 and 30 bar, the dehydrogenation reaction could be switched to the hydrogenation reaction, using the same catalyst Pt/ Al_2O_3 . Here, 0.3 wt % Pt/ Al_2O_3 was used. Four hydrogenation/dehydrogenation reaction cycles were performed. Dehydrogenation productivity decreased strongly over the first few cycles but appeared to stabilize later (see Figure 2.11). Heavy by-products increased per cycle, from 0.9 to 2.1 wt %, while light by-products remained <0.3 wt %. In the case of H18-DBT dehydrogenation, thermal cracking of the molecule produces high-boiling-point compounds (heavy by-products). The catalyst activity decreased with an increase in heavy by-products. The heavy by-products are bulkier molecules that can block the catalyst's active sites. Therefore, formation of heavy by-products account for the observed deactivation.

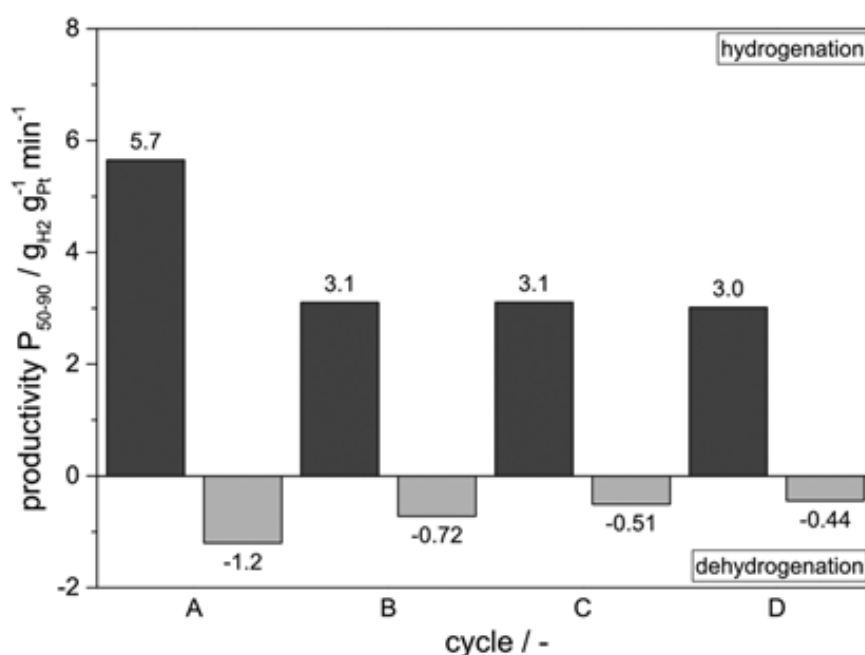


Figure 2.11: Catalyst efficiency (0.3 wt % Pt/ Al_2O_3) in terms of hydrogen productivity for reversible hydrogenation of DBT, using a two-in-one reactor. Adapted from ref. [85], with permission from The Royal Society of Chemistry.

2.3 LOHC process integration

Various methods by which heat is provided for the endothermic dehydrogenation reaction are now discussed. Calculations for the following scenarios are calculated from electricity-to-electricity efficiencies as published by Teichmann et al. [86].

Electrical heating by means of using a share of the electricity output from a proton exchange membrane fuel cell (PEMFC) is the most inefficient way to dehydrogenate a charged LOHC system. In this operation, some of the electrical energy is converted to heat, which reduces the efficiency of the system to a maximum of 24% (electrical output of PEMFC vs. LHV of LOHC hydrogen). Alternatively, a hydrogen burner can be applied to provide the dehydrogenation heat. Here, a share of the hydrogen produced by a LOHC is burned to supply heat to the dehydrogenation system, and the remaining hydrogen is supplied to the PEMFC. This process has a maximum efficiency of about 34%, hence it is a better option than electrical heating.

A system that utilizes a hydrogen burner for supplying the dehydrogenation heat has been installed by Hydrogenious Technologies (currently operating in Stuttgart, Germany). This system is suitable for off-grid energy supply; it contains a hydrogen burner, LOHC dehydrogenation system producing 33 Nm³/h hydrogen (~100 kW based on the LHV of hydrogen) and a 30-kW PEMFC [27]. Furthermore, this company has already delivered two dehydrogenation systems to the United Hydrogen Group (UHG), one dehydrogenation system used for the cooling of power plant generators and the other for hydrogen supply to UHG customers [87]. H₂ Mobility GmbH (Germany) will install a first hydrogen refueling station in Erlangen (Germany), supplied by Hydrogenious' LOHC technology. Operation is anticipated for early 2020 [88]. In the HySTOC project, funded by the European Community, a LOHC-based filling station delivering high purity hydrogen (ISO 14687:2-2012) will be demonstrated in Voikoski (Finland) [89].

The integration of solid oxide fuel cell (SOFC) and endothermic LOHC dehydrogenation systems has the advantage of heat integration between the high-temperature exothermal SOFC process and the endothermal dehydrogenation reaction. During SOFC operation, exhaust heat of >600 °C is produced. Upon the introduction of cold air, the temperature can be reduced to the optimum operation temperature (300 °C) of the LOHC dehydrogenation system, thus enabling efficient heat integration. In this way, the LOHC system produces hydrogen for the SOFC operation, providing electricity, while the SOFC operation produces heat for the LOHC dehydrogenation reaction. The efficiency of the conversion of bound hydrogen into electricity in the dehydrogenation + SOFC sequence is reported to be 45% [90]. The effect of LOHC vapours on the SOFC performance was also studied. The experimental results indicated that these vapours do not harm the performance of the SOFC, and operation times of >10 years have been simulated without any performance degradation [90].

Figure 2.12 gives a schematic representation of the heat integration between SOFC operation and LOHC dehydrogenation.

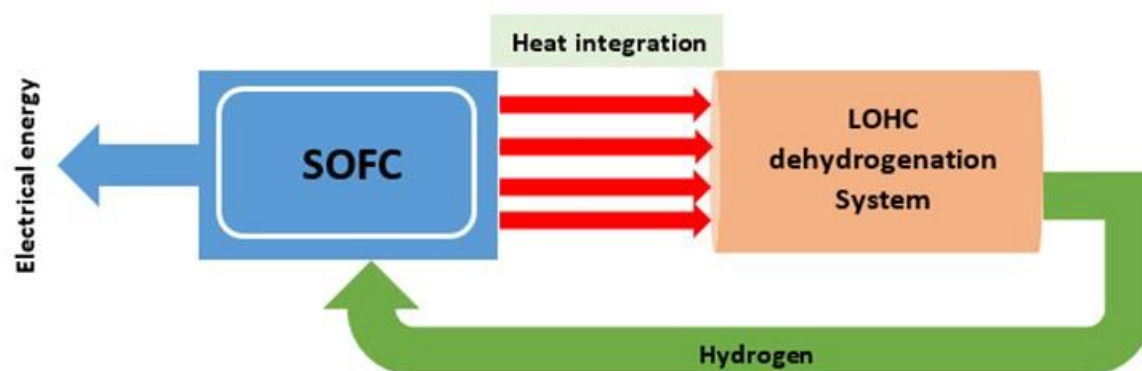


Figure 2.12: Heat integration between LOHC dehydrogenation and SOFC operation.

2.4 Reactors for LOHC dehydrogenation

Several types of reactors have been proposed for performing the LOHC dehydrogenation reaction, as already reported. See Figure 2.13. They include, but are not limited to, spray pulsed [45–47], fixed bed [59], batch-type continuous stirred [63,64], 3D structured monolith (SEBM) [69], tubular [70] and pressure swing [85] reactors. In LOHC dehydrogenation, the reactor has to cope with the high volume of hydrogen formed. For example, 1 ml of H18-DBT produces >650 mL of hydrogen gas. The reactor is basically a gas generation device. It is clear that the high volume of hydrogen can displace the LOHC, which will then reduce the LOHC contact with the catalyst, resulting in poor heat and mass transfer, as well as in reduced residence times of the liquid in the reactor.

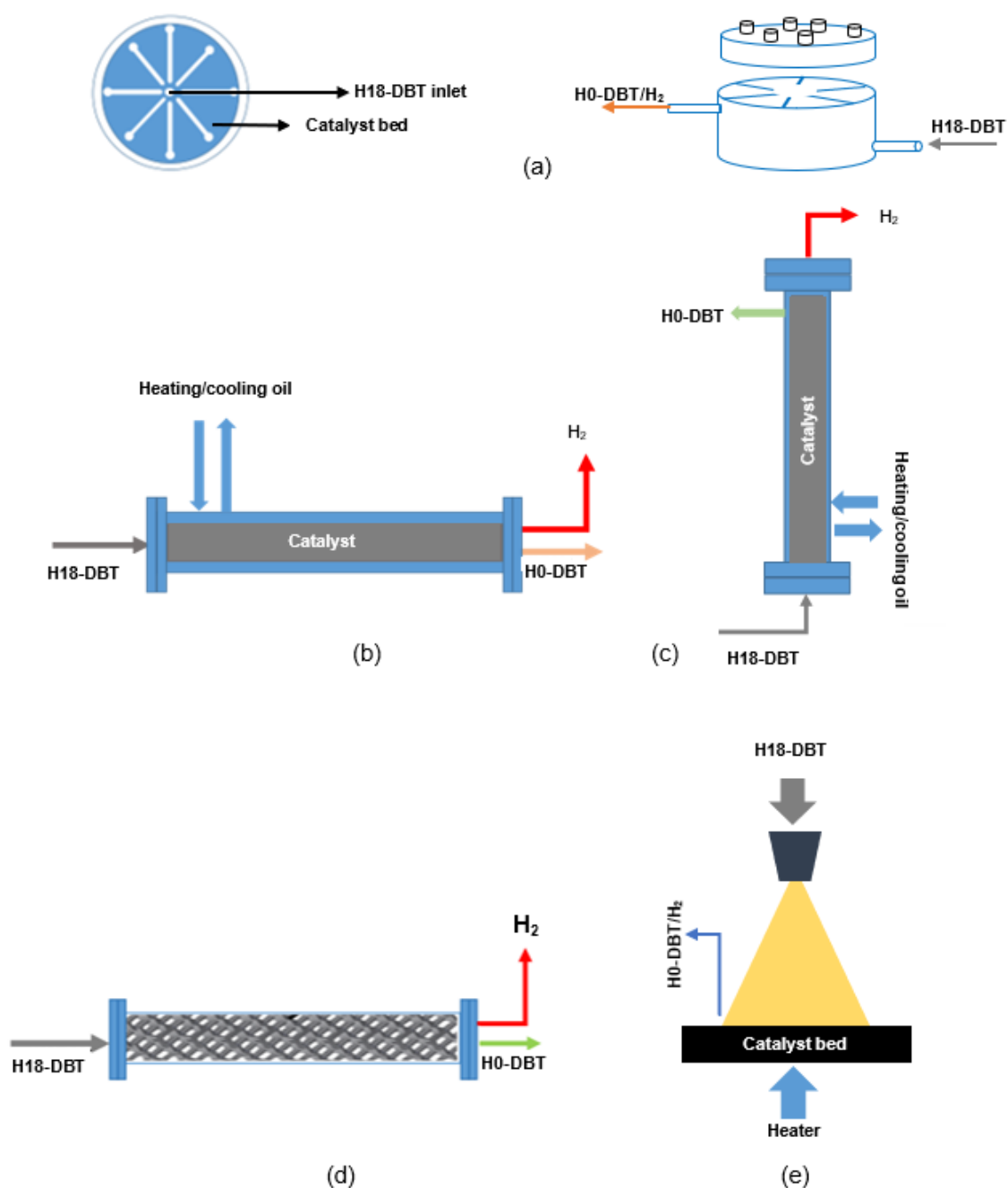


Figure 2.13: Examples of reactors used for dehydrogenation of LOHCs: (a) radial flow, (b) horizontal tubular, (c) fixed bed, (d) 3D structured monolith (SEBM) and (e) spray pulsed reactor.

Horizontal tubular reactors have the advantage of separating the two phases (gas/liquid). While hydrogen escapes vertically into an empty gas volume, the liquid flows horizontally through the fixed bed of catalyst pellets. Interestingly, hydrogen evolution creates turbulence in the liquid, which strongly improves the heat transfer from the hot wall into the liquid. Multi-tubular reactors or plate reactors can be more efficient for larger systems. A radial flow reactor has been recently proposed to release hydrogen from the LOHC. However, such a reactor has not yet been used in large LOHC systems. Herein, the liquid flow is radially directed outwards by the use of a

microstructure. This can counteract the increase in volume caused by the continuous production of gas, and it also simplifies the discharge of the gas from the multiphase flow [91].

Table 2.2 gives an overview of published LOHC dehydrogenation experiments, indicating the applied reactor systems and the performances achieved.

Table 2.2: Comparison of catalytic processes for the dehydrogenation of various LOHC compounds and reactor types applied

LOHC	Catalyst	Reactor type	Reaction conditions	Results	Reference
Cyclohexane	10 wt % Pt/CFF-1500S	SPR	330 °C	P=0.51 mol/g _{Pt} /min, F _{H₂} =55 mmol/min	[45]
	3 g/m ² Pt/Al ₂ O ₃	SPR	350 °C	P=3,8 mol/g _{Pt} /min, F _{H₂} =89 mmol/min	[45]
	20 wt % Ni/ACC	SPR	300 °C	P=8.5 mmol/g _{cat} /min	[46]
	20 wt % Ni/ACC + 0.5 wt % Pt	SPR	300 °C	P=12,75 mmol/g _{cat} /min	[46]
	0.5 wt % Pt/ACC	SPR	300 °C	P=0,21 mmol/g _{cat} /min	[46]
	10 wt % Ag/ACC	SPR	300 °C	P=6.8 mmol/g _{met} /min	[46]
	10 wt % Ag/ACC + 1 wt % Pt	SPR	300 °C	P=14.2 mmol/g _{met} /min	[47]
	Ni-Cu/SiO ₂ (17.3 mol % Ni, 3.6 mol % Cu)	PFR	250 °C	P=58 mmol/h/g _{cat} , X _{CHE} =95.0%, S _{CHE} =99.4%	[48]
	Ni-Cu/SiO ₂ (17.3 mol % Ni, 3.6 mol % Cu)	PFR	350 °C	P=54 mmol/h/g _{cat} /min, dod=87.8%, S _{CHE} =99,9%	[48]
	Ni-Cu/SBA-15 (4.9 wt % Ni, 3.5 wt % Cu)	PFR	325 °C	P=61 mmol/h/g _{cat} , dod=99.7%, S _{CHE} 99%	[49]

Methylcyclohexane	2 wt % Pt/AC	BR	300 °C	P=910 mmol/g _{met} /min	[50]
	3.82 wt % Pt/Al ₂ O ₃	BR	300 °C	P=1800 mmol/g _{met} /min	[50]
	Ni/Al ₂ O ₃	-	127 °C	X _{MCH} =16.5%	[53]
	Ni/Al ₂ O ₃ -TiO ₂	-	127 °C	X _{MCH} =99,9%	[53]
	1 wt % Pt/La _{0.7} Y _{0.3} NiO ₃	SPR	350 °C	P=45.76 mmol/g _{met} /min	[55]
	Pt/LaO ₃	SPR	350 °C	P=21.1 mmol/g _{met} /min	[55]
	Pt/V ₂ O ₅	SPR	350 °C	-	[55]
	Pt/Y ₂ O ₃	SPR	350 °C	X _{MCH} =98%	[55]
	1 wt % Pt/CB	FBR	300 °C	P=342 mmol/g _{met} /min, X _{MCH} =95%	[56]
	5 wt % Pt/8wt% Mo-SiO ₂	FBR	400 °C	-	[57]
	1 wt % Pt/Al	MR	225 °C	dod=70%	[58]
	1 wt % Pt/SC-CNT	FBR	315 °C	dod=90%	[59]

	0.25 wt % Pt/SC-CNT	FBR	315 °C	dod=90%	[59]
Decalin	1 wt % Pt/Al ₂ O ₃	FBR	315 °C	dod=90%	[59]
	1 wt % Pt/AC-Sn	FBR		dod=74%, S _{Naph} =90%	[62]
	3 wt % Pt/C	BR	210 °C	P=45.4 mmol H ₂ /g _{Pt} /min	[63]
	Pt/C	BR	260 °C	P=220 mmol H ₂ /g _{Pt} /min	[64]
	Pt/CB	BR	260 °C	P=100–140 mmol H ₂ /g _{Pt} /min	[64]
	Pt/Al ₂ O ₃	PFR MR	-	P=0,2 gH ₂ /g _{Pt} /min P=1,5 gH ₂ /g _{Pt} /min, X _{NEC} =90%	[68] [68]
	Pt/Al ₂ O ₃	SEBMR	250 °C, 1,7 bar, F _{feed} =30 mL/min, 48 h	P=1,12 gH ₂ /g _{Pt} /min	[69]
	Pt/Al ₂ O ₃	SEBMR	260 °C, F _{feed} =4 mL/min, 48 h	P=1,27 gH ₂ /g _{Pt} /min	[69]

Dodecahydro-N-ethylcarbazole					
	1.87 mg Pt/Al ₂ O ₃	TR	260 °C, F _{feed} =0,4 mL/min	P=4 gH ₂ /g _{Pt} /min, Y _{H2} =26%	[70]
	1.87 mg Pt/Al ₂ O ₃	TR	260 °C, F _{feed} =0,8 mL/min	P=5 gH ₂ /g _{Pt} /min, Y _{H2} =21,9%	[70]
	0.82 mg Pt/Al ₂ O ₃	TR	260 °C, F _{feed} =0,8 mL/min	P=10,9 gH ₂ /g _{Pt} /min, Y _{H2} =20,9%	[70]
	0.82 mg Pt/Al ₂ O ₃	TR	260 °C, F _{feed} =0,4 mL/min	P=7,3 gH ₂ /g _{Pt} /min, Y _{H2} =35%	[70]
	5 wt % Pd/SiO ₂	BR	170 °C, 17 h	X _{NEC} =100%, Y _{H2} =60%	[72]
	0.5 wt % Pt/Al ₂ O ₃	BR	270 °C	dod=75%	[83]
	1 wt % Pt/C	BR	270 °C	dod=96%	[83]
Perhydrodibenzyltoluene	1 wt % Pt/C	BR	270 °C	dod=71%	[83]
	0.3 wt % Pt/Al ₂ O ₃	PSR	291 °C	P=1.2 gH ₂ /g _{Pt} /min	[85]

Abbreviations: SPR - Spray pulse reactor; BR - Batch reactor; PMR - Palladium membrane reactor; FBR - Fixed bed reactor; TR - Tubular reactor; PFR - Plug flow reactor; MR - Microchannel reactor; SEBMR- Selective electron beam melting reactor; PSR- Pressure swing reactor; F_{H2} - Hydrogen flow; F_{feed} - Feed flow; X – Conversion; P – Productivity; S – Selectivity; Y_{H2} - Hydrogen yield; dod - Degree of dehydrogenation

The H0-DBT/H18-DBT LOHC system, meanwhile, has progressed to commercial application. Table 2.3 summarizes relevant performance data recorded for this system. It is evident that long-term application data are still missing from the open literature. This is in contrast with for example, published performance data for >8000 h operation time for MCH dehydrogenation systems, as published by Chiyoda Corporation (use made of the Pt/Al₂O₃ catalyst). Thus far, all successful catalysts reported for H0-DBT/H18-DBT are eggshell-based catalyst systems. The active shell of the catalyst pellet (20–100 μm thick) contains typically >95% of the applied Pt.

The LOHC durability is defined as the number of cycles that a liquid carrier molecule can withstand given the quantity of by-products formed per cycle, if any. For example, if the quantity of by-products produced per cycle is high, the LOHC properties will be altered, and the LOHC material life cycle will be affected. Furthermore, high dehydrogenation temperature is also one of the critical challenges. This therefore opens the door to further research into LOHCs molecules with lower enthalpy of reaction and also to the development of new/improved catalysts.

Table 2.3: H0-DBT/H18-DBT LOHC system: performance data

Parameters	Units	Performance	Reference
Catalyst efficiency	gH ₂ /gPt/min	1.2	[85,92]
Operating temperature	°C	290	[92]
Selectivity	%	99.8	[85]
Conversion factor/ degree of dehydrogenation	%	96	[83]
Catalyst durability	h	-/405	[92]
LOHC durability	Number of cycles	13	[92]

2.5 *Ab initio* calculations for improving the LOHC technology

There has been a significant increase in the application of *ab initio* modelling techniques such as density functional theory (DFT) in catalysis and catalytic studies. This is mainly due to the increase in computational power as well as algorithmic refinements which have enabled these techniques to probe increasingly larger systems. DFT, is frequently adopted in many aspects of catalysis, such as high-throughput screening of different catalyst surfaces, rational design of new catalysts, and the investigation of catalytic reaction pathways on different catalytic species and surfaces. This is mainly because the DFT technique is not computationally expensive. DFT has therefore been used to complement experimental investigations as well as to predict properties that might be used to guide experiments. Hence DFT techniques have also been used to explore LOHCs and their interactions with different catalytic species and surfaces. DFT investigations usually entail understanding the adsorption characteristics of the reactants and products of a particular reaction. This is done via calculation of the adsorption energies of the different reactants and products on the catalyst surfaces, and the reaction and activation energies of the associated catalytic reaction processes.

A typical calculation is exemplified in the following example for the catalytic dehydrogenation of octahydroindole. The reactant is first adsorbed on the catalyst surface. Once this is done, the adsorption energy is calculated. The same calculation is performed for the products; in this example both hydrogen molecule(s) and the LOHC in its hydrogen-lean form, indole. However, there are two ways in which the adsorption of the products can be carried out. One can investigate the adsorption of products in two ways. The first will be by performing a simultaneous adsorption of all the products on the same surface and the other is by adsorbing each of the products separately on the surface (see Figure 2.14). In the case of the dehydrogenation of octahydroindole, where the products will be four molecules of hydrogen and indole, the following applies. According to method 1, all the products will be adsorbed on the same surface, simultaneously, as shown in Figure 2.14. If method 2 is used, then all the products will be adsorbed separately, with both hydrogen and indole on one surface (see Figure 2.15) or on different surfaces (see Figure 2.16).

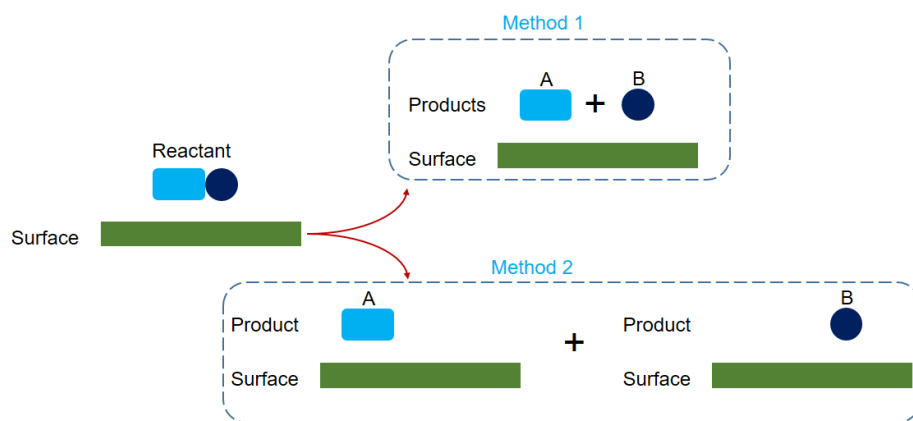


Figure 2.14: Schematic: Investigating the adsorption of products of a reaction on a surface.
Adapted from ref. [93], with permission from Elsevier.

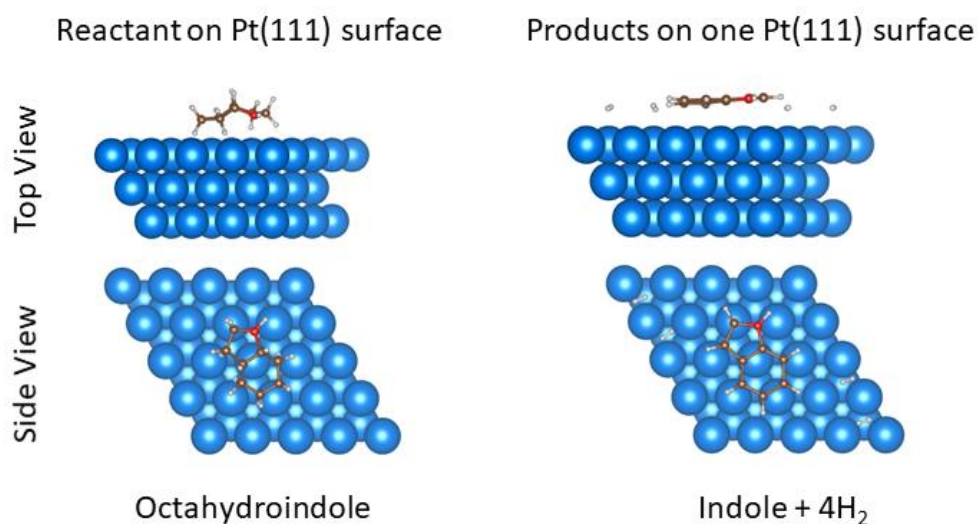


Figure 2.15: Modelling the catalytic dehydrogenation of octahydroindole: Atomic structures,
where both products, indole and dehydrogenated H₂ molecules, are simultaneously adsorbed
on the same surface.

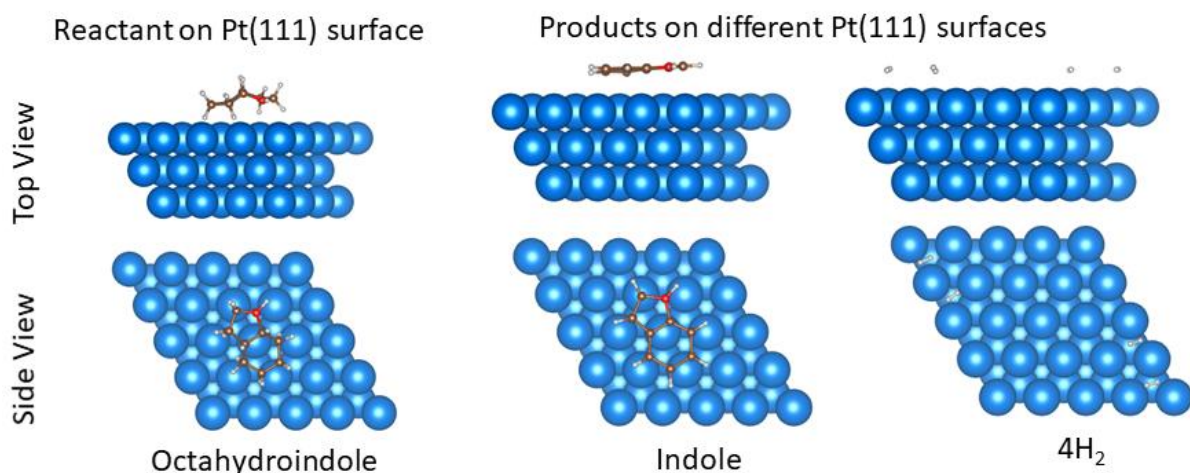


Figure 2.16: Modelling the catalytic dehydrogenation of octahydroindole: Atomic structures, where the products indole and dehydrogenated H₂ molecules are adsorbed on separate surfaces.

The adsorption energies of any of the adsorbed species on the catalyst surface can be obtained. See Eq 1.

$$E_{\text{ADS}} = E_{\text{S+A}} - E_{\text{S}} - E_{\text{A}} \quad (1)$$

where $E_{\text{S+A}}$ is the total energy of the surface and adsorbate, E_{S} is the total energy of the surface alone, and E_{A} is the total energy of the adsorbate alone. The adsorption energies calculated can be used to determine the adsorbate binding strength on the catalyst surface. The calculated total energies can also be used to obtain the reaction energy for the dehydrogenation of octahydroindole. See Eq 2.

$$E_{\text{R}} = \frac{[E_{\text{H0}} + nE_{\text{H2}} - E_{\text{H8}}]}{n} \quad (2)$$

where E_{H0} , E_{H2} , and E_{H8} are the DFT calculated total energies of surface–indole, surface–hydrogen, and surface–octahydroindole systems, respectively, and n is the number of dehydrogenated hydrogen molecules. In this case, the energies presented here are overall barriers. Two dehydrogenation reaction pathways of octahydroindole to indole have been proposed in which the main difference is the presence of indoline as an intermediate. Using DFT calculations with van der Waals corrections, the dehydrogenation of octahydroindole to indole was found to be 57.57 kJ/mol, without indoline as an intermediate, and 60.51 kJ/mol for

octahydroindole dehydrogenation to indoline. The reaction energy for indoline dehydrogenation to indole was found to be 43.32 kJ/mol [93].

DFT has been also used to investigate CHE hydrogenation and dehydrogenation. In some instances, the DFT results have been found to be consistent with experimental observations [94]–[98]. While investigating benzene hydrogenation, Saeys et al [94] were able to identify the most favorable benzene hydrogenation pathway as well as calculate reaction barriers that were in quantitative and qualitative agreement with experimental observations. Investigations carried out by Delbecq et al. [95] for the dehydrogenation of CHE on ordered Pt-Sn surface alloys, using DFT, also yielded results consistent with experimental observations [94]. Other DFT studies carried out by Tsuda et al. [96], [97] and Humbert et al. [98] have also provided insight into CHE dehydrogenation on Pt and bimetallic surfaces. MCH structure sensitivity on supported Ir particles has also been explored using DFT and these results have been compared with results of experimental observations [99].

A combined DFT and experimental study was used to investigate the catalytic dehydrogenation from decalin to tetralin to naphthalene over Pd and Pt supported catalysts [100]. Here, DFT was mainly used to explore the energy profile of the dehydrogenation process. DFT predicted the first dehydrogenation step, from decalin to tetralin, to highly favour the use of a Pt supported catalyst over a Pd catalyst. However, in the second dehydrogenation process, from tetralin to naphthalene, the reverse applied. This prediction was confirmed by experimental observations, also reported in the same study. Ghadami et al. [101] reported that DFT predictions were consistent with experimental observations on the adsorption, dehydrogenation, and passivation of naphthalene on Ni (111). Furthermore, they pointed out that such a model (naphthalene on a Ni (111) surface) can be used as a good starting point in the rational design, development, and optimization of a catalyst surface. In their study, scanning tunnelling microscopy was used to confirm *ab initio* results obtained using van der Waals corrected DFT, on the adsorption, diffusion, and rotation of naphthalene on a Pt (111) surface.

Deuterium exchange experiments combined with DFT calculations have also been used to investigate the reaction profile for the aromatization (dehydrogenation) of tetrahydrocarbazole [102]. DFT calculations predicted the highest reaction barrier as the one involving the first H abstraction. Both DFT calculations and experimental results indicated that

the aromatization of tetrahydrocarbazole is largely dominated by the cleavage of the carbon-hydrogen bonds at specific carbon atom positions.

Dehydrogenation kinetics of H12-NEC dehydrogenation on Pd supported catalysts were investigated by Sotoodeh et al., using both DFT and experimental techniques [103]. In their study, both DFT and experimental results indicated that catalytic dehydrogenation of H12-NEC and dodecahydrocarbazole were structure sensitive. DFT was used to explain why the dehydrogenation rate was slower in the case of dodecahydrocarbazole dehydrogenation compared with the dehydrogenation of H12-NEC. DFT calculations revealed that in the case of dodecahydrocarbazole there was strong adsorbate adsorption on the surface. DFT has also recently been used to give insights on the adsorption behaviour of different isomer and regioisomers on different planar surfaces ((100), (110) and (111)) of Pd, Pt, and a 50:50 Pd-Pt alloy [104]. Despite all exhaustive experimental work done on hydrogenation and dehydrogenation of LOHCs, to the best of our knowledge DFT studies are still lacking.

2.6 Key market participants and activities

Early studies on the LOHC technology focussed on their direct use in vehicles combined with hydrogen combustion in internal combustion engines. Well established companies such as Air Products, Bayerische Motoren Werke (BMW) and General Motors (GM) pursued development projects within this objective. By around 2010, when the idea of on-board hydrogen combustion in an engine became less popular due to the related NO_x emissions, the scope of the LOHC technology broadened to targets, such as stationary hydrogen and energy storage, industrial hydrogen logistics, and delivery of hydrogen to refuelling stations. With renewable energies becoming more and more competitive against traditional power plant technologies, the LOHC technology is seen as a key link between locations with a very high potential of renewable energy and global areas with very high industrial activities. Green hydrogen stored in LOHC systems is a tradable, storable and transportable form of renewable energy that can play a key role in the expected transition from a fossil fuel-based to a renewable, emission-free energy system. In this context it is very important, that the LOHC technology can make full use of the established infrastructure for liquid fuels, thus enabling step-wise and rapid introduction of the technology around the globe.

2.6.1 Air Products

The US based company Air Products, founded in the 1940s, is one of the largest hydrogen suppliers in the world today. Air Products has a long history of hydrogen innovation which stems from its relationship with NASA in the 1950s [105]. Air Products pioneered the supply of liquid hydrogen to industry and gained a leading market position [105]. Furthermore, in South Africa, Air Products holds a leading hydrogen position (to be discussed in more detail later). Between the mid-1990s and late 2000s, Air Products pursued involvement in US DoE funded research programmes to develop a better understanding of and expertise in the field of LOHCs [106]. This interest, shown by one of the world's largest hydrogen companies, galvanised much discussion around the topic and led to the filing of several "basic" patents. Once interest in on-board vehicle systems began to fade, Air Products scaled back on its development efforts. In recent years, they are looking to license their LOHC technology portfolio using the term "liquid battery" [107,108].

2.6.2 Chiyoda Corporation

Chiyoda, also founded in the 1940s, has expanded from a fossil-based engineering, procurement, and construction company to one which leads the global liquefied natural gas (LNG) sector [109]. More recently, it has diversified into sustainable energy, water management, and clean-up technologies with in-house catalysis capabilities [109]. Chiyoda sees sustainable energy as a future core business. From this basis they developed an interest in LOHC-based hydrogen storage. Chiyoda's LOHC activities began towards the end of the work of Air Products in this area. The company focussed on the challenge of global distribution of renewable energy using MCH as hydrogen-rich carrier. Initial catalysis testing delivered suitable, stable, long-term performance to allow the building of a pilot facility that came online in 2013. A follow-on project, connecting the pilot facility to renewable energy and integrating a SOFC is due to be completed this year. The success of these pilot facilities enabled Chiyoda to form a consortium of companies, including Mitsubishi, Mitsui, and Nippon Yusen Kabushiki Kaisha, to form the Advanced Hydrogen Energy Chain Association for Technology Development (AHEAD) [110]. AHEAD is a hydrogen supply chain demonstration project. The group has three specific goals:

- Gather the expertise to design, build, own, and operate supply chains for hydrogen.

- Confirm the robustness of the hydrogenation/dehydrogenation plants in actual operating environments.
- Confirm the overall international supply chain capability via operation.
- AHEAD has developed a project that will supply a maximum of 210 megatons of hydrogen from Brunei to Japan in time to coincide with the 2020 Olympic Games [110]. At this stage, however, the participating companies have not confirmed any further action.

2.6.3 Hydrogenious Technologies

Hydrogenious Technologies, founded in 2013, is the main European pioneer of LOHC technology. It is a spin-off of the Friedrich-Alexander University of Erlangen-Nuremberg, where much of the basic LOHC research has been undertaken and is still going on [82]. Hydrogenious gained notoriety after an investment from Anglo American. This secured the start-up and enabled the development of commercial demonstrator units. To date, a dozen of such units is in commercial operation or in pre-commercial field tests, all of them using the H0-DBT/H18-DBT LOHC system. Main business activities are currently in Europe, USA and China. In the US a commercial hydrogen logistics project has been recently realized with the UHG [87]. The offered commercial products include hydrogenation units with charging capacities of up to 12 tons of hydrogen per day (16 MW based on the LHV of the bound hydrogen). With respect to dehydrogenation units the offered units are smaller reflecting the decentralized nature of hydrogen delivery. The commercial units offered by Hydrogenious have daily capacities ranging from 12 to 500 kg released hydrogen (33 to 700 kW).

2.6.4 Framatome

Framatome, which counts Electricité de France, Mitsubishi and Assystem as its shareholders, is interested to continue AREVA's activities in LOHC-based hydrogen storage and transport for their future business [111]. Obviously, there is now a crossover between the Chiyoda project and Framatome's European developments as both involve Mitsubishi at a high level.

Framatome has been undertaking demonstration work on their technology since 2014. Field tests using the H0-DBT/H18-DBT LOHC system have been performed on pilot scale (deployed in Arzberg, Germany) in the context of a power-to-hydrogen-to-power

demonstrator. Beyond this original demonstration, Framatome has been building small laboratory scale systems predominantly for supply to the HySA Infrastructure (a South African based programme) [112]. Having PEM electrolysis, PEMFC and LOHC technologies within its energy business offers Framatome the opportunity to rapidly scale their current pilot technology to bigger applications [112].

2.6.5 Hynertech Co. Ltd

Hynertec, established in 2014, is one of the new entrants to the LOHC market; however, its roots go back to the work undertaken by Air Products [113]. Its founder, Prof. Hansong Cheng [114], worked within the Air Products LOHC development team in the USA. Prof. Hansong Cheng repatriated to China and saw the opportunity to position LOHC technology within the Chinese market. In 2015 Hynertech rolled out an initial dehydrogenation system and followed it up with a pilot unit in 2016 [114]. In 2016, an on-board LOHC-hydrogen system was demonstrated. It was integrated within a car and a small fuel cell bus—a world first. The Chinese government sees LOHC technology as one of the game-changing technologies which they wish to support as fuel cell electric vehicles begin to enter the market. Hynertech appears to be fully focussed on the Chinese market, with little or no activity beyond its borders. Hynertech began testing the first production location for their LOHC technology in January 2018. This company announced the building of two new production facilities during the first half of 2018 in Wuhan (China). A focus of the Chinese LOHC development plan is to reduce dehydrogenation temperatures to ~180 °C.

2.7 Opportunities in South Africa

In the following we want to expand on attractive application scenarios for the LOHC technology for the particular case of South Africa. Addressing the specific needs of the South African economy, the LOHC technology can be useful to provide hydrogen to mining equipment, such as extra low profile (XLP) mining dozers, locomotives etc., when the principle is used to power fuel cell vehicles for emission-free, underground service. Other options for on-board use of LOHC as a fuel include but not limited to city busses, cars, ships, heavy duty trucks and trains. Once the LOHC technology is tested and has passed strict underground mining regulations then it will be easier for it to be adopted anywhere. Moreover, a wide range of stationary power

applications could be sustained by the LOHC technology in South Africa, for example, for grid support or energy self-supply for off-grid applications. For the last example, the combination of renewable energy harvesting and energy storage in LOHC systems is most attractive to replace diesel-powered generators.

2.7.1 The mining industry

Diesel-powered vehicles are extensively used in the mining industry. Two examples are shown Figure 2.17: XLP dozer and load haul dump (LHD) machine. The mining sector therefore faces a number of challenges such as high operating costs associated with maintenance of diesel equipment, ventilation costs, particle emissions from diesel engines, and lack of automation in tele-remote operations. The World Health Organization (WHO) classifies diesel engine exhaust as “carcinogenic to humans,” based on sufficient evidence that it is linked to an increased risk of lung cancer. Thus, underground mine workers are at particular high risk as air exchange in the mine is limited. The safety aspects and codes for hydrogen application in the mining environment need further development and validations. There is a need to detail the requirements for hydrogen handling in a mine and to demonstrate on-site the key elements of a mining hydrogen infrastructure, such as hydrogen production and delivery. The disadvantages associated with diesel equipment has resulted in the development and testing of fuel cell equipment by a number of international key players in this sector, including Anglo American Platinum. LOHC technology offers one of the promising technologies for the safe handling of hydrogen in underground applications. It provides the required energy density and greatly reduces the risk of hydrogen-caused explosions.



Figure 2.17: Examples of mining equipment that could be converted make use of the LOHC technology (left, XLP dozer; right, LHD machine).

The map in Figure 2.18 shows mines currently using LHD machines and trucks, to a lesser or greater extent in South Africa. These types of earthmoving vehicles are currently powered by diesel engines and are contributors to the high heat and particle pollution underground. Therefore, being the main production vehicles within an active mine, they are ideal candidates for fuel cell retrofitting with LOHC fuelling.

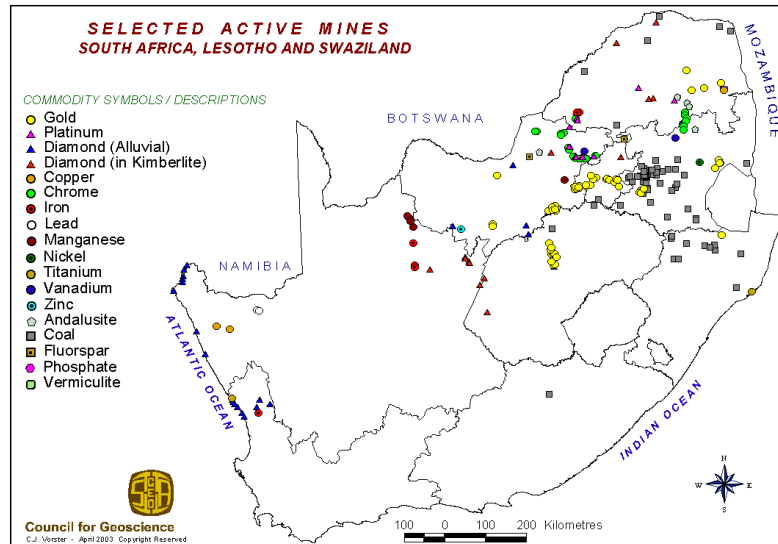


Figure 2.18: Map showing all operating and open mining activities within South Africa and neighbouring countries where diesel-powered machinery is currently used underground [115].

Vehicle's emissions are controlled by underground ventilation, which is the responsibility of mine management. Vehicles may operate on condition that strict attention and adherence is paid to the ventilation requirements within Mine Health and Safety regulations and best industry practice. All existing vehicle exhaust system are equipped with catalytic fuel convertors and fume dilution devices. In addition, the soft rock mines are equipped with additional scrubbing systems and safety systems to decrease the exhaust temperatures and emissions. If these vehicles were to be equipped with battery or fuel cell systems then the heat and emissions levels could be further reduced, which would have a dramatic impact on the total mine ventilation costs. Furthermore, all trackless mines make use of these vehicles. An alternative power source will be required when the pending legislation pertaining to emissions is implemented by the Department of Mineral Resources (DMR) in South Africa. There is a total of 409 dump trucks and 2061 LHDs that are diesel powered and operating in different

mining locations in South Africa. The vehicles mentioned do not constitute an exhaustive list of machines that may require clean energy power systems but represent only the first phase of replacement or retrofitting of the mining fleets within the RSA, when the pending legislation is passed. Most of the machines do not even comply with the diesel particulate matter legislation of 2015 instituted by the DMR. Several mining houses are investigating the use of fuel cell technology in mining units where high numbers of diesel units are being used.

2.7.2 Hydrogen logistics for stationary power applications

South Africa has the natural resources that can make it an international “powerhouse” for renewable energies in the future energy market—and LOHC can play an important part to store, transport and trade these renewable energies. The government has the goal to supply all its communities with energy. To achieve this using grid connected power will take decades and will challenge infrastructure providers and the landscape alike. The use of diesel inflates CO₂ levels, hence the solutions offered by LOHCs appear attractive. If a central production model is used, it will need an initial commercial user to create the supply chain. Once this is in place, it can be expanded, with government support, to bring solutions to these communities. However, without the initial business model being founded within a business community, it is unlikely that the government will see this form of energy supply as a possible longer-term solution for one of their core goals.

A decentralized LOHC system could also be envisaged with local community energy schemes being developed based on renewables. Here, LOHCs can act as a community energy storage resource—a “community battery”. This could allow communities to share locally produced energy resources and ensure they are completely CO₂ neutral. This will probably cost more in the short term but should offer wider and more inclusive benefits over a longer term. LOHC technology also presents South Africa with an international trading opportunity. One of the leading LOHC compounds is manufactured by Sasol, admittedly outside the country, but the revenues flow back, and manufacturing could be expanded locally if the market was there.

Potentially combining the efforts of Sasol and Anglo American should provide a strong, financially secure base for business model investigation and delivery. It should also help to increase lobbying potential towards the government for strong support. The combination of these two players should be seen in the same way than the Japanese government has

encouraged the AHEAD consortium and positioned funding to support LOHC technology. South Africa is home to some leading solar energy research. Combining this with LOHC development and research, which is underway at HySA Infrastructure, could offer attractive ways to overcome the challenge of providing the heat of dehydrogenation by simple solar thermal installations. This could create global license income for South Africa if successfully developed. South Africa has a wealth of naturally occurring renewables which could be used as source for creating a long-term replacement for internationally traded energy, with LOHC being positioned as the most suitable hydrogen carrier to distribute the harvested energy globally using existing tank ship capacities. This could deliver local electrical grid benefits and would also bring a need for an expanded electrolysis industry. Local production and assembly of LOHC systems and electrolyzers could be foreseen, subsequently providing jobs, first in the higher skilled sector which in turn will contribute to the economy. Wide deployment of the mentioned systems will deliver future improved wealth and employment.

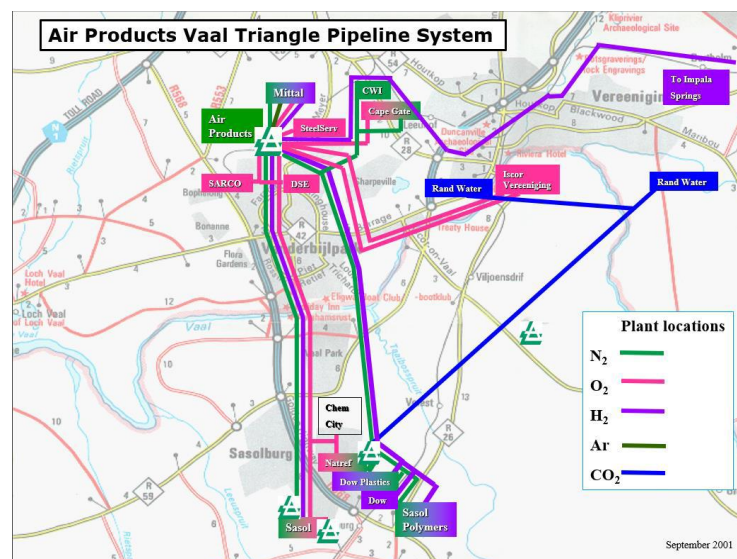
Globally, expansion of fuel cell buses is accelerating, and one interesting fact is that Hynertech Co. Ltd has already developed a fuel cell bus fuelled by LOHC [116]. Many train routes in Germany are not electrified, particularly on local transport links. For this reason, Scientists from the Helmholtz Institute Erlangen-Nürnberg for Renewable Energy Production (HIERN), a branch office of Forschungszentrum Jülich, aim to equip trains with LOHC technology [117]. This could be adopted globally given the fact that Alstom has already launched the first H₂ fuel cell train in the world in Sept 2018 [118]. The interest is also growing in the direction of refuelling of ships with LOHC, the storage of the energy carrier on board as well as the process of power generation on-board of the vessel [119]. Heavy duty fuel cell-based trucks are also gaining momentum, Toyota, Nikola, Dongfeng and Hyundai are already taking lead in this project [120]. All fuel cell-based vehicles mentioned could be converted to use the LOHC technology.

2.8 Market study for application of LOHC-bound hydrogen in South Africa

To assess the market for LOHC-bound hydrogen in South Africa, we first need to consider the existing market positions. The South African third-party hydrogen supply is dominated by Air Products and Sasol (see Figure 2.19). The main supply exists around Vanderbijlpark, via a comprehensive network of hydrogen pipelines, and stems from a close working relationship between the two main players.

2.8.1 Production/Large-scale demand

The majority of hydrogen is sourced via an impure hydrogen stream from Sasol. This product is purified by a pressure swing adsorption clean-up system, owned by Air Products. The supply is then split between the two parties. Sasol supplies hydrogen via a 110-km-long pipeline, owned by Air Products, to Impala Platinum in Springs. Excess is spilt to the Natref refinery in Sasolburg. Air Products then has rights to a further 12,000 kg/day for their own pipeline and tube trailer to supply their customers. Afrox (a business combination between Linde and Praxair) has a minor production position, providing about 600 kg/day, while Air Liquide has little or none.



Source: Air Products South Africa

Figure 2.19: Air Products pipeline system for different customers in Vaal Triangle (South Africa).

Electrolytic hydrogen production is scarce (although it is understood that Afrox is running a system) due to the high cost of power vs. the Sasol route. On-site or pipeline customers are on long-term supply agreements (generally 15-year duration). Most large hydrogen applications in recent times come via the refinery sector. In South Africa, there has been little addition in this sector for many years. However, the refineries themselves do not have excess hydrogen to offer to the market. Air Products has detailed knowledge here, as they supply and manage the hydrogen clean-up membranes for Sasol, Natref, and Chevron.

2.8.2 Merchant trucked hydrogen

Here, once again, Air Products dominates, but the market itself is not large. Air Products operates a limited fleet of about 10 vehicles operating at 200 bar with a payload of 250 kg, delivering approximately 5000–6000 kg/month or 200 kg/day. Air Products also supplies a limited volume to Air Liquide (SA) (~500 kg/month). Afrox is thought to have only a single tube trailer remaining in the country, mainly due to Air Products' successful pipeline connections programme in recent times. Delivery costs for gaseous hydrogen in South Africa are similar to those in Europe, ca. 1.3–1.5 Euro/km. Therefore, given that hydrogen pricing will be the same for either type of delivery system employed, we can assume that applications will follow a similar set of cost criteria for LOHC to be of interest in the market. The main difference between Europe and South Africa is that the density of hydrogen sources countrywide is much less than in Europe and the employed gaseous technology here is at lower pressure. Therefore, applications in more remote areas should benefit from the increased payloads that LOHC tankers can offer.

2.9 Conclusions

Hydrogen storage using LOHC systems is attracting steeply increasing interest, with more industrial examples coming on-stream. Key drivers for this development include the following: a) the improved availability of renewable energy with hotspots located typically in locations with low population and thus low energy demand; b) the further development of electrolyzer technologies; c) the strongly increasing interest in green, emission-free technologies, in particular for the mobility sector, provoking the need to make renewable energy a globally tradable commodity; d) interest in using existing industrial assets (such as tank trucks, tank farms or tank ships), also in a renewable world; e) the significant progress in the effectiveness of LOHC hydrogenation and dehydrogenation technologies as well as in process concepts that make use of heat integration potentials between heat-generating and heat-consuming processes in the process chain. It was the purpose of this review to present selected recent developments in this context and to make the reader aware of the growing application potential created by the recent findings.

Further research and development is needed and the optimization potential offered by the technology is far from fully explored. For example, the catalyst performance for both

hydrogenation and dehydrogenation catalyst could be further improved towards highly effective conversion at minimal by-product formation. The modification of chemical and textural properties of the supports (e.g., acidity, porosity, and wetting), the use of promoters and the further optimization of catalyst preparation method (polyol vs ion-exchange, calcination and activation temperatures) are very rewarding approaches for the ongoing and future research activities. To decrease high dehydrogenation temperature, LOHC molecules with lower enthalpy of reaction should be considered. Reports on important computational and kinetic studies for the dehydrogenation of H18-DBT are still lacking in the open literature.

From the reactor point of view, the key challenges are associated with the large gas volumes formed and with the need for effective transfer of dehydrogenation heat to the catalytic site in a reactor that is essentially filled with gas. Here, the use of heat transfer plates coated with catalyst and optimization of hydrodynamics by structured catalysts are recommended optimization strategies.

From the process point of view, the intelligent coupling of exothermal hydrogen consumption (fuel cell, engine) and hydrogen upgrade (e.g., compression) steps with the endothermal hydrogen release from the LOHC carrier will help to further improve the efficiency of the overall process.

As all hydrogen purification step will consume energy, it is a very important requirement to reduce any sort of by-product formation. The latter efforts also contribute to an excellent recyclability of the LOHC carrier, which is a relevant factor in hydrogen storage economics.

Market research for the example of the South African economy has indicated that there are numerous opportunities where the LOHC technology can be applied, for example, in mining, hydrogen logistics companies and rural electrification.

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CHAPTER 3: ANALYSIS OF REACTION MIXTURES OF PERHYDRO-DIBENZYL TOLUENE USING TWO-DIMENSIONAL GAS CHROMATOGRAPHY AND SINGLE QUADRUPOLE GAS CHROMATOGRAPHY

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OVERVIEW

The isomeric nature of dibenzyltoluene makes it challenging to analyse and measure degree of hydrogenation (doh) using conventional gas chromatography. Hence, reliable, precise and accurate methods need to be developed. This is important for determining the efficiency of the catalyst for overall process optimization. Perhydrodibenzyltoluene was dehydrogenated at temperatures from 270 to 300 °C using a horizontal plug flow reactor to deliberately produce reaction mixtures of different degree of hydrogenation. Comprehensive two-dimensional gas chromatography coupled with time of flight mass spectrometry (2D-GC-TOF-MS) and single quadrupole-mass spectrometry gas chromatography (GC-SQ-MS) were used to determine the effect of temperature on distribution of isomer fractions and doh. These equipment were also used to identify isomers and to predict the dehydrogenation reaction pathway. Proton nuclear magnetic resonance and direct analysis in real time mass spectrometry equipment were used to confirm the doh and molecules analysed by 2D-GC-TOF-MS and GC-SQ-MS. The results indicate each isomer fraction loses three molecules of hydrogen (3 H₂) until all rings are aromatic. GC-SQ-MS was also used to determine the decomposition by-products which are due to possible side reactions.

3.1 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 at very low temperature (-253 °C) in the case of liquefied hydrogen [3–5]. These methods create risks and require energy-intensive compression and liquefaction procedures [6]. Marlotherm SH (a commercially available heat-transfer fluid; Sasol) is an isomeric mixture of dibenzyltoluenes (H0-DBTs) which is used today as an alternative hydrogen storage material [7]. Among other liquid organic hydrogen carriers (LOHCs), the H0-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]. Hydrogen is chemically bound in the aromatic rings of H0-DBT through a reversible hydrogenation process [10]. The resulting hydrogen-rich LOHC (perhydro-dibenzyltoluene; 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 H0-DBT 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 proton nuclear magnetic resonance spectroscopy (^1H NMR) and single quadrupole-mass spectrometry gas chromatography (GC-SQ-MS) analyses. GC-SQ-MS analysis is also used to quantify and qualify decomposition products. Quadrupoles of GC-MS are mass analyzers which consist of four rods to which DC and RF voltages are applied [19]. An ion of a specific mass-to-charge ratio (m/z) stabilizes and passes 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.

3.2 Materials and methods

3.2.1 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. H18-DBT (95%, certified hydrogenation grade) was supplied by Hydrogenious Technologies GmbH (Germany) and used as a feed for the dehydrogenation. All dehydrogenation experiments were carried out using a platinum on alumina support (0.5 wt % Pt loading; Hydrogenious Technologies). H0-DBT 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.

3.2.2 Dehydrogenation experiment

Briefly, the experimental dehydrogenation system here comprised a liquid feed loop for hydrogen-rich LOHC, a horizontal plug flow reactor (PFR) made of quartz glass equipped with an electrical heater and a system control loop (see Figure 3.1). The hydrogen-rich substrate is pumped via a peristaltic pump into a horizontally orientated PFR 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/Al₂O₃, 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 was kept constant at 4.5 ml/min and 90 min resident time, only the temperature was varied.

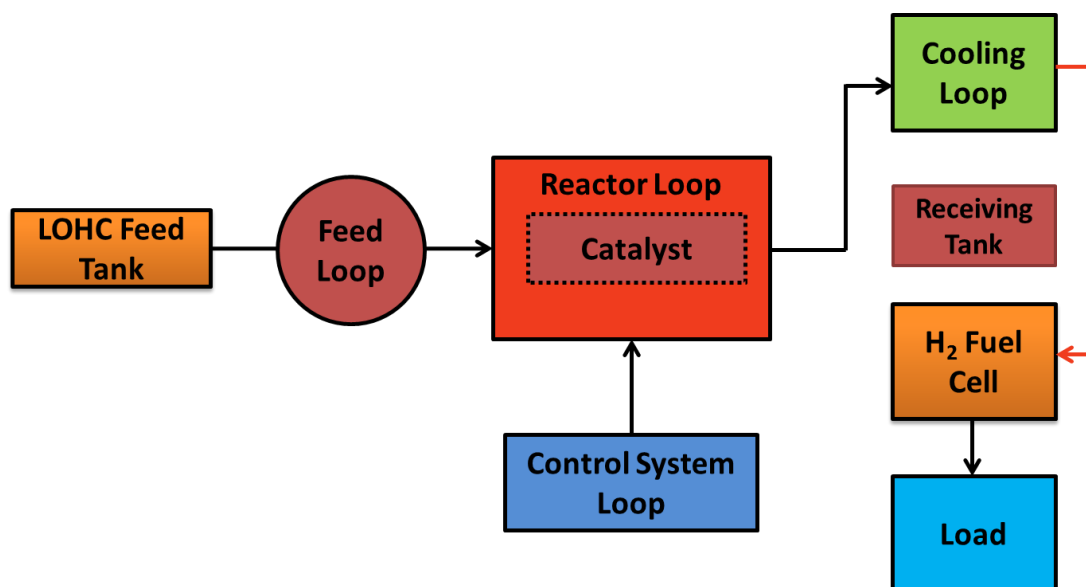


Figure 3.1: Process flow diagram of the dehydrogenation unit.[§]

3.2.3 Two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (2D-GC-TOF-MS)

In this study, 2D-GC-TOF-MS was used to analyse commercial LOHCs and their dehydrogenation reaction mixtures. Chromatographic analyses of samples were carried out in the 2D mode using an Agilent 6890N GC × GC coupled to a TOF mass spectrometer (Leco Pegasus 4D), equipped with an Agilent 7683 B Series auto sampler. A cryogenic modulator located between two columns ensured improved compound separation (see Figure 3.2). All samples of the LOHC reaction mixtures were diluted with chloroform (1:100 wt/wt) and 1-μL quantities were injected using an autosampler. Helium was used as a carrier gas at a constant flow rate of 1 ml/min. The injector temperature was held constant at 300 °C for the entire run. A Restek Rxi-5Sil MS capillary column (30 m, 0.25 mm i.d., 0.25 μm d_f) served as the primary column. Compound separation was achieved by programming the primary oven as follows: initial temperature of 150 °C for 2 min, followed by an increase of 10 °C/min to a temperature of 300 °C, and maintained for 1 min. A shorter Restek Rxi-17Sil column (1.79 m, 0.15 mm i.d.,

[§] Detailed P & ID diagram and a picture of dehydrogenation system can be found in appendix section (Figure A8 and A9).

0.15 μm d_i) served for the second-dimension separation of the compounds. The secondary oven was programmed with an identical temperature gradient to that used for the primary column, only now with an offset of +15 $^{\circ}\text{C}$.

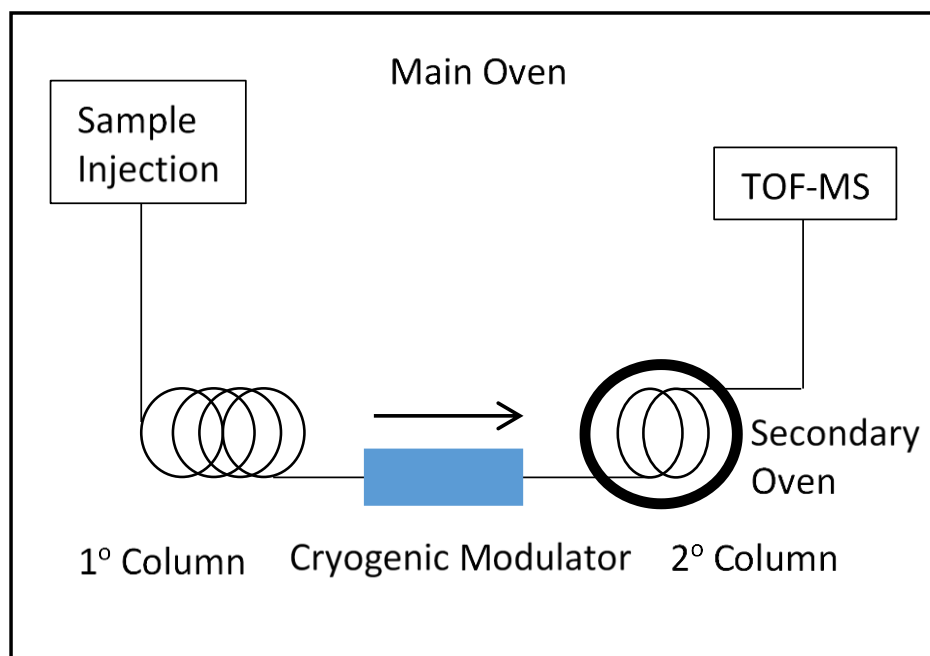


Figure 3.2: Diagram showing comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (2D-GC-TOF-MS).

Cryo-modulation and a hot pulse of nitrogen gas of 0.7 sec and 0.3 sec cooling time between stages was used to control the effluent emerging from the primary column onto the secondary column. The transfer line was held at a constant 290 $^{\circ}\text{C}$ and the ion source temperature at 200 $^{\circ}\text{C}$, for the entire run. The detector voltage was 1600 V and the filament bias -70 eV. Mass spectra were collected at an acquisition rate of 200 spectra per second from 50–600 m/z . ChromaTOF software (version 4.32; Leco Corporation) was used for peak finding, mass spectral deconvolution (spectral determination) and peak identification.

3.2.4 Single quadrupole-mass spectrometry gas chromatography

GC-SQ-MS analysis of decomposition products and reaction mixtures was performed using a Scion 436 GC-SQ-MS instrument. The system was equipped with a CP 8400 auto sampler

(7683 D), a GS-Tek GsBP-50+MS column (30 m, 0.25 mm i.d., 0.25 μ m d.f.) and a single quadrupole mass spectrometer. The single quadrupole mass spectrometer consists of an ion source, where the sample is ionized, and then the ions are focused by mass analyser (Q_0) to the quadrupole rods (Q_1) for mass filtering (SIM) (see Figure 3.3). Quantification and identification were carried out with an extended dynamic range detector. All samples were diluted with hexane (1:100 wt/wt) and 1- μ L quantities of each sample were injected at a split ratio of 1:100. The injector temperature was 300 $^{\circ}$ C and the oven program was as follows: 70 $^{\circ}$ C for 2 min, followed by an increase of 40 $^{\circ}$ C/min to 160 $^{\circ}$ C, then by 2.5 $^{\circ}$ C/min to 300 $^{\circ}$ C, with the final holding time of 20 min. Helium was used as a carrier gas at a constant flow rate of 1 ml/min. The transfer line to the source was held at 250 $^{\circ}$ C. The source temperature was 200 $^{\circ}$ C and the electron energy was -70 eV. MS Workstation 8 with NIST library was used to process data. Mass spectral data were collected in the m/z range 40–450.

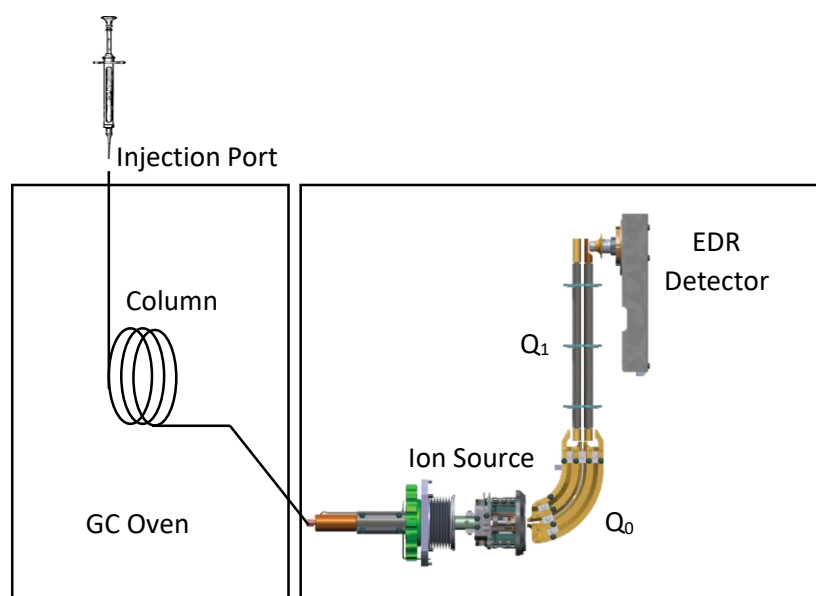


Figure 3.3: Diagram showing single quadrupole-mass spectrometry gas chromatography system (GC-SQ-MS) with extended dynamic range (EDR) detector.

3.2.5 Direct analysis in real time mass spectrometry

Direct analysis in real time mass spectrometry (DART-MS) analysis of reaction mixtures was carried out using a Jeol AccuTOF-DART-MS instrument. A sample was introduced manually using a glass pipet, the tip of which was wetted with the sample. The ionization was done in ESI+ mode using a stream of helium at 200 °C from the ion source. The distance between the ion source and the inlet orifice was set to 1,5 cm. The mass spectra were recorded from $m/z = 100$ to 1000.

3.2.6 Proton nuclear magnetic resonance spectroscopy

^1H NMR spectra of the reaction mixtures were recorded on a Jeol ECX 400 instrument. Chloroform- d was used as solvent. Processing and integration of the spectra was performed using the Jeol Delta 5.0.4 software.

3.3 Results and discussion

3.3.1 Two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (2D-GC-TOF-MS)

The compounds in the first chromatographic column in 2D-GC exhibit similar peak distribution as in conventional GC; overlapping peaks can be further separated in the second chromatographic column. This is because the non-polar 1st dimension column separates compounds according to their boiling point while separation on the mid-polar 2nd dimension column is based on aromatic selectivity. Commercially available H0-DBT consists of a mixture of 8 structural isomers; it is not readily available as a pure compound [20]. A sample of commercial H0-DBT was analysed using 2D-GC-TOF-MS in an effort to understand the nature of this compound and its purity. Since in the non-polar primary column the elution order or separation generally follows the boiling points, the peaks of H0-DBT isomers observed overlap each other. There are some unresolved peaks in the 1D chromatogram that suggest relatively close boiling point isomers (see Figure 3.4). All peaks were confirmed by TOF-MS. They belong to the hydrogen-lean H0-DBT. No other impurities were detected by this technique. We also confirmed eight isomers of H0-DBT by counting horizontally in the first dimension of the chromatogram and excluding tailing isomers. Commercially available perhydro-

dibenzyltoluene (hydrogen-rich) from Hydrogenious Technologies was also analysed using 2D-GC-TOF-MS.

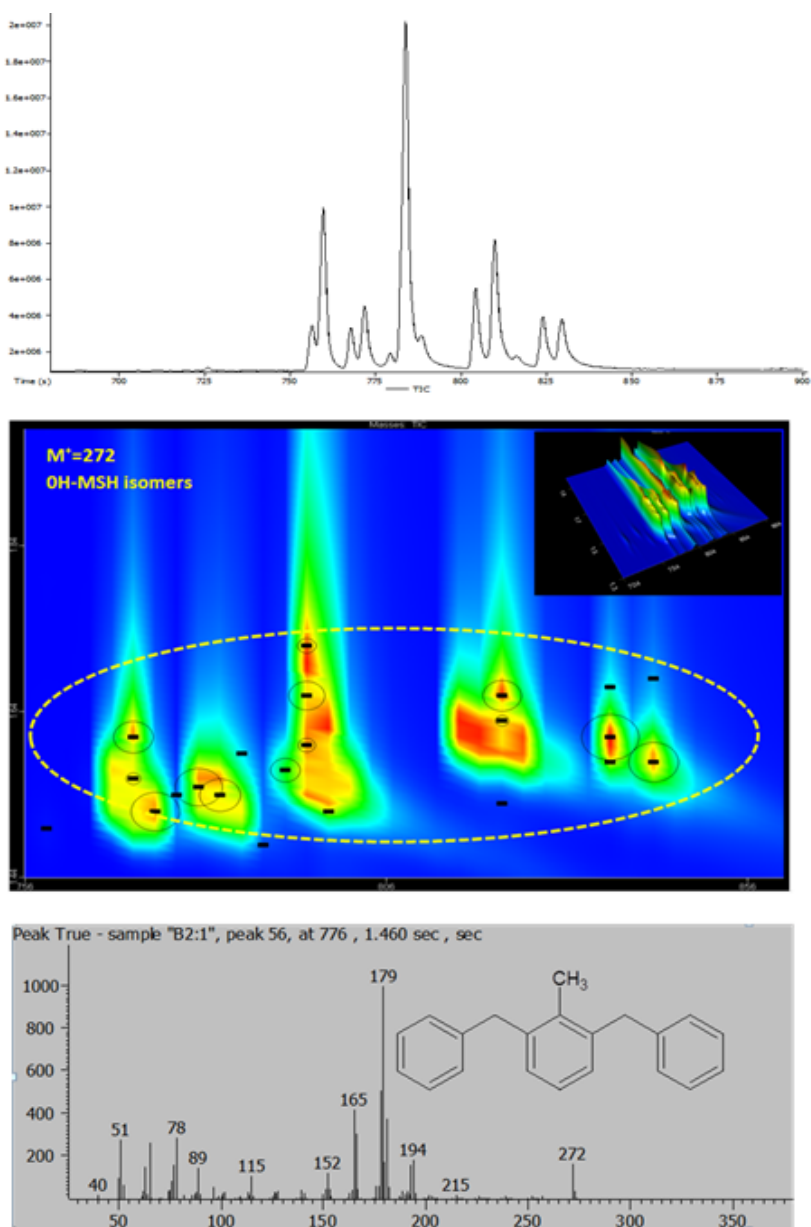


Figure 3.4: Chromatograms (1D, 2D, 3D) and mass spectra of dibenzyltoluene (Sasol).

In Figure 3.5, the 1st dimension chromatogram shows overlapping peaks of isomers and isomer fractions, and thus no distinctive separation. However, on the 2D-GC contour plot, the secondary column separates the H18-DBT into two fractions. With the aid of a TOF-MS detector, the two fractions shown on the contour plot indicate $m/z = 290$ and 284 , with the high molecular weight retained first in the secondary column. This also indicates that the compound is not fully hydrogenated, due to the presence of a dodecahydro-dibenzyltoluene (H12-DBT) $m/z = 284$ fraction, seen on the contour plot (see Figure 3.5). Hexahydro-dibenzyltoluene (H6-DBT) could also appear depending on the effectiveness of the hydrogenation process.

To understand the LOHC dehydrogenation process, hydrogen-rich H18-DBT was pumped at 4.5 ml/min to the dehydrogenation reactor containing 120 g of 0.5 wt % Pt/Al₂O₃ catalyst at temperatures ranging from 270 to 300 °C. For example, the reaction mixture obtained after dehydrogenation at 290 °C showed four fractions on the 2nd dimension (y-axis) of the contour plot (Figure 3.6). The 1st dimension chromatogram of this sample showed more unresolved peaks due to isomers and isomer fractions. The TOF-MS detector also confirmed the presence of isomers of a fully hydrogenated fraction ($m/z = 290$, 6.2 wt % H₂), a partially hydrogenated fraction ($m/z = 284$, 4.1 wt % H₂ and $m/z = 278$, 2.1 wt % H₂) and, lastly, a fully dehydrogenated fraction ($m/z = 272$, 0 wt % H₂).

On the other hand, the secondary column, which is mid-polar (aromatic selective), showed an increase in the aromaticity of the LOHC as dehydrogenation takes place (Figure 3.6). DBT is non-polar and it has the highest number of double bonds and therefore delocalized electrons. It is reported, however, that polycyclic H18-DBT is more hydrophobic (more non-polar) than H0-DBT, due to the absence of delocalized electrons [21]. Therefore, we assumed that the non-polarity strength of fully hydrogenated and dehydrogenated LOHC follows the order H18-DBT ($m/z = 290$) > H12-DBT ($m/z = 284$) > H6-DBT ($m/z = 278$) > H0-DBT ($m/z = 272$).

In Figure 3.7, a surface plot comparison of reaction mixtures obtained at different temperatures for commercial hydrogenated and unhydrogenated LOHCs are depicted. Both the reaction mixtures, obtained at 270 °C and 280 °C, show three isomer fractions ($m/z = 290$, 284 , 278); however, the fraction obtained at 280 °C, with $m/z = 278$, has more isomers than the one obtained at 270 °C. When the reactor temperature was further increased to 290 °C the fully dehydrogenated isomer fraction ($m/z = 272$) appears, leading to four isomer fractions. The reaction mixture obtained after dehydrogenation at 300 °C shows the absence of $m/z =$

290 isomer fraction and a reduced number of the $m/z = 284$ isomers. Furthermore isomers of the $m/z = 272$ fraction increased in number, compared with the isomers of other reaction mixtures. This suggest that the dehydrogenation becomes more efficient at higher temperature. As is evident in Figure 3.7, in all steps of the dehydrogenation reaction each isomer fraction loses three molecules of hydrogen (3 H_2) until all rings are aromatic. All isomer fractions appear at the same second-dimension retention time for reaction mixtures and commercial products. The 2D peaks were integrated using the ChromaTOF software.

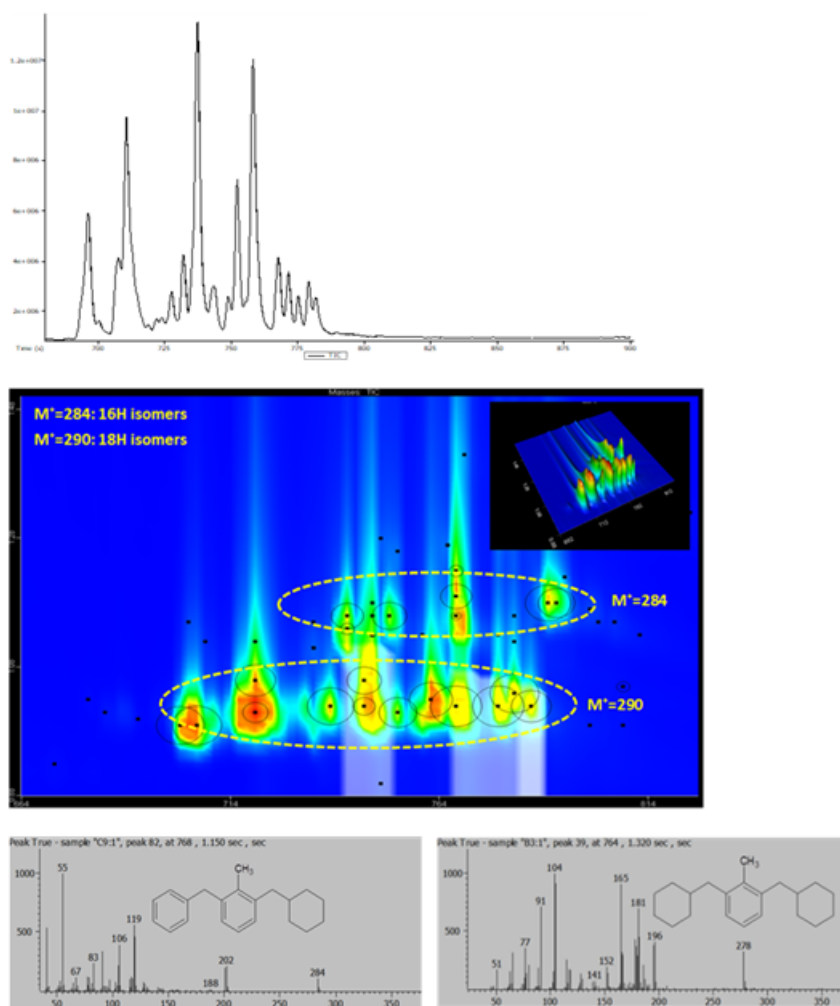


Figure 3.5: Chromatograms (1D, 2D, 3D) and mass spectra of 95% perhydro-dibenzyltoluene (Hydrogenious Technologies).

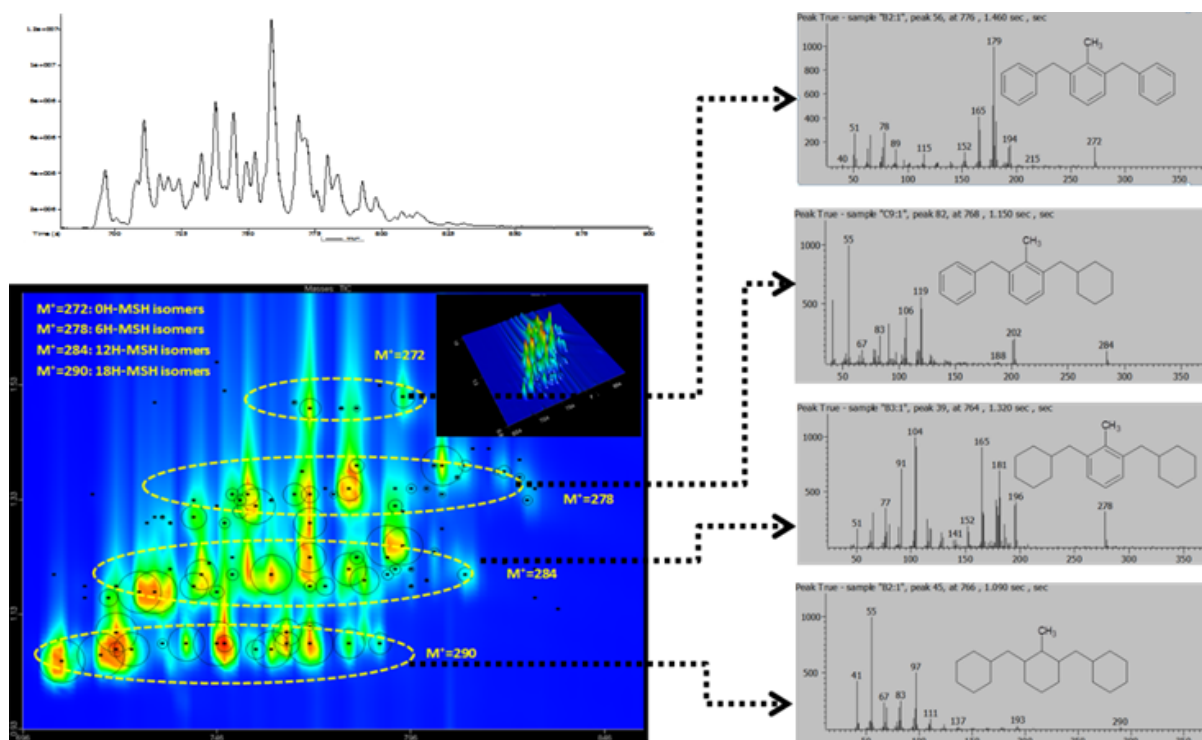


Figure 3.6: Representative chromatograms (1D, 2D, 3D) and mass spectra of a reaction mixture obtained after dehydrogenation at 290 °C.

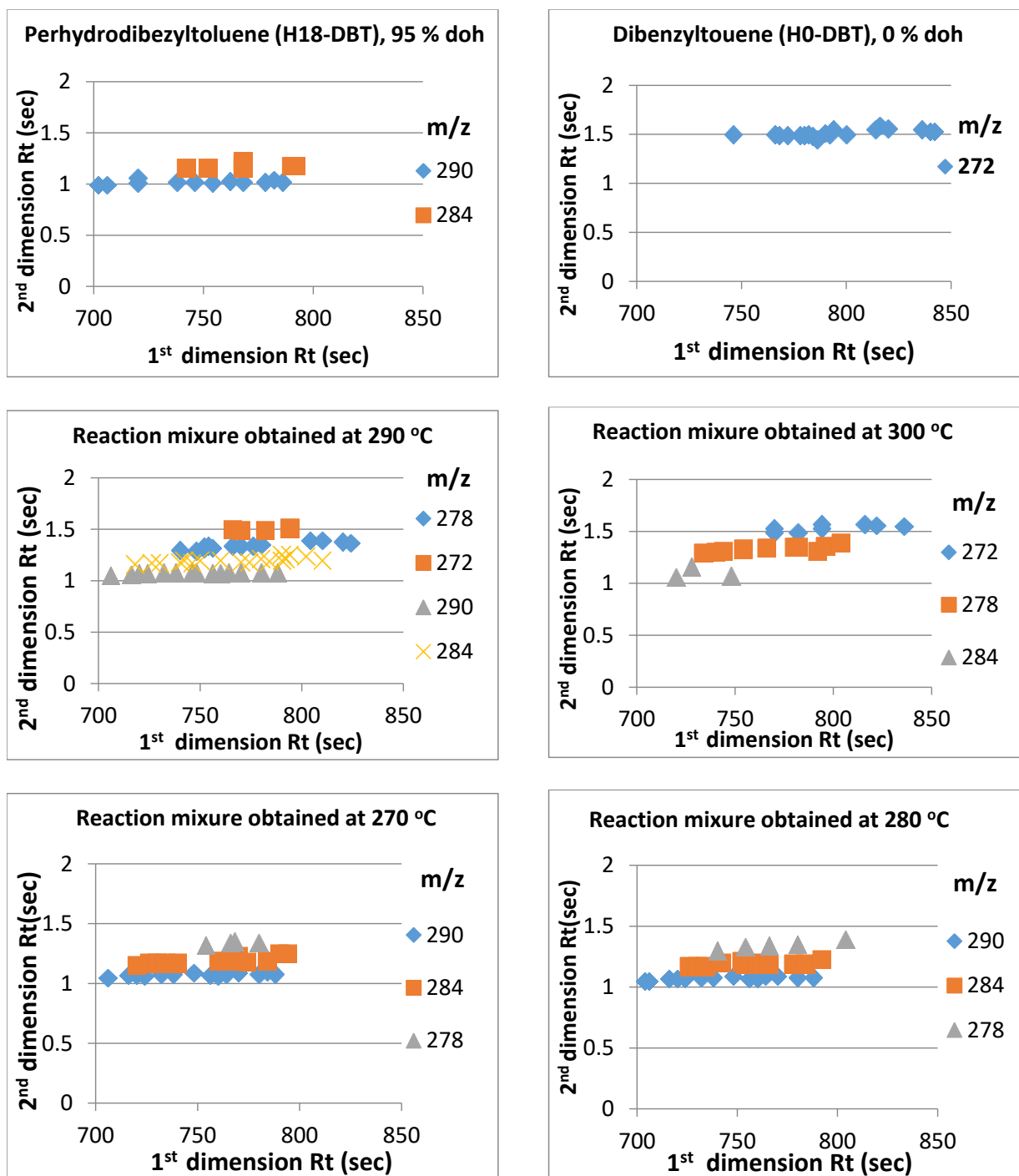


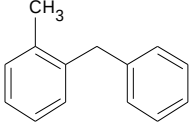
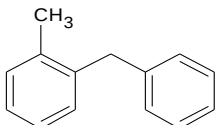
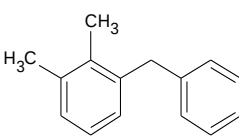
Figure 3.7: 2D-GC surface plots of perhydro-dibenzyltoluene, dibenzyltoluene and reaction mixtures obtained after dehydrogenation at temperatures in the range 270–300 °C. Rt (retention time)

3.3.2 Single quadrupole-mass spectrometry gas chromatography (GC-SQ-MS)

The LOHC process conditions, temperature for example, need to be optimized to avoid the decomposition of carrier molecules over long periods of use of the liquid carrier. For the purpose of GC-SQ-MS analysis we here define decomposition products as any molecules with an $m/z < 272$ (molecular weight of H₀-DBT). We then investigated the effect of reaction temperature on the decomposition of the carrier molecules (see Table 3.1). The reaction mixtures obtained at 280 °C and below showed no decomposition products; however, at 290 °C a peak with $m/z = 182$ appears at 13.6 min (see Figure 3.8). Furthermore, the reaction mixture obtained at 300 °C showed the presence of a peak with $m/z = 182$ peak, and three more peaks of the same mass ($m/z = 196$) (see Figure 3.9). All these products described above eluted before the parent molecule (H₀-DBT).

It is expected that the last isomer fraction to elute will be H₀-DBT ($m/z = 272$). However, we observed another fraction of $m/z = 270$ eluting after the H₀-DBT fraction (see Figure 3.10). The long retention time fraction of $m/z = 270$ is attributed to high-boiling-point molecules. This compound with a high boiling point or long retention time may be of the benzyl-methylfluorene type, stemming from a dehydrogenative cyclization of the parent LOHC molecule. Therefore, high and low boilers occurring at 290 and 300 °C are due to thermal cracking and cyclization of the liquid carrier molecules as a result of harsh reaction condition [22–24]. The total percentage of decomposition products obtained from the reaction mixtures at 290 and 300 °C yielded 0.73% and 7%, respectively. Hence, an effective catalyst that can perform dehydrogenation at 280 °C or below will be most suitable because harsh reaction conditions lead to fast dehydrogenation reactions, which shortens the LOHC lifetime—lower temperatures lead to longer lifetimes. Doh between 10 and 85 % were reached [25], so that the usable LOHC capacity in this experiment is more than 4.6 wt %.

Table 3.1: Identification and quantification of decomposition products obtained at different dehydrogenation temperatures

Reaction mixture temperature, °C	Decomposition products	Quantity in the mixture, %
270	Not detected	
280	Not detected	
290	 $M^+ = 182$	0.73
	 $M^+ = 182$	1.80
300	 $M^+ = 196$	1.94
	$M^+ = 270$: structure not identified; possibly benzyl-methylfluorene	3.63

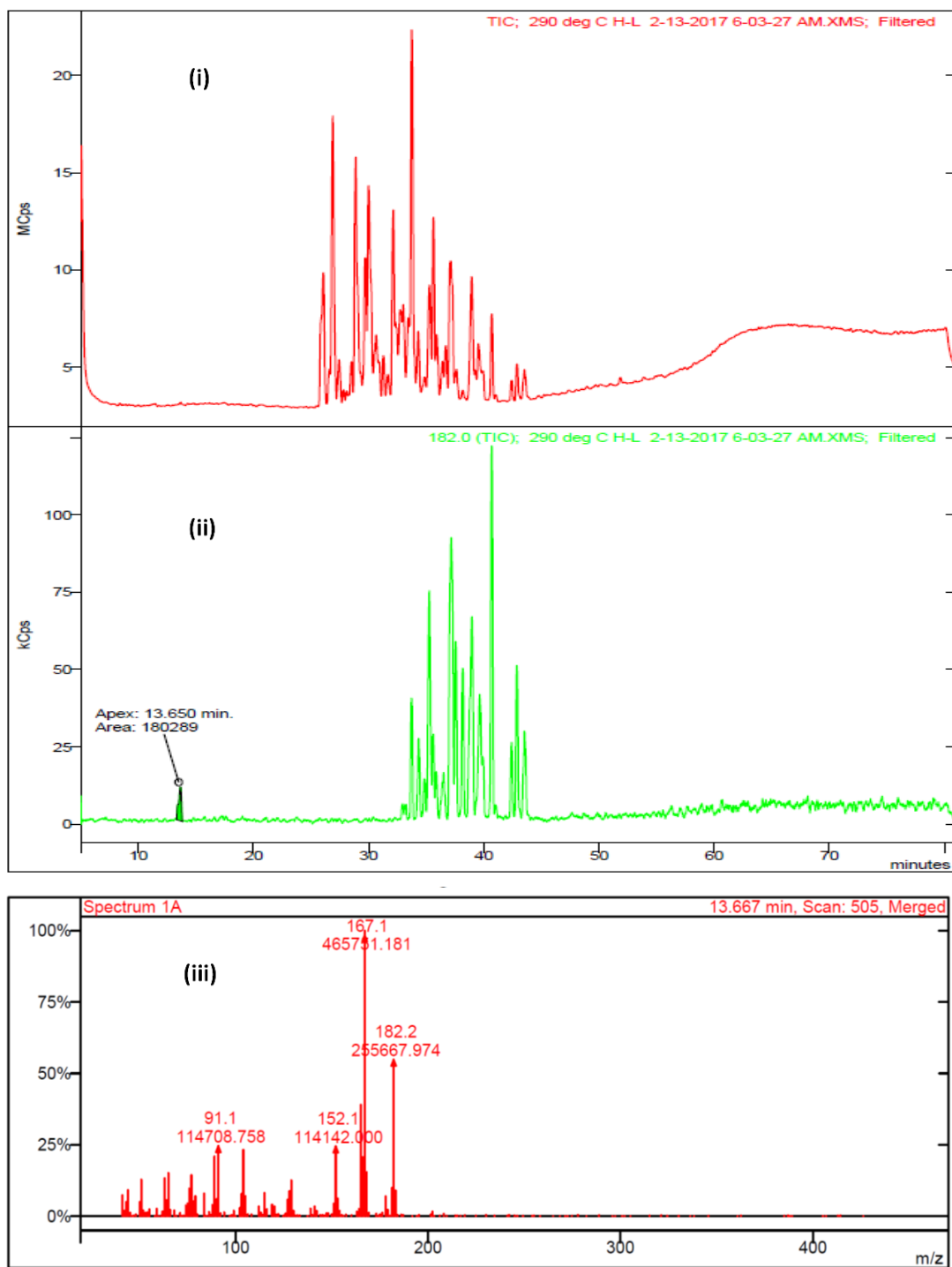


Figure 3.8: (i) Full scan chromatogram, (ii) SIM mode and (iii) mass spectra showing a decomposition product ($m/z = 182$) of a reaction mixture obtained after reaction at 290 °C.

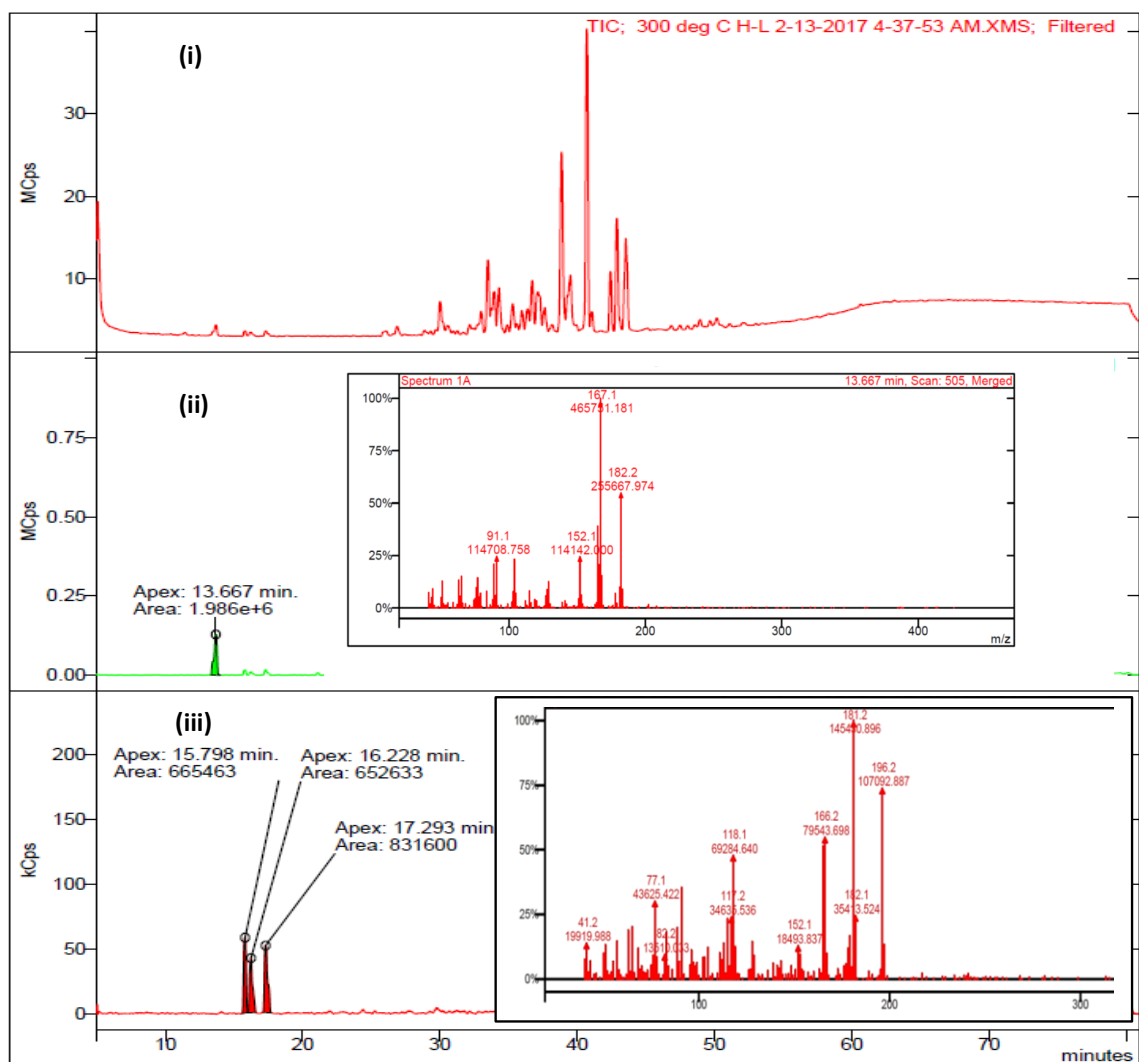


Figure 3.9: (i) Full scan chromatogram, SIM mode and mass spectra of decomposition products (ii) $m/z = 182$ and (iii) $m/z = 196$, of a reaction mixture obtained after reaction at 300 °C.

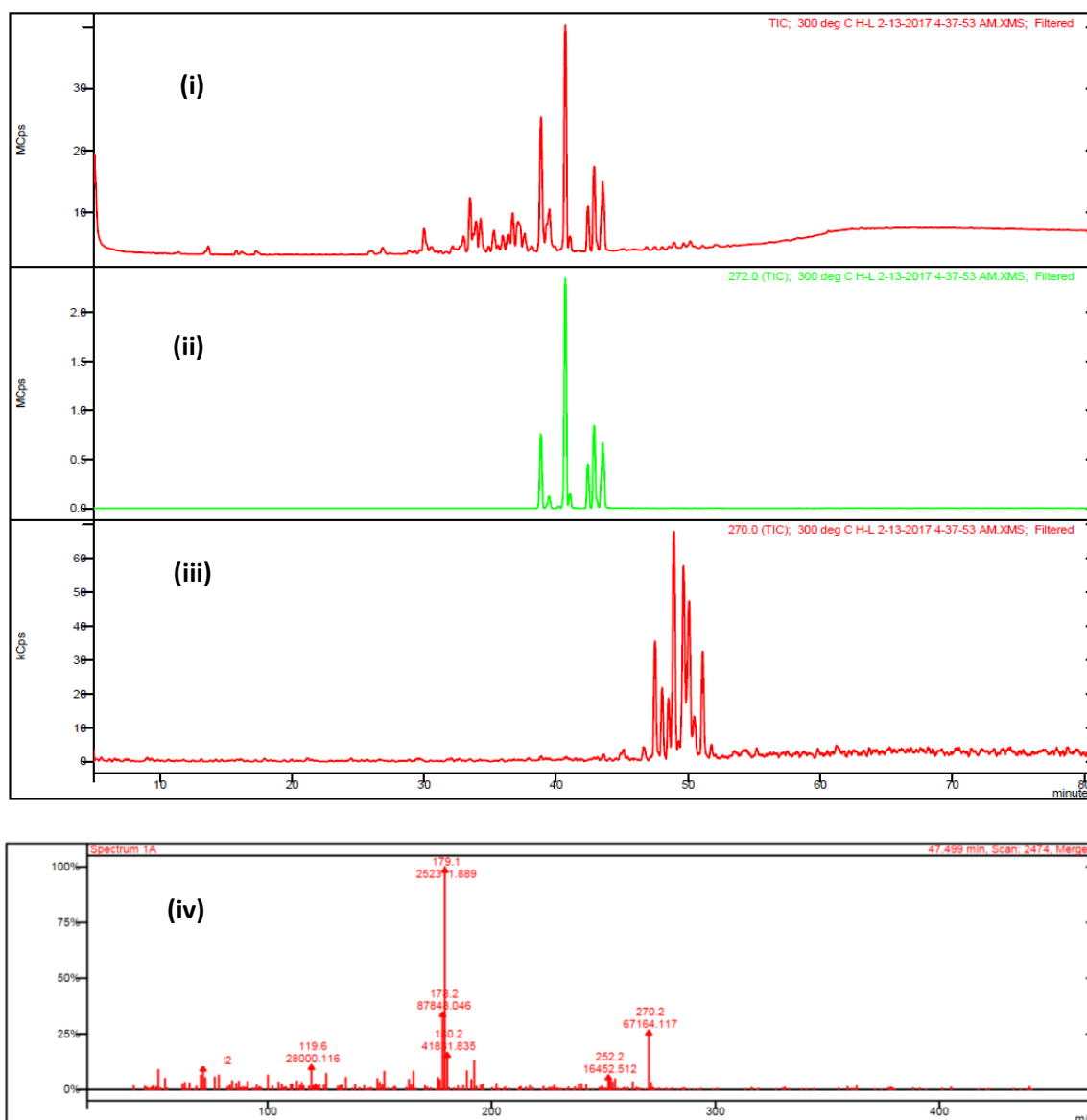


Figure 3.10: (i) Full scan chromatogram SIM mode of isomer fractions of (ii) $m/z = 272$ (iii) decomposition product ($m/z = 270$) and (iv) mass spectrum, for a reaction mixture obtained after reaction at 300 °C.

Here, the SIM mode of GC-SQ-MS is discussed as applied for the separation of chromatograms into fractions. In SIM mode, a fixed set of DC and RF voltages was applied to the quadrupole—thus only ions of a selected m/z can pass. Ions with different m/z values are filtered out. We have previously indicated the problem of overlapping chromatogram peaks, due to close boiling points of components of an isomer mixture of H0-DBT, has been

mentioned. See the full scan in Figure 3.11. Here, the non-polar GC column separates according to the analyte's boiling point and SQ-MS isolates only ions or isomer fractions of interest using SIM mode. Hence isomer fractions of the reaction mixture obtained at 290 °C show separate fractions of stepwise dehydrogenation from H18-DBT to H0-DBT ($m/z = 290-272$). See results for the SIM mode in Figure 3.11. Moreover, the elution order of isomer fractions obtained in SIM mode resembles that obtained from 2D-GC-MS.

Understanding individual isomer fraction depletion and formation using GC-SQ-MS offers more insight into the dehydrogenation process. As shown in Figure 3.12 and Figure 3.13, there is depletion of H18-DBT and subsequent formation of H12-DBT. Furthermore, there is depletion of the latter as the reaction temperature is increased to 300 °C. The H12-DBT fraction depletion yields H6-DBT, which is also depleted to form H0-DBT. Hence, at low temperatures the quantity of H0-DBT is low, but at 300 °C more than 60% of this fraction is formed. H0-DBT is a fully dehydrogenated fraction which can be achieved in a mixture together with other fractions or as a pure compound if a more active catalyst is used.

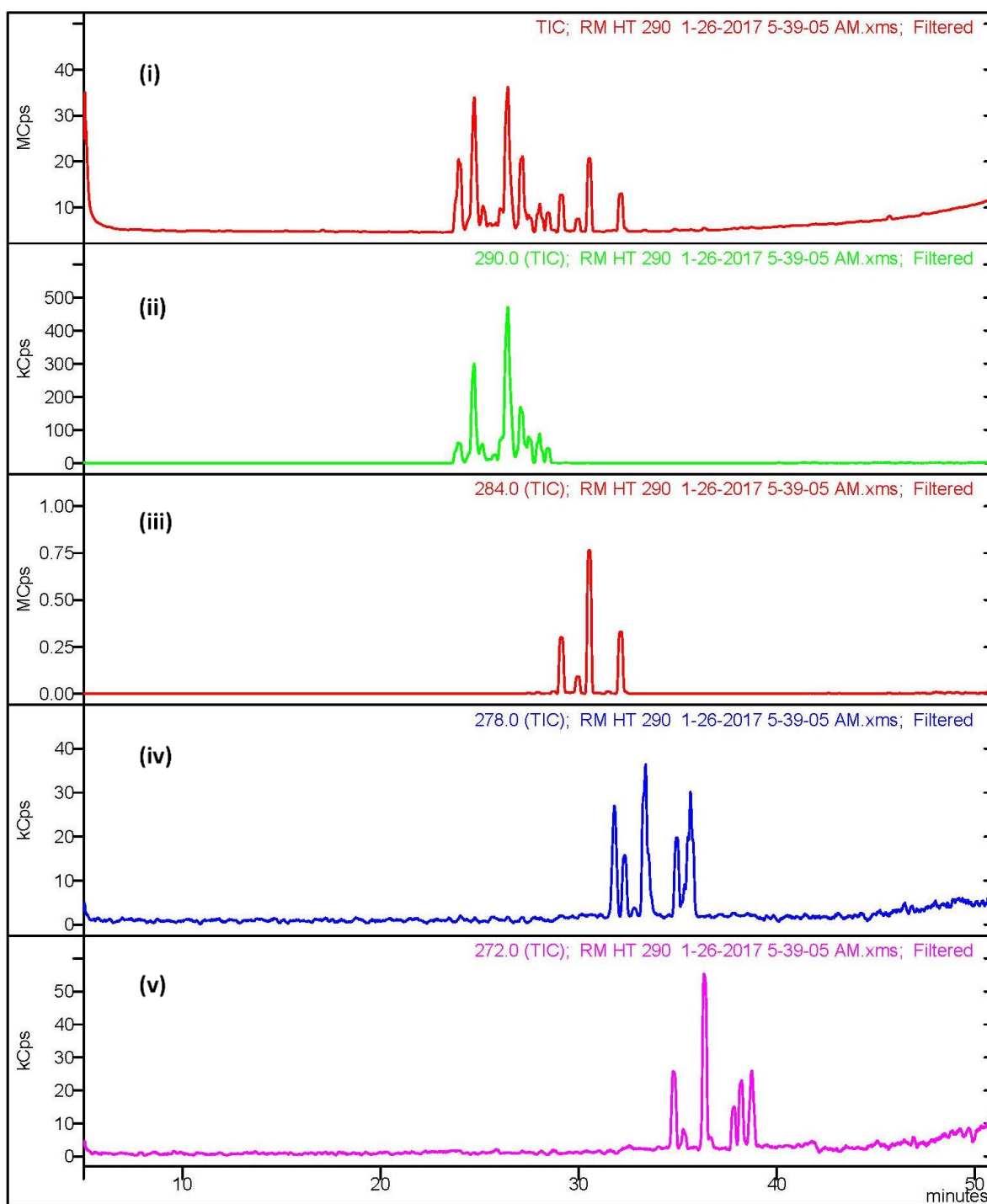


Figure 3.11: Representative chromatograms of a reaction mixture obtained after reaction at 290 °C: (i) full scan, SIM mode of (ii) H18-DBT, (iii) H12-DBT, (iv) H6-DBT and (v) H0-DBT.

3.3.3 Direct analysis in real time mass spectrometry (DART-MS)

To determine the possible presence of products that are not detected by GC methods and to further confirm the findings of the previously discussed GC-MS methods, a DART-MS analysis of the reaction mixtures was performed. Figure 3.12 to Figure 3.17 show a comparison of the MS plots of the reaction mixtures. In no cases were signals with $m/z > 600$ obtained; hence the spectra are scaled accordingly. The molecules already detected by the GC method were confirmed by the DART-MS spectra. The mass spectra show distinct groups of peaks, centred on the expected m/z values of different hydrogenated species and their decomposition products. The existence of peaks besides the molecular ion peaks is due to the loss or the addition of proton. This phenomenon is more pronounced with the substances containing aromatic rings. In the mass spectrum of the reaction mixture obtained at 270 °C, the dominant peak is at $m/z = 284$ for H12-DBT; the peak groups around $m/z = 278$ and 272 indicate the presence of H6-DBT and H0-DBT, respectively.

The single peak at $m/z = 290$ arises from the aliphatic compound H18-DBT. The much smaller signals around $m/z = 194$ and 182 show the presence of some amounts of dodecahydro-benzyltoluenes and benzyltoluenes. With increasing reaction temperatures, a shift of the mass-to-charge ratio peaks to lower m/z can be observed. This corresponds well to the findings from the GC quantitation. An increase in benzyltoluenes with increasing reaction temperature is also observed. It should be noted that almost no hexahydro-benzyltoluene is detected at $m/z = 188$. The most remarkable feature of the mass spectrum of the reaction mixture obtained at a reaction temperature of 300 °C is the still-present base peak of $m/z = 290.19$, corresponding to H18-DBT (see

Figure 3.16). According to GC analysis, this compound is not present in the reaction mixture. DART-MS has a tendency to form adducts with atmospheric water; hence a peak at $m/z = 290.19$ could be a mixture of an adduct and water. Therefore, the peak at 290.19 can best be explained with the formation of $[M+H_2O]^+$: addition of water ($m/z = 18.011$) to the non-hydrogenated material ($m/z = 272.16$). An experiment with a higher de-clustering voltage of 50 V is used to eliminate water, see Figure 3.17.

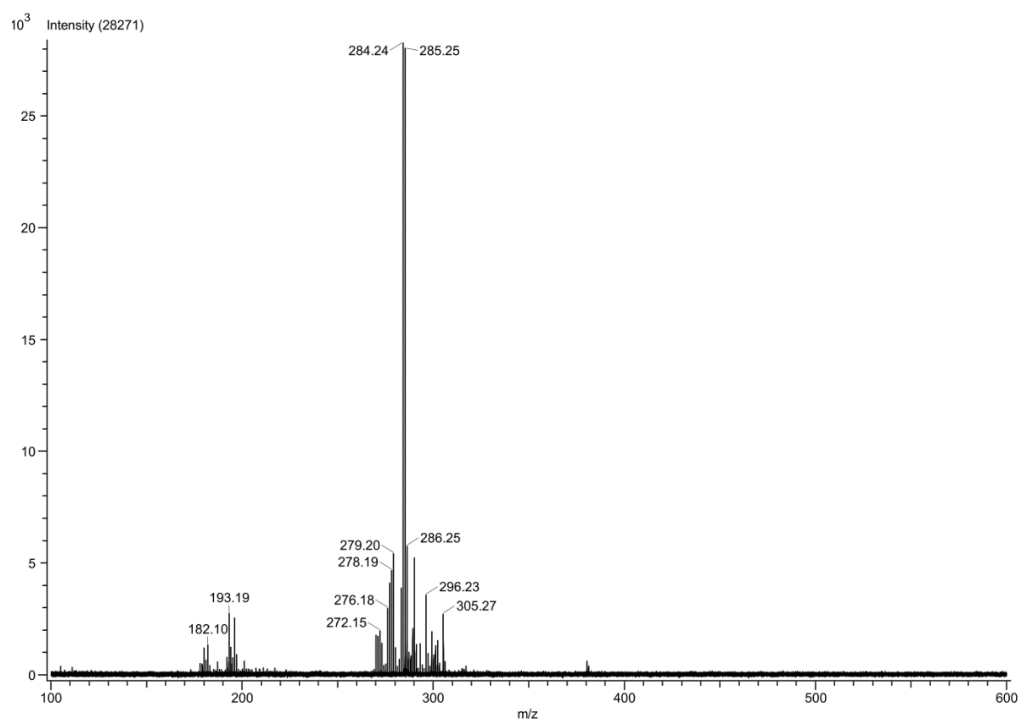


Figure 3.12: DART-MS spectrum of a reaction mixture obtained after reaction at 270 °C.

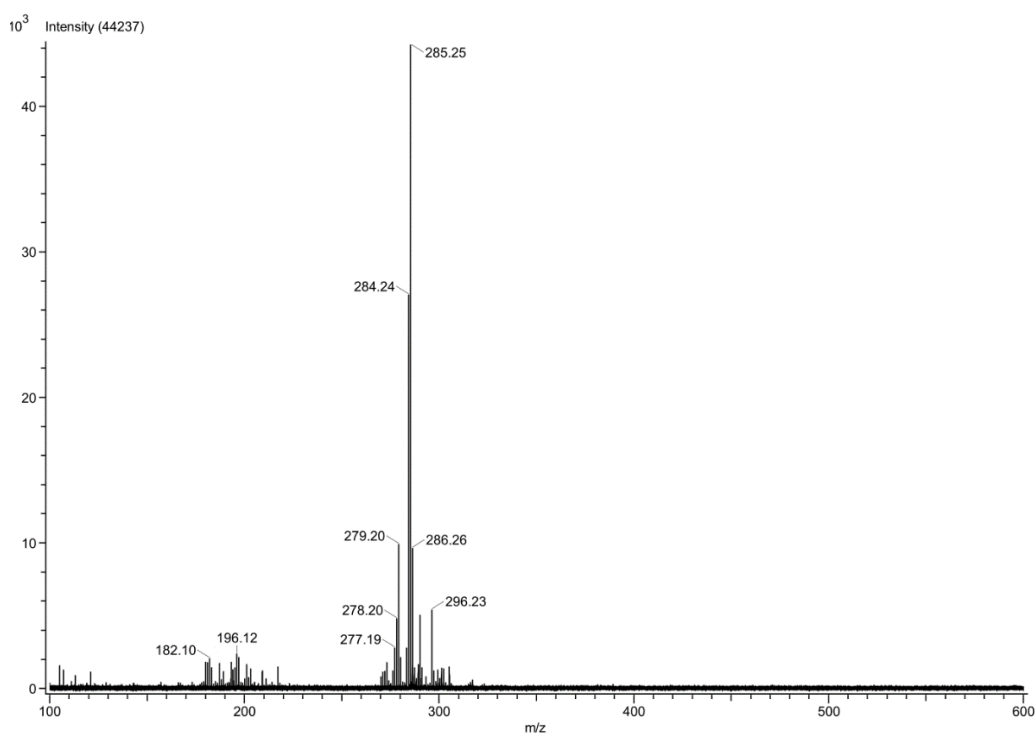


Figure 3.13: DART-MS spectrum of a reaction mixture obtained after reaction at 280 °C.

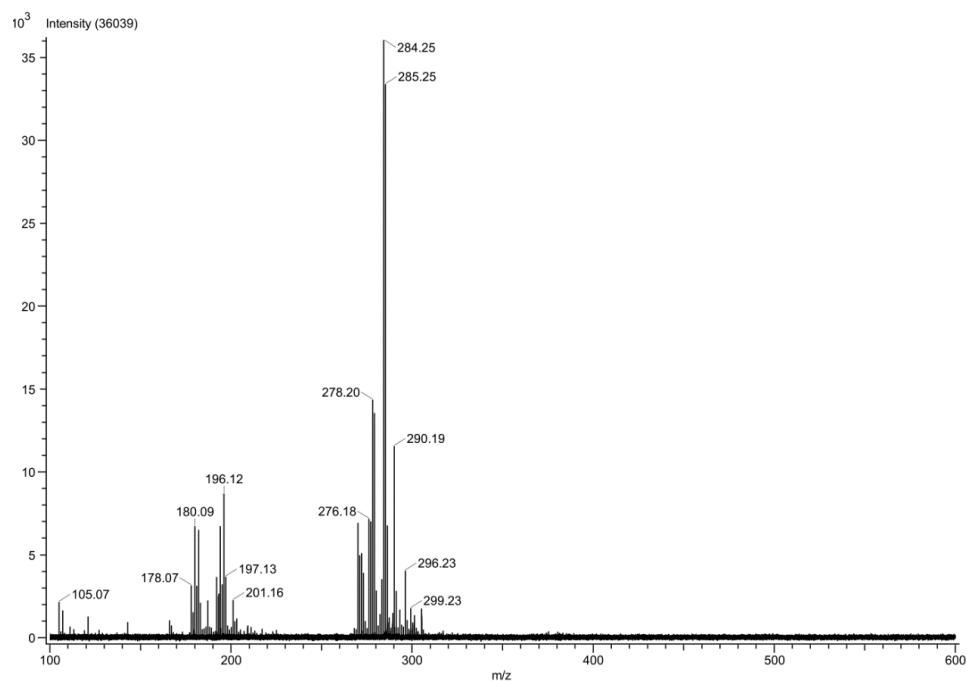


Figure 3.14: DART-MS spectrum of a reaction mixture obtained after reaction at 290 °C.

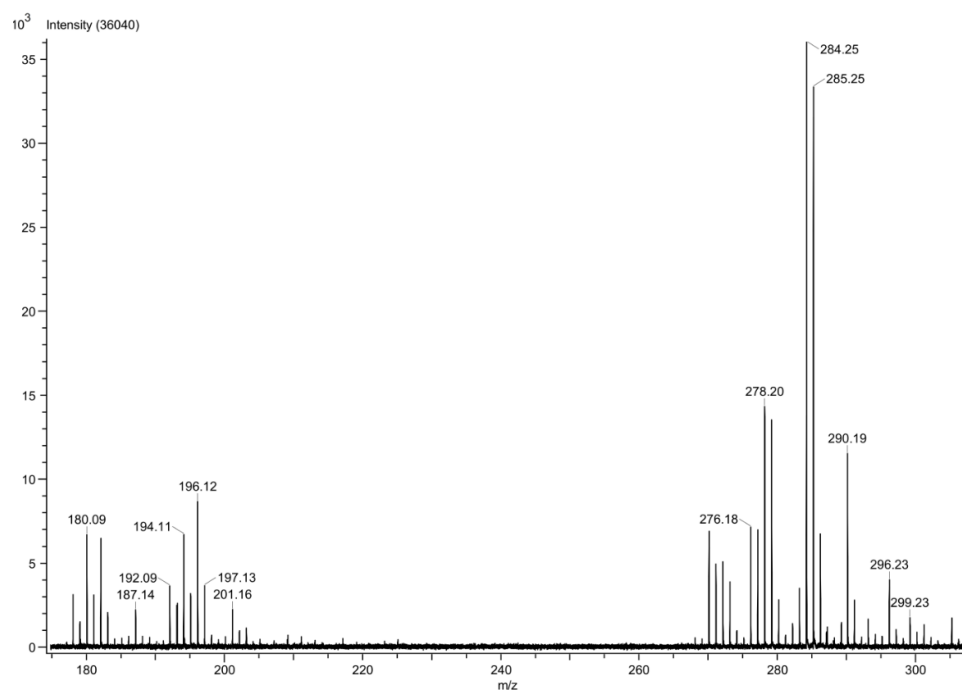


Figure 3.15: Magnification of Figure 3.14.

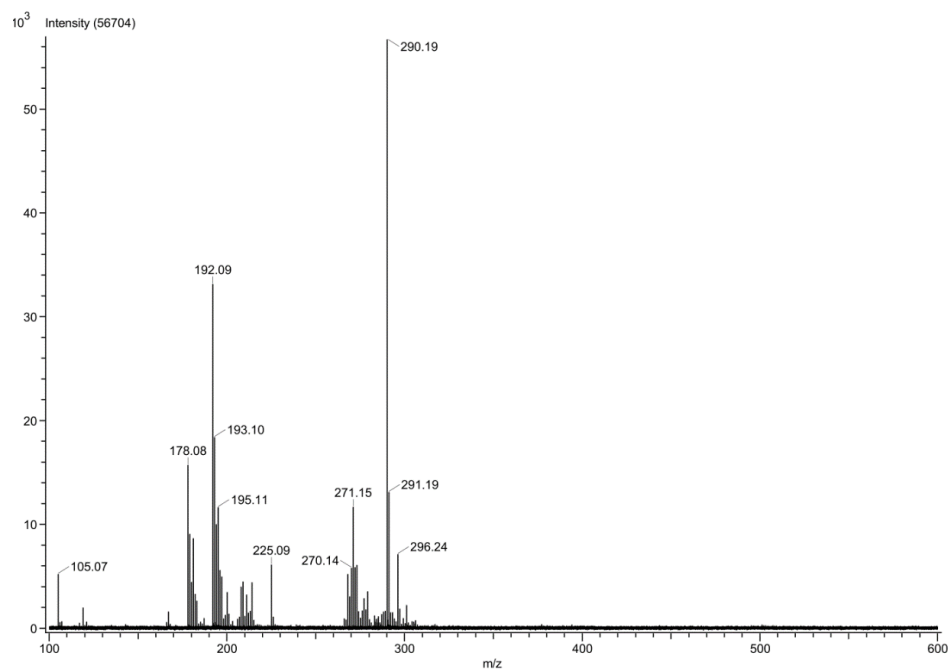


Figure 3.16: DART-MS spectrum of a reaction mixture obtained after reaction at 300 °C.

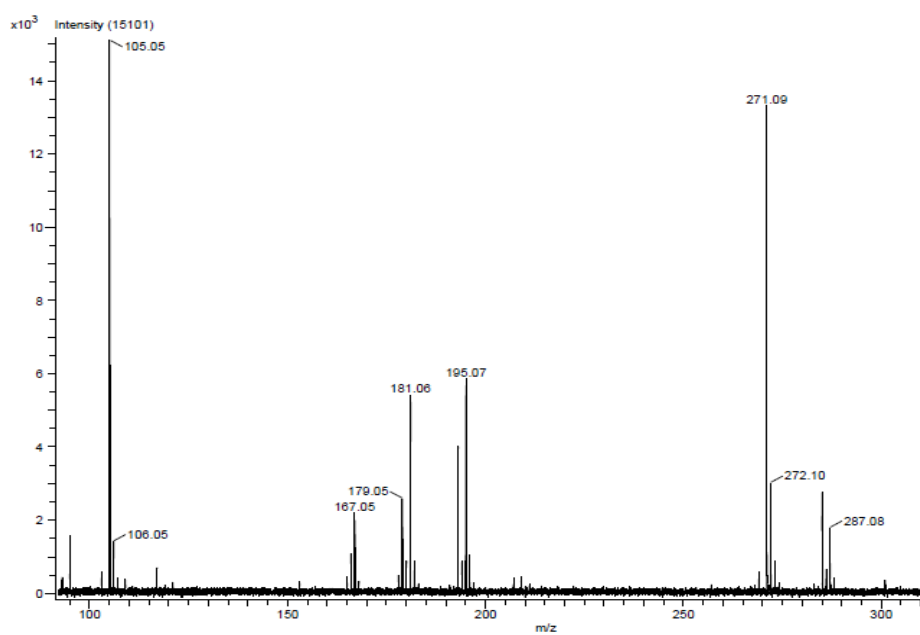


Figure 3.17: DART-MS spectrum of a reaction mixture obtained after reaction at 300 °C, after application of higher declustering voltage to remove atmospheric water.

3.3.4 Determination of the degree of hydrogenation

The doh can be determined using Eq. 1 [26], where X is the mole fraction.

$$doh = [0.33(X_{H6-DBT}) + 0.67(X_{H12-DBT}) + X_{H18-DBT}] \times 100 \quad (1)$$

The mole fraction (X) of each compound, or the reaction mixture in this case, is determined by integration of the contour plot peaks to obtain the peak area of all fractions of isomers.

$$X = \frac{\text{Total isomer fraction peak area}}{\text{Total fractions peak area}} \quad (2)$$

Conversely, a series of standards were used to generate a calibration curve by the multilevel (5) external standard method. The SIM mode was used to filter masses corresponding to H18-DBT to integrate peak areas for all standards. The relative standard deviation (RSD) of the response factor, calculated from GC-SQ-MS, was 1%, with a correlation coefficient value of 0.9947. For 2D-GC-MS-TOF the RSD was 1.9%, with a correlation coefficient of 0.9998.

The doh values determined using Eq. 1 were compared with results from the calibration method, see Table 3.2. As shown in Table 3.2, the doh decreases with an increase in reaction temperature; however, dehydrogenation is lower at 270 °C and 280 °C than at higher temperatures [27]. The results obtained from comprehensive 2D-GC-MS-TOF are comparable to those from GC-SQ-MS, when Eq. 1 is used for both techniques (see Figure 3.18 and Figure 3.19). The precision of the NMR measurements was not determined in this study, but was estimated, based on [28], to be better than 3%.

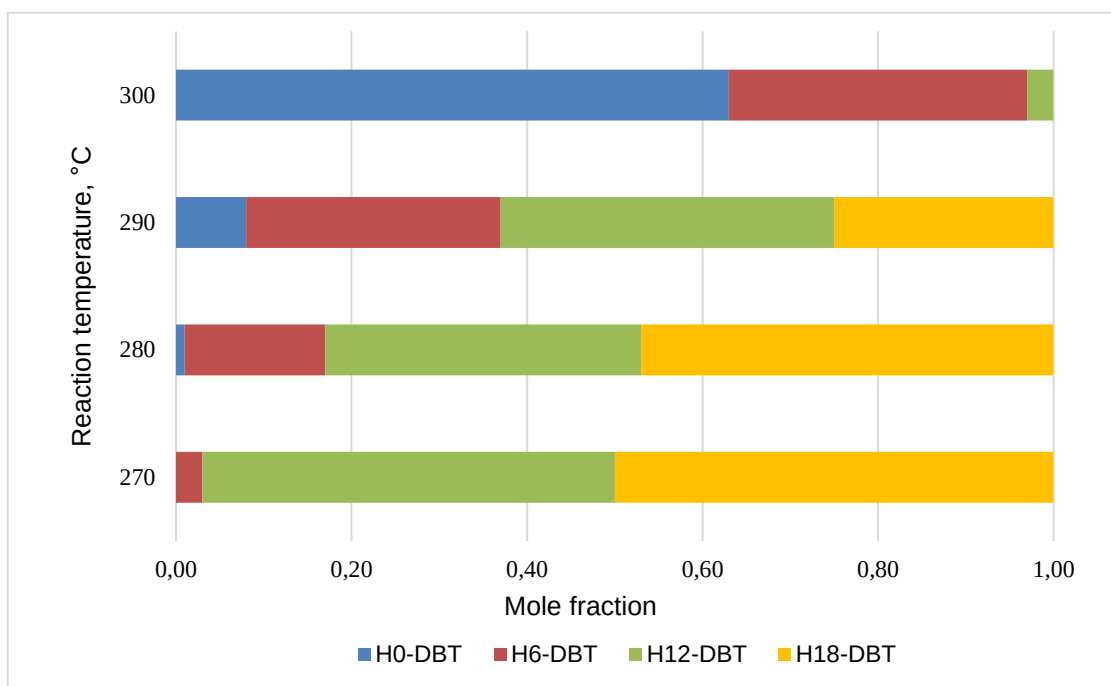


Figure 3.18: Fractions obtained at different reactions temperatures using 2D-GC-TOF-MS.

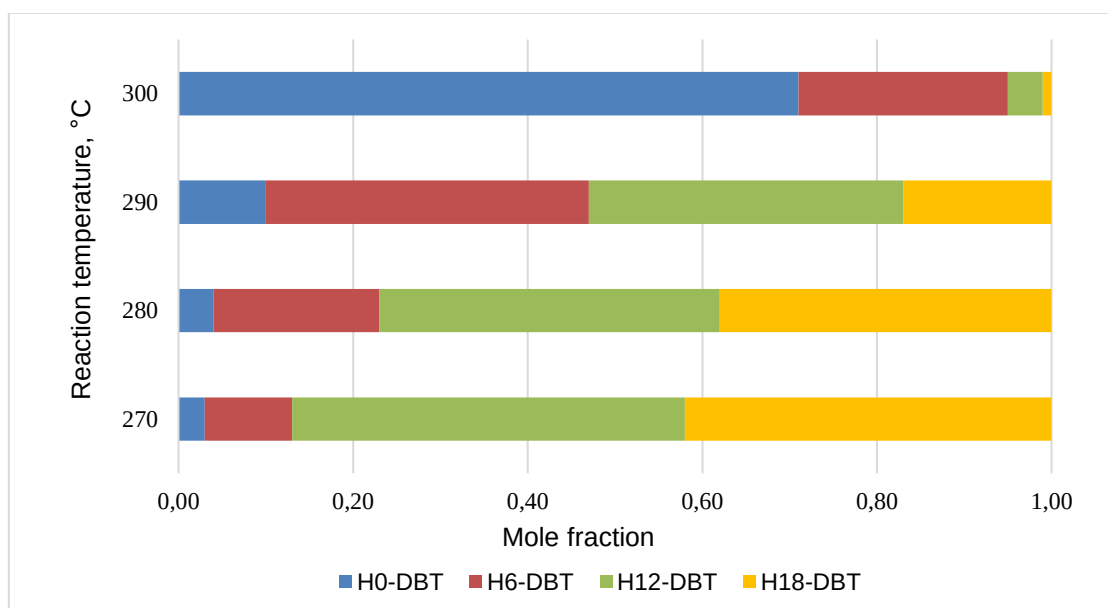


Figure 3.19: Fractions obtained at different reaction temperatures using GC-SQ-MS.

Table 3.2: Comparison of doh values obtained using 2D-GC-TOF-MS and GC-SQ-MS techniques

Adduct	Mole fraction								doh GC-SQ- MS	doh 2D-GC-MS- TOF	doh NMR
	H0-DBT		H6-DBT		H12-DBT		H18-DBT		Equation 1 {Calibration curve}		
	2D-GC-MS	GC-SQ-MS	2D-GC-MS	GC-SQ-MS	2D-GC-MS	GC-SQ-MS	2D-GC-MS	GC-SQ- MS	%	%	%
SASOL(Marlotherm-SH)	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0 {0}	0 {0}	0
Reaction mixture: 300 °C	0.63	0.71	0.34	0.24	0.03	0.04	0.00	0.01	12 {19}	13 {17}	18
Reaction mixture: 290 °C	0.08	0.10	0.29	0.37	0.38	0.36	0.25	0.17	53 {69}	60 {71}	65
Reaction mixture: 280 °C	0.01	0.04	0.16	0.19	0.36	0.39	0.47	0.38	70 {77}	76 {79}	82
Reaction mixture: 270 °C	0.00	0.03	0.03	0.10	0.47	0.45	0.50	0.42	75 {88}	82 {86}	84
Hydrogenious Technologies	0.00	0.02	0.00	0.02	0.36	0.44	0.64	0.52	82 {90}	88 {91}	93

3.4 Conclusions

Analysis by conventional GC is inadequate for the determination of doh because reaction mixtures of partially dehydrogenated H18-DBT show overlapping peaks of isomers and isomer fractions. Such complex mixtures can be successfully separated by comprehensive 2D-GC-TOF-MS, with a suitable selection of first- and second-dimension column polarity. Results of 2D-GC-TOF-MS reveal that isomer fractions lose three molecules of hydrogen (H18-DBT, H12-DBT, H6-DBT and H0-DBT) until dehydrogenation is completed. The degree of hydrogenation decreases with an increase in reaction temperature; for example, 84% hydrogenation was obtained at 270 °C and 18% at 300 °C. Furthermore, by making use of GC-SQ-MS, it is possible to identify and isolate isomer fractions, by using the so-called selective ion mode option (filtering masses of interest). Results were comparable to those obtained with comprehensive 2D-GC-MS. Products that resulted from the thermal cracking of molecules of the parent isomeric mixture were observed only after dehydrogenation at 290 °C and 300 °C. This suggests that higher temperatures may reduce the life cycle of H0-DBT-based LOHC. Quantitative analysis of LOHC reaction mixtures using GC-SQ-MS and 2D-GC-MS-TOF reveal that values for the degree of hydrogenation obtained by the calibration method are comparable to values obtained when ^1H NMR was used as reference.

3.5 Acknowledgements

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3.6 References

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CHAPTER 4: EVALUATION OF CATALYST ACTIVITY FOR RELEASE OF HYDROGEN FROM LIQUID ORGANIC HYDROGEN CARRIERS

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OVERVIEW

This contribution investigates the effect of parameters for the production of hydrogen by catalytic dehydrogenation of perhydro-dibenzyltoluene (H18-DBT). The sensitivity of the dehydrogenation reaction to temperature (290–320 °C) is justified by an increase in the degree of dehydrogenation (dod) from 40 to 90%, and hydrogen flow rate from 5 to 23 NL/h, when using 1 wt % Pt/Al₂O₃ catalyst. However, the increase in temperature accelerates the formation of by-products, hence a decrease in hydrogen purity is observed. In addition, a dod of 96% was obtained when 2 wt % Pt/Al₂O₃ was used at 320 °C. The dod obtained for Pd, Pt, and Pt-Pd catalysts is 11, 82 and 6%, respectively. Therefore, Pd is not a metal of choice for the dehydrogenation of H18-DBT, in both monometallic and bimetallic systems. The *ab initio* density functional theory (DFT) calculations are consistent with this observation. Furthermore, dehydrogenation of H18-DBT followed 1st order reaction kinetics and the activation energies for 1 wt % Pt/Al₂O₃, 1 wt % Pd/Al₂O₃ and 1:1 wt % Pt-Pd/Al₂O₃ catalysts were 205, 84 and 66 kJ/mol, respectively.

4.1 Introduction

Hydrogenation and dehydrogenation of organic compounds are well established industrial processes that have been extensively used for various applications. Catalysts commonly used for these processes include platinum, palladium, ruthenium, nickel, copper and others [1–4]. The noble metal catalysts are deposited in small quantities (0.3–5 wt %) on porous supports

such as SiO_2 , Al_2O_3 , TiO_2 and V_2O_5 [5–7]. $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts are typically used for the dehydrogenation of cycloalkanes to their corresponding aromatic compounds, whereas nickel and copper systems, containing much higher loadings (~50 wt %), are typically used for the hydrogenation of aromatic compounds [8]. The low volumetric density of gaseous hydrogen makes it challenging to store. The conventional technologies are liquefied ($2.4 \text{ kWh}_{\text{th}}/\text{L-H}_2$) and compressed hydrogen at 350 or 700 bar (0.8 or $1.3 \text{ kWh}_{\text{th}}/\text{L-H}_2$) [9–11]. These technologies offer only limited benefits due to safety concerns, low storage density, heavy transportation, boil-off losses and relatively high costs.

Hydrogen storage by means of hydrogenation of aromatic compounds, commonly known as the liquid organic hydrogen carrier (LOHC) technology, has recently attracted much attention [12]. Amongst several other LOHCs systems, dibenzyltoluene (H0-DBT) has excellent hydrogen storage properties (reported elsewhere [13–17]). The most remarkable properties of H0-DBT are its high boiling point (390°C), hydrogen capacity of 6.2 wt % and a storage density of $56 \text{ kg-H}_2/\text{m}^3$ -H18-DBT (equivalent to $2.06 \text{ kWh}/\text{kg-H18-DBT}$) [18–21]. The hydrogenation of H0-DBT produces a corresponding hydrogen-rich compound perhydro-dibenzyltoluene (H18-DBT), which can be dehydrogenated to release the stored hydrogen. Remarkably, hydrogenation and dehydrogenation reactions of H0-DBT and H18-DBT can be carried out in the same temperature range (290 – 310°C), where hydrogen pressure is used to control the equilibrium between hydrogen loading and release [22].

Compared with other hydrogen storage technologies, LOHC technology is attractive in terms of safety, scalability and transportation. However, improvements in catalyst development, reactor design and overall process optimization are required in order to bring the LOHC technology to fruition. To this end, there is also the need for both experimental and theoretical approaches towards the catalytic reactions. Theoretical studies, especially those based on *ab initio* density functional theory (DFT), can offer fundamental insight into the different processes and reactions that take place on the surfaces of different catalysts, as well as the screening of metal catalysts [23,24]. A suitable catalyst and reactor configuration for LOHC dehydrogenation is required to meet hydrogen fuel cell specifications. This refers to the production of fuel-cell-grade hydrogen, including the flow and pressure requirements.

The catalyst efficiency depends on the metal loading and the structural properties, i.e., porosity, surface area, particle size, active surface area, pore diameter and volume [25–29]. Okada et al. [30] reported that alumina with controlled pore size has good Pt dispersibility for

impregnation compared to uncontrolled pore size of alumina. This has been proven by the high conversion (>95%) of methylcyclohexane to toluene and a selectivity of >99.9% when Pt/Al₂O₃ with controlled pore size is used. Biniwale et al. [31] compared the use of the following two catalysts for the dehydrogenation of cyclohexane: 20 wt % Ni/ACC (ACC: activated carbon cloth) and 0.5 wt % Pt/ACC + Pt-promoted nickel catalyst (20 wt % Ni/ACC + 0.5 wt % Pt). Their results revealed that the bimetallic (Ni/Pt) activity (12.75 mmol.g_{cat}.⁻¹min⁻¹) was 60 times higher than that of monometallic Pt/ACC (0.21 mmol.g_{cat}.⁻¹min⁻¹) and 1.5 times higher than that of 20 wt % Ni/ACC (8.5 mmol.g_{cat}.⁻¹min⁻¹). Furthermore, operating parameters such as feed flow or contact time, reaction temperature and pressure also affect the overall system performance [19].

In this work, monometallic catalysts Pt/Al₂O₃ and Pd/Al₂O₃, as well as the bimetallic counterparts Pt-Pd/Al₂O₃, are evaluated for dehydrogenation H18-DBT. The effects of the dehydrogenation temperature (290–320 °C), metal loading (0.5, 1 and 2 wt % Pt) and bimetallic catalyst (Pt-Pd) were investigated using a batch reactor setup. This was followed by determination of the activation energy using the Arrhenius model. The purity of the released hydrogen and the composition of by-products were qualified and quantified by gas chromatography (GC). Furthermore, the catalysts were characterized using temperature-programmed reduction (TPR), CO pulse chemisorption, Brunauer–Emmett–Teller (BET) analysis and transmission electron microscopy (TEM) to determine their properties. DFT studies are also performed to complement the experimental results.

4.2 Experimental

4.2.1 Materials and methods

Dibenzyltoluene (traded as Marlotherm SH) was supplied by Sasol Germany GmbH and further hydrogenated (in a pilot plant) to obtain perhydro-dibenzyltoluene (99% degree of hydrogenation (doh)). Briefly, a hydrogenation reactor packed with Ni catalyst was heated to 140 °C and pressurized with hydrogen up to 30 bar. The reactor was fed with H0-DBT, to produce H18-DBT. The following gases were supplied by Afrox South Africa: He (99.999%), Ar (99.999%), CO/He (10%) and H₂/Ar (10% H₂). These gases were used in the TPR and CO pulse chemisorption experiments. Furthermore, the following dehydrogenation catalysts (1.6-mm cylindrical extrudes), all supported on Al₂O₃, were supplied by Mintek, South Africa: 0.5

wt % Pt, 1 wt % Pt, 2 wt % Pt, 1 wt % Pd and 1:1 wt % Pt-Pd. These catalysts were prepared by a conventional wet impregnation method as described in open literature [32]. Calibration standards of hydrogenated compounds were supplied by the Institute of Chemical Reaction Engineering of Erlangen University (Prof. Wasserscheid, Germany).

4.2.2 Catalytic activity tests

For the dehydrogenation of H18-DBT (99% doh), a 200 ml three-neck round bottom flask was used as a batch reactor. The flask was attached to a cooling condenser with a downstream filter made of glass wool and activated carbon for capturing any discharged vapours. A mass flow meter (El-Flow F11B-500-AGD-22V, Bronkhorst; max. flow 30 NL/h) was connected to the filter outlet and used to measure the hydrogen flow rate. For analysis of the reaction mixture, a sample was drawn at the sample port. Prior to each of the dehydrogenation experiments, air was removed from the reactor by purging with Ar gas. This was followed by reduction of the catalysts at 350 °C using a 10% H₂/Ar mixture. The reactor was heated externally using a heating mantle with a digital feedback controller (WHM-C10D, Daihan Scientific), while the cooling condenser was continuously cooled to 10 °C using a cryostat (FED-12, Julabo).

The temperature and hydrogen flow rate data were logged using LabVIEW software. From this data, the degree of dehydrogenation (doh) was calculated based on the total hydrogen produced vs. the theoretical maximum hydrogen to be released from H18-DBT. As this calculation is based on released hydrogen gas, liquid samples of the H18-DBT reaction mixtures were further analysed using a calibrated refractometer (Abbemat 300, Anton Parr) ** to confirm the doh. The theoretical maximum amount of hydrogen ($V_{H_2,max}$) that can be released from H18-DBT was determined using Eq. 1, where $n_{H_2,max}$ is the maximum number of molecules of hydrogen in one molecule of H18-DBT and V_m is the molar volume of hydrogen

** A calibrated refractometer provides measurements regarding the doh (i.e., available amount of hydrogen in the molecule) or the dod (i.e., the amount of hydrogen released from the molecule), at a fast turn-around time than gas chromatography methods. This is possible because the reaction mixture samples of dibenzyltoluene based LOHC obtained at various reaction temperatures have different refractive indices and doh values. The doh values are first determined using chromatography methods. Therefore, the refractive index values can be correlated with the respective doh values to generate a calibration curve, as shown in Figure A1 of supplementary information.

$$V_{H_2,max} = n_{H_2,max} \cdot v_m = \frac{9 \cdot m_{H_{18}-DBT}}{M_{H_{18}-DBT}} \cdot 22.414 \frac{l}{mol} . \quad (1)$$

The dod was calculated using Eq. 2

$$dod = \frac{V_{H_2, released}}{V_{H_2, max}} \cdot 100. \quad (2)$$

Productivity (P) is defined as the mass of released hydrogen per mass of platinum per minute, calculated using Eq. 3 [33]

$$P = \frac{m_{H_2}}{m_{Pt}} \left[\frac{g_{H_2}}{g_{Pt} \min} \right]. \quad (3)$$

4.2.3 Characterization

Gas analysis (H_2 purity) was performed using a gas chromatograph (SRI-8610C GC, USA) equipped with a 0.9-m molecular sieve column and a thermal conductivity detector (TCD) detector. During dehydrogenation experiments, the gas samples were collected in 1 L sampling bags (Restek). The GC was calibrated to qualify and quantify gases such as H_2 , CH_4 , CO and CO_2 , using Ar as a carrier gas. Analysis of liquid-based by-products was performed using a single quadrupole gas chromatograph (436-GC-SQ-MS; Scion, Netherlands). The system is equipped with a CP 8400 auto sampler (7683 D), a GS-Tek GsBP-50+MS column (30 m, 0.25 mm i.d., 0.25 μ m d.f.) and a single quadrupole mass spectrometer. Helium was used as a carrier gas. To perform liquid analysis, samples of the reaction mixture were drawn from the reactor, diluted with hexane (1:100 wt/wt), then 1- μ L quantities of each sample were injected at a split ratio of 1:100.

TPR was performed using an automated chemisorption analyser (AutoChem II 2920, Micromeritics, USA). A sample of each catalyst (~0.3 g) in powder form was loaded in a quartz U-tube fitted with quartz wool at the bottom. This was fixed in the furnace of the instrument. TPR analysis of the catalysts was carried out in a flow of 10% H_2 /Ar gas mixture (flow rate 50 ml/min). Each sample was flushed for 30 min at room temperature, using 10% H_2 /Ar (flow rate 50 ml/min). Thereafter, the furnace was ramped at 10 $^{\circ}$ C/min up to 800 $^{\circ}$ C, whilst recording the hydrogen consumption with a thermal conductivity detector.

CO pulse chemisorption experiments were also conducted using the abovementioned AutoChem II 2920. The quartz U-tube reactor was loaded with 0.6 g of catalyst pellets. All catalysts samples were reduced in 10 % H₂/Ar at 350 °C for 2 h and allowed to cool to room temperature before carrying out CO pulse chemisorption experiments. Chemisorption was carried out at 35 °C under a stream of He (flow rate 50 ml/min) using a pulsed chemisorption technique, where 0.5 ml pulses of CO were injected. Nitrogen adsorption/desorption isotherms at -196 °C were recorded using a Micromeritics instrument (ASAP 2020). Samples were degassed at 300 °C for 8 h prior to recording measurements.

Transmission electron microscopy (TEM) analysis was carried out using a FEI Tecnai G2 20 instrument equipped with a LaB6 filament and operating at an accelerating voltage of 200 kV. Image J software was used to determine particle size distribution.

4.3 Results and discussion

4.3.1 Catalyst evaluation

During the course of the dehydrogenation of H18-DBT, the temperature of the external heating source is always higher than the content of the reactor. This is due to the endothermic nature of the dehydrogenation reaction, which is reported to consume 65.4 kJ/mol-H₂ [34].^{††} The data presented in this work was collected after the catalyst had stabilized, in this case after three reaction cycles. In order to determine the effect of temperature on the dehydrogenation of H18-DBT, the reactor temperature was varied from 290 to 320 °C at atmospheric pressure. The reaction was allowed to proceed for 1 h 40 min. Use was made of 20 ml of H18-DBT (99 % doh) and 5 g of 1 wt % Pt/Al₂O₃ as a catalyst.

Due to the temperature sensitivity of the dehydrogenation reaction, the increase in the reaction temperature is beneficial for the doh. After 1 h 40 min, the doh had increased from 40% (2.5 wt % H₂) to 90% (5.6 wt % H₂), with an increase in temperature from 290 to 320 °C. See Figure 4.1. A similar trend was observed by Shi and co-workers [35] after 300 min; the dehydrogenation content increased from 50.8 to 81.3% with an increase in temperature from

^{††} The reaction enthalpy value (65.4 kJ/mol) reported in the cited reference [34] is valid for standard conditions. Since the reaction enthalpy has a small temperature dependence, the value (65.4 kJ/mol calculated at 298.15 K) will slightly be higher at elevated temperature. The establishment of a range of the specific values was not in the scope of the thesis. .

270 to 320 °C, when using 5 wt % Pt/Al₂O₃ and H18-DBT. Furthermore, at a reaction temperature of 270 °C, when using 0.5 wt % Pt/Al₂O₃, Bruckner and co-workers noted a dod of 40% after 2 h [36]. Therefore, for specific applications, a reaction temperature can be used to control the hydrogen production.

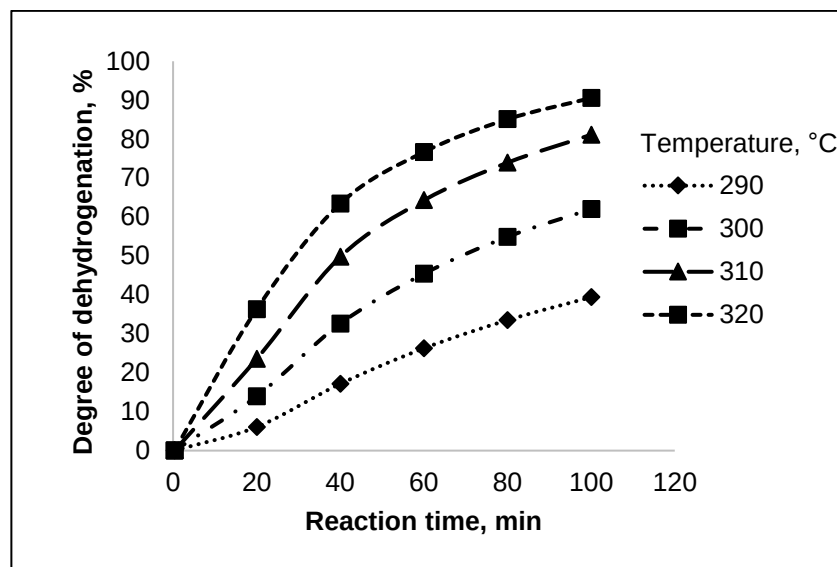


Figure 4.1:The effect of temperature variation (290–320 °C) on dehydrogenation of H18-DBT (99% DoH; 63 mmol (20 ml)) using 0.4 mol % of Pt as 5 g of 1 wt % Pt/Al₂O₃.

In experiments to determine the effect of Pt loading (0.5, 1 and 2 wt %) on the dehydrogenation of H18-DBT, the reaction temperature was then fixed at 320 °C. For the reaction time of 1 h 20 min, the dod results obtained were 50% (0.5 wt % Pt), 80% (1 wt % Pt) and 96 % (2 wt % Pt). See Figure 4.2. This clearly indicated that the dehydrogenation of H18-DBT take a much longer time when using the 0.5 wt % Pt loading. Furthermore (as seen in Figure 4.2, insert), 96% dod is obtained after 7 h when 0.5 wt % Pt is used, whereas this could be achieved within 1 h 20 min when 2 wt % Pt is used. The increase in the dod results from an increase in the number of active sites due to the increase in the metal loading.^{‡‡}

^{‡‡} The active sites on the catalyst surface are only available to partake in the heterogenous reactions and our experiments indicate that dod increases with increasing Pt metal loading. Later in this chapter, we will discuss the effect of metal loading in terms of turnover frequency based on the chemisorption results.

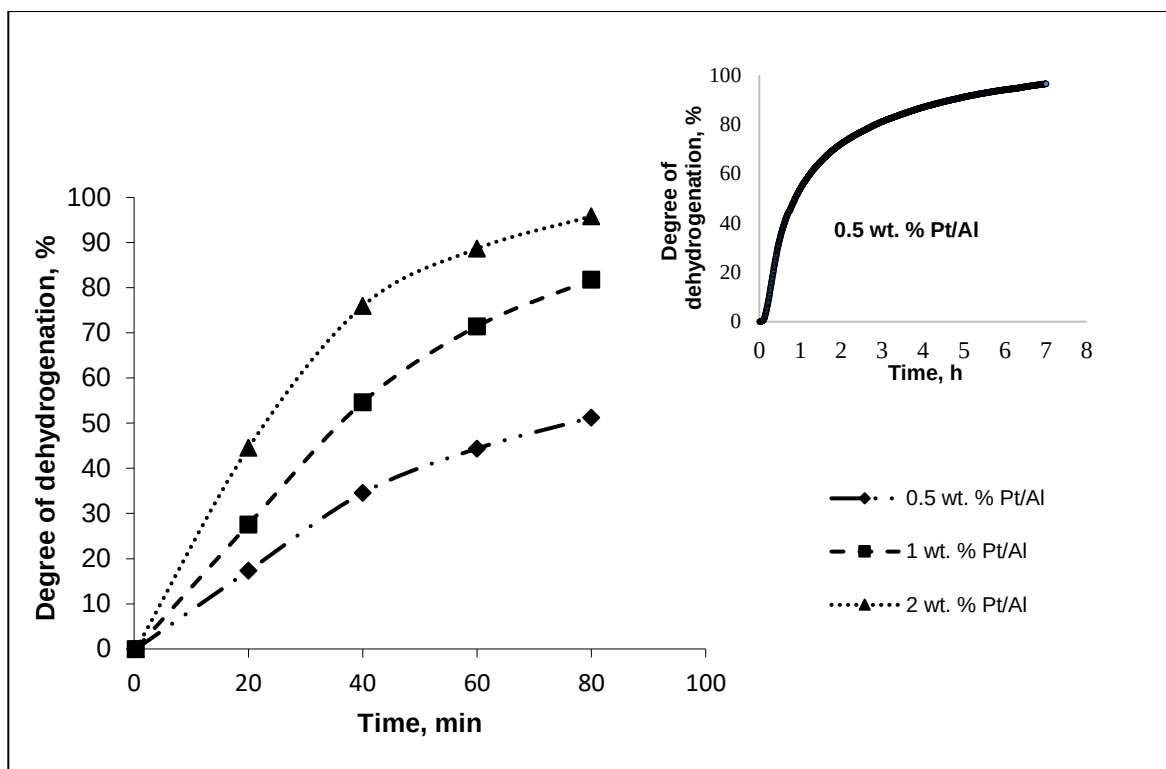


Figure 4.2: Effect of metal loading on dehydrogenation of H18-DBT (99% DoH; 20 ml) using 5 g of each catalyst at 320 °C. Insert shows 96% dod achieved within 7 h when 0.5 wt % Pt/Al₂O₃ is used.

Platinum is known to have good adsorption and desorption properties for hydrogen, and Pd nanoparticles have high reactivity and durability [37]. Therefore, upon a combination of Pt and Pd, synergistic effects between nanoparticles is expected to improve the dehydrogenation performance. For the first time, a bimetallic catalyst 1:1 wt % Pt-Pd/Al₂O₃ catalyst is evaluated for the dehydrogenation of H18-DBT. The activity of 1:1 wt % Pt-Pd/Al₂O₃ was compared to that of monometallic 1 wt % Pt/ Al₂O₃ and 1 wt % Pd/Al₂O₃. As Figure 4.3 shows that the catalytic activity of Pt was five times higher than that of Pd alone and the catalytic activity of Pt-Pd was much lower than that of Pt and Pd alone. This performance degradation, when Pd is incorporated, has been observed elsewhere for the dehydrogenation of cyclohexane [38]. It is proposed to be due to competition between Pd and Pt to occupy the oxidation centres of the alumina surface during reduction. Hence, here, the incorporation of Pd did not improve the dehydrogenation activity of H18-DBT, it actually lead to a decrease in the overall performance.

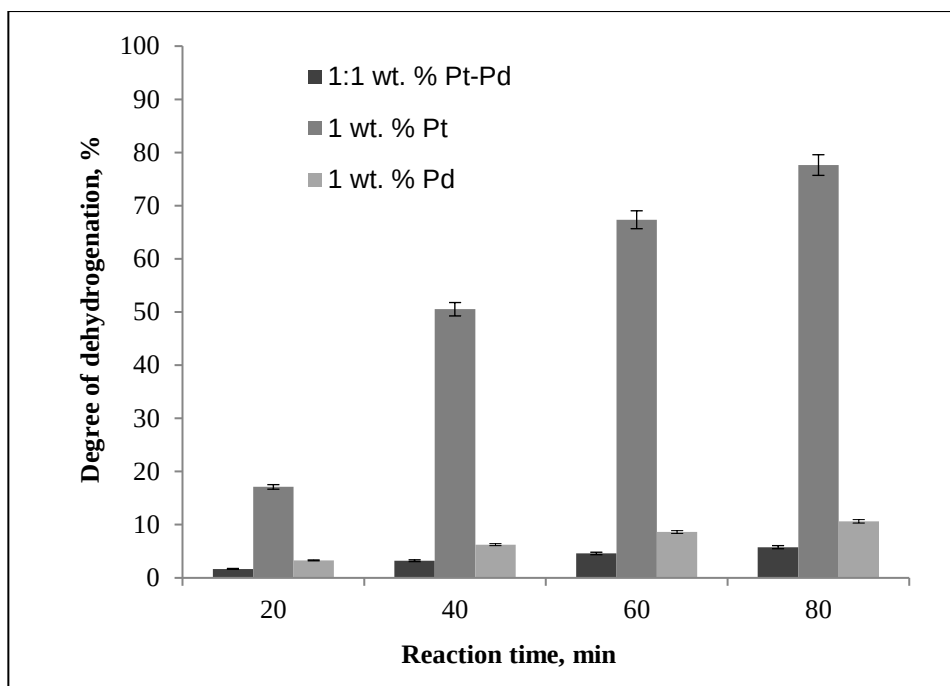


Figure 4.3: Comparison of monometallic and bimetallic catalysts for the dehydrogenation of H18-DBT (99% doh; 20 ml), using 5 g of each catalyst at 320 °C.

The reaction kinetics of the H18-DBT dehydrogenation reaction over time were determined for the catalysts 1 wt % Pt/Al₂O₃, 1 wt % Pd/Al₂O₃ and 1:1 wt % Pt-Pd/Al₂O₃. First, the apparent rate constants (k_A) were determined at temperatures ranging in the range 260–290 °C. See Figure 4.4A. This temperature range was selected because the rate constants are usually recorded at low conversions (dehydrogenation levels). The experimental data fitted well with the first order reaction kinetics. The Arrhenius plot, in which the natural logarithm of k_A is plotted at different reaction temperatures, was obtained for the catalysts. The Arrhenius plot is derived from Eqs 4 and 5.

$$k_A = Ae^{-\frac{E_a}{RT}} \quad (4)$$

$$\ln(k_A) = \ln(A) - \frac{E_a}{RT} \quad (5)$$

where, k is the rate constant, T is the absolute temperature, E_a is the activation energy, A is the pre-exponential factor and R is the ideal gas constant.

Therefore, apparent activation energy is calculated from the slope of a plot of $\ln(k)$ versus $1/T$, (Figure 4.4B). The apparent activation energies (E_a) obtained for the dehydrogenation of H18-DBT for 1 wt % Pt/Al₂O₃, 1 wt % Pd/Al₂O₃ and 1:1 wt % Pt-Pd/Al₂O₃ are 205, 84 and 66 kJ/mol, respectively. As shown in Figure 4.4B, the reaction with a higher E_a has a steeper slope (1 wt % Pt/Al₂O₃). This is because the reaction rate is very sensitive to change in temperature. Furthermore, the reaction with a lower E_a (1:1 wt % Pt-Pd/Al₂O₃) is less sensitive to a temperature change.

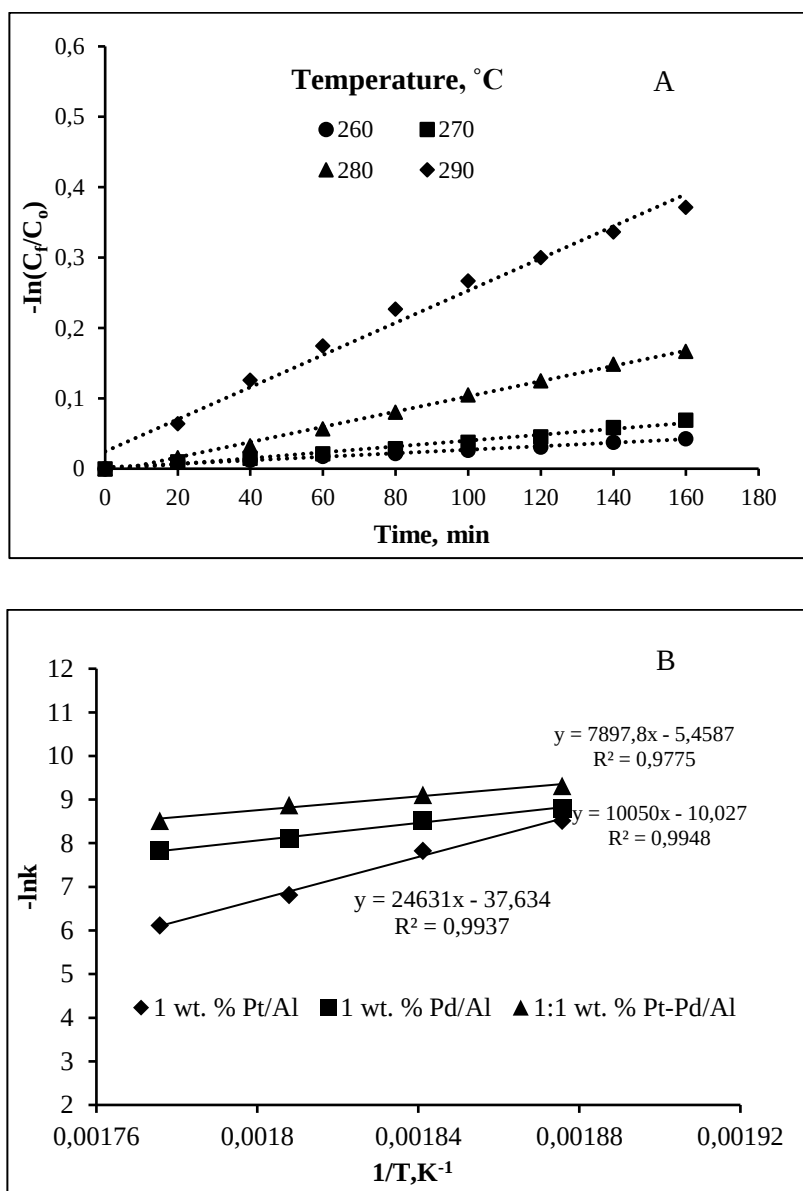


Figure 4.4: (A) Representative 1st order reaction kinetic model for dehydrogenation of H18-DBT using 1 wt % Pt/Al₂O₃. (B) Arrhenius plot for calculation of apparent activation energy for dehydrogenation of H18-DBT, for 1wt % Pt/Al₂O₃, 1 wt % Pd/Al₂O₃ and 1:1 wt % Pt-Pd/Al₂O₃ catalysts

4.3.2 LOHC reaction mixture and gas analysis

In this section, both gas and liquid analyses were performed to determine the purity of hydrogen and the reaction mixture by-products vs. productivity. The performance trend of the catalyst (1 wt % Pt/Al₂O₃) was investigated for 12 dehydrogenation runs. After each run, each ~1.5 h long, a spent LOHC is discarded and replaced by a fresh LOHC. A fresh catalyst is only used for the first run and the same catalyst is reused up to the twelfth run, with the reaction temperature kept constant at 300 °C. In the first run, productivity reached a maximum of 0.76 gH₂.gPt⁻¹.min⁻¹ and 0.1% of by-products were produced. See Figure 4.5. The second run showed a significant drop in productivity, by 74%; however, from the third to the sixth runs the productivity stabilized at ~0.24 gH₂.gPt⁻¹.min⁻¹, which is about 68% drop from the first run. From the second to the sixth runs, the by-products decreased to <0.02%. After the sixth run, the catalyst was placed in a Soxhlet extraction apparatus for 6 h, where hexane was used as a washing solvent.

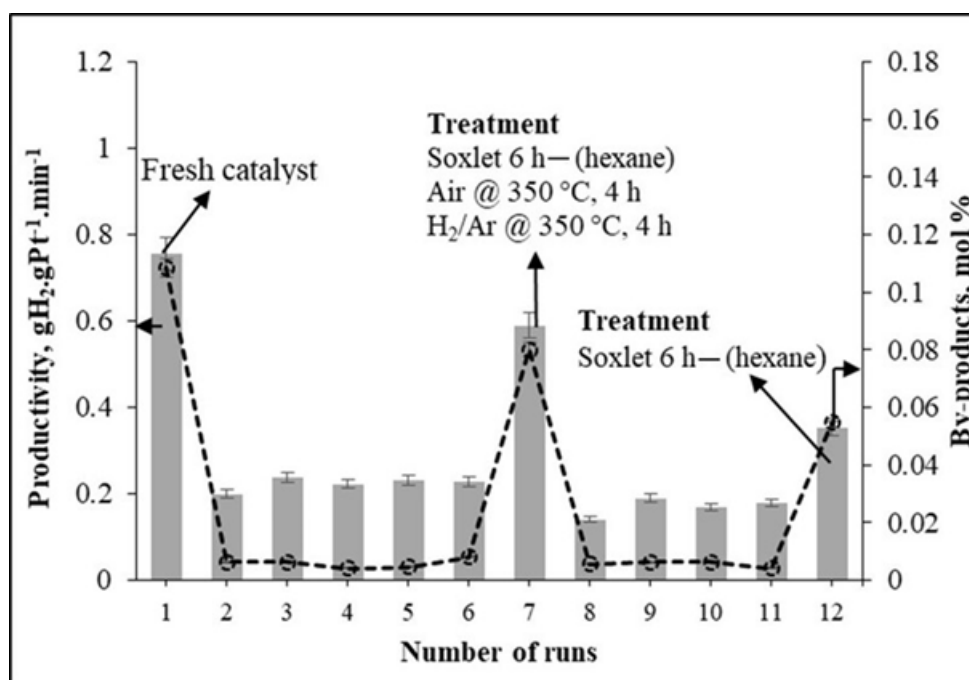


Figure 4.5: The influence of liquid by-products and catalyst regeneration on productivity when using 5 g of 1 wt % Pt/Al₂O₃ as catalyst and 20 ml of H18-DBT at 300 °C.

The catalyst was then treated with air in a furnace at 350 °C so that any form of carbonaceous material in the catalyst is removed by reacting with O₂ from air to form CO₂. The catalyst was further reduced using a 10% H₂/Ar mixture. See Figure 4.5. After this treatment, and re-evaluation, the productivity increased to 0.56 gH₂.gPt⁻¹.min⁻¹ (42% improvement) in the seventh run and the by-products increased to 0.08 mol %. These by-products are low- and high-boiling compounds, resulting from thermal cracking of the H18-DBT [39]. In the eighth run, the productivity dropped lower than in the second run and it stabilized at ~0.19 gH₂.gPt⁻¹.min⁻¹ (9th to 11th run). After the eleventh run, the catalyst was only washed with hexane for 6 h in a Soxhlet apparatus. Hence, in the twelfth run, the productivity improved to 0.35 gH₂.gPt⁻¹.min⁻¹ and the by-product increased to 0.055 mol %. This scenario suggest that the catalyst deactivation could be due to the formation of by-products—after treatment they are removed and the activity is improved although not fully restored. At this point, it remains unknown how this type of catalyst deactivation can be minimized.

To determine hydrogen purity, 1 wt % Pt/Al₂O₃ catalyst was used for the dehydrogenation of H18-DBT at temperatures ranging from 290 to 320 °C. First of all, as the reaction temperature is increased from 290 to 320 °C, the maximum achievable hydrogen flow rate increases 5 to 23 NL/h. See Figure 4.6. At each temperature, gas samples were collected using sampling bags, followed by analysis using GC. The maximum hydrogen purity >99.99% was obtained at 290 °C. A further increase in temperature to 320 °C reduced the hydrogen purity to 99.96%. In addition, a gaseous by-product methane was also detected and its concentration increased with an increase in reaction temperature from 290 to 320 °C. See Figure 4.6. The concentration of liquid by-products also increases with an increase in temperature [39]. The presence of methane suggests the occurrence of side reactions having taken place during the dehydrogenation reaction, as already indicated by the liquid analysis. According to the current standards (ISO 14687-2 and SEA J2719) for the quality of hydrogen fuel intended for fuel-cells(FCs), methane levels should not exceed 100 ppm [40]. Therefore, further purification of the hydrogen released from H18-DBT is required to meet the current standards of FCs.

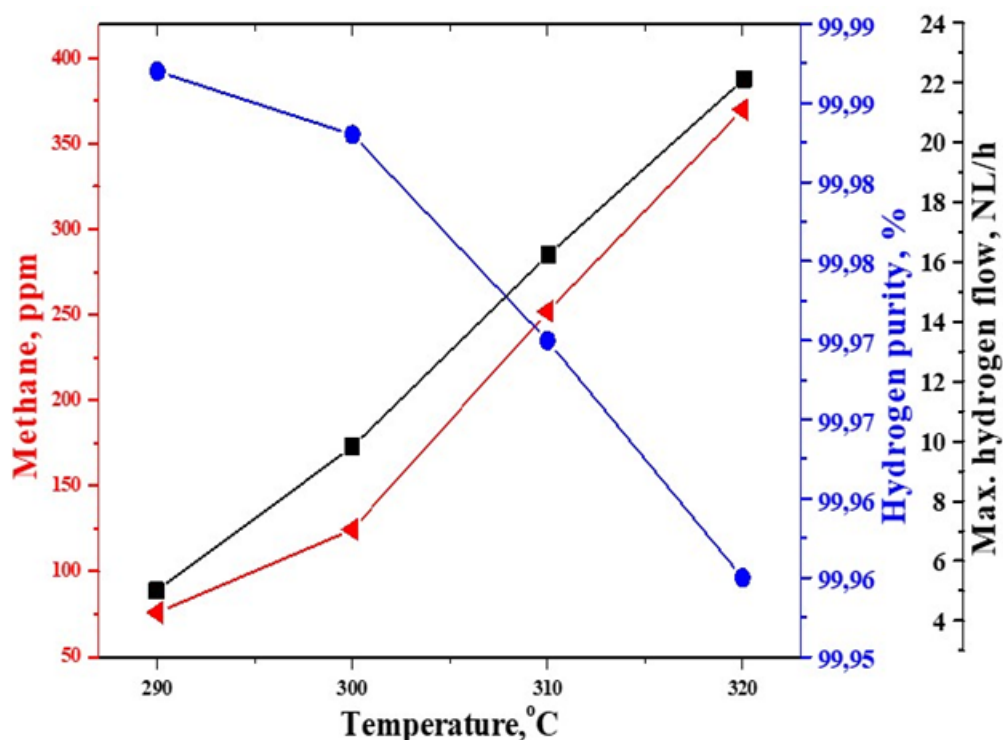


Figure 4.6: Effect of temperature on the concentration of methane, hydrogen purity and hydrogen flow rate when using 5 g of 1 wt % Pt/Al₂O₃ as catalyst and 20 ml of H18-DBT.

4.3.3 Catalyst characterization

The temperature-programmed reduction of Pt/Al₂O₃ catalysts is characterized by two main peaks, as evident in Figure 4.7 [41,42]. The peak at lower temperature (<250 °C) is due to the reduction of platinum oxide (PtO and PtO₂) to Pt. The TPR peak at high temperature (>250 °C) indicates strong support interaction with Pt, possibly leading to the formation PtAl₂O₄ spinel [41]. The area under the curves (H₂ consumption) increases as the Pt loading increases, as is also evident in Figure 4.7. This occurrence clearly indicates an increase in the number of reducible species. The catalyst performance (the *dod*) has also improved. See Table 4.2. Profiles for both the Pd/Al and Pt-Pd/Al catalysts indicate negative peaks around 70 °C, associated with the desorption of weakly adsorbed hydrogen from the Pd surface, and H₂ decomposition of palladium hydride (Pd-H) species formed upon initial supply of H₂ [43]. Here, surprisingly broad reduction peaks are observed at around 300 °C, but they are small

(indicating a very low H_2 consumption), when compared to results with the 1 wt % Pt/ Al_2O_3 catalyst.

Pulse chemisorption analysis revealed that with an increase in metal loading there is a decrease in the dispersion of active metal particles. See Table 4.2. Dispersion of metal particles is inversely proportional to the metal particle size; therefore, the larger the metal particles the lower the dispersion [41]. Metallic particle dispersion correlates well with productivity—the higher the dispersion the higher productivity. Table 4.2. This is because both dispersion and productivity represent the efficiency of metal utilization. Conversely, as the particles size increases, the metallic surface area increases, which affords a wider area upon which the hydrogenation reaction can take place—consequently, the d_{od} increases. However, for Pd and Pt-Pd catalysts, the above statements do not hold; both catalysts were reported to be less active for the dehydrogenation of H18-DBT. Figure 4.7 shows TPR profiles for 0.5 wt % Pt/ Al_2O_3 , 1 wt % Pt/ Al_2O_3 , 2 wt % Pt/ Al_2O_3 , 1 wt % Pd/ Al_2O_3 and 1:1 wt % Pt-Pd/ Al_2O_3 catalysts.

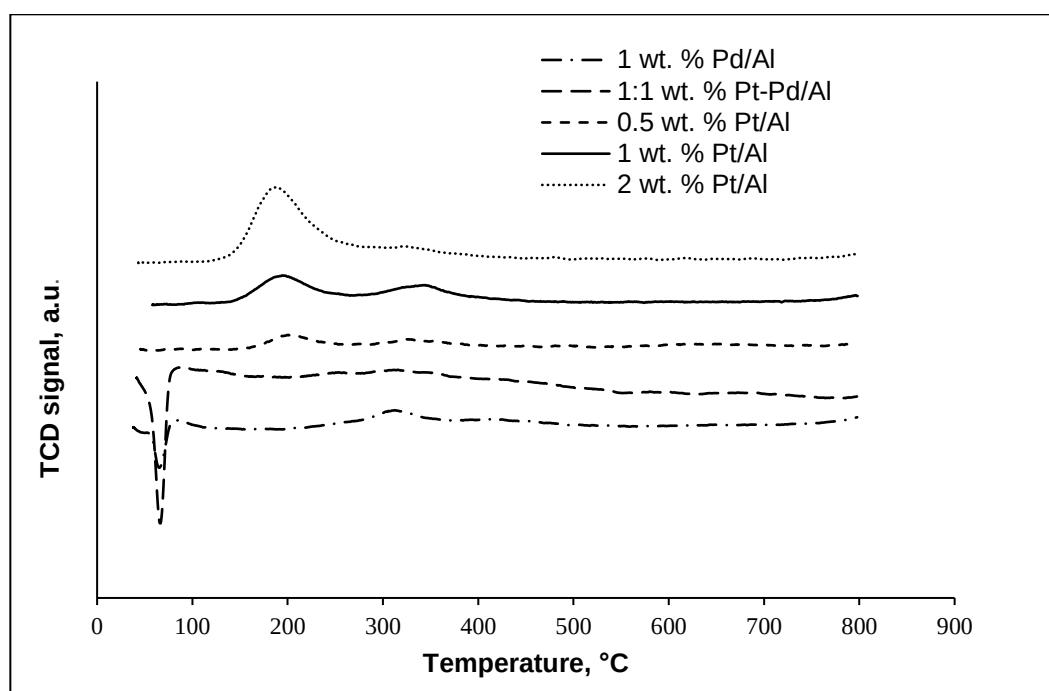


Figure 4.7: Temperature-programmed reduction profiles for Pt, Pd and Pt-Pd catalysts in the dehydrogenation of H18-DBT.

The textural properties, based on the adsorption/desorption isotherms, are shown in Table 4.1. Figure 4.8 shows that Al_2O_3 exhibits an isotherm of type IV with hysteresis loops of type

H1. Properties of the Al_2O_3 support were compared before and after the loading of Pt, Pd and Pt-Pd. It is clear that after metal loading there were no significant changes in the textural properties of the catalyst. These catalysts display narrow pore size distributions with the maxima centred around 10.9–11.4 nm for all metal loadings, and slightly higher maxima (11.6 nm) for the Al_2O_3 support. See Figure 4.8. This clearly indicates that the catalyst retains its mesoporous structure after metal loading.

Table 4.1: Textural properties of Al_2O_3 supports before and after loading of metallic catalysts

Catalyst	BET surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$) ^a	Pore size (nm) ^a
Al_2O_3	186	0.641	11.6
1 wt % Pt/ Al_2O_3	190	0.606	10.9
1 wt % Pd/ Al_2O_3	192	0.619	11.1
1:1 wt %Pt-Pd/ Al_2O_3	185	0.605	11.4

^aDetermined using the Barrett–Joyner–Halenda (BJH) method

The morphology and particle size distribution of Pt-based catalysts were determined using TEM. The particles of 0.5 wt % Pt/ Al_2O_3 could not be seen in the TEM images. This could indicate that the particles are very small and buried within the alumina support. Furthermore, the particle sizes obtained from CO pulse chemisorption experiments did not correspond with results obtained from TEM analysis. For example, the 1 wt % Pt/ Al_2O_3 particle size distribution is shown in Figure 4.9. There, the highest particle diameter is not greater than 5 nm, with an average particle diameter of 2 nm, whereas results of pulse chemisorption give an average diameter of 7 nm for 1 wt % Pt/ Al_2O_3 . Similar deviation is also reported in literature [44]. Indications are therefore that TEM imaging is applicable to selected sample areas, to measure and calculate the mean size of particles—it may not reflect the total particle size distribution of the whole sample. On the other hand, CO pulse chemisorption is be used to obtain results based on the total volume of CO adsorbed by Pt particles.

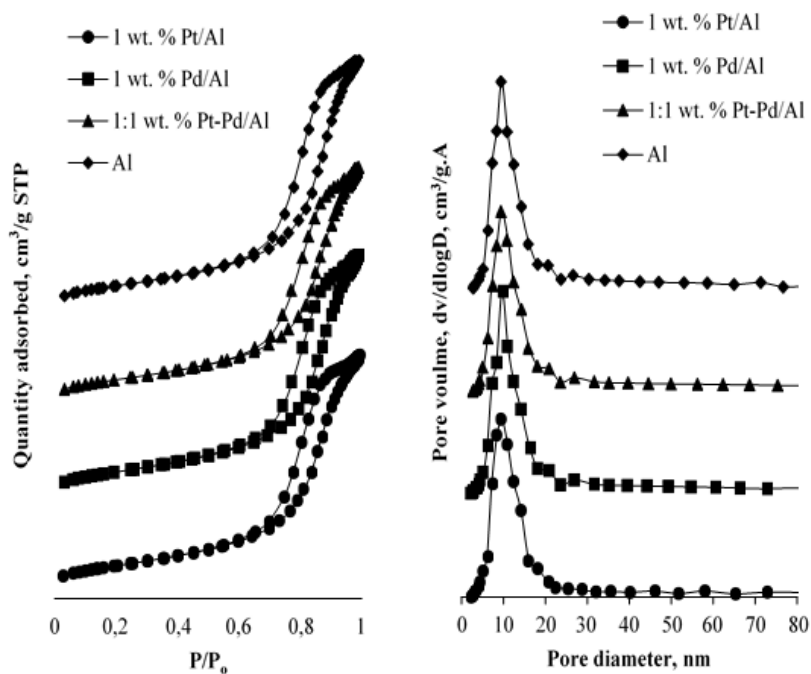


Figure 4.8: N₂ adsorption/desorption isotherms and pore size distributions of various catalysts and Al₂O₃ (Al) support.

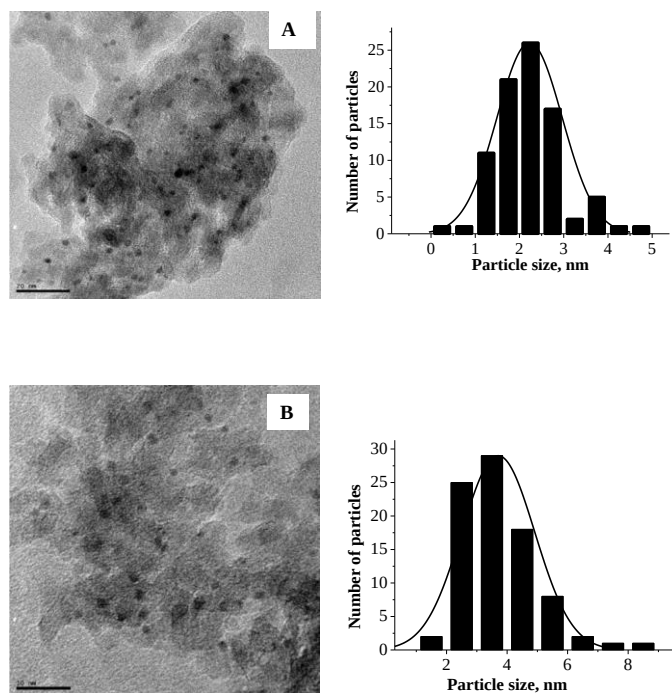


Figure 4.9: TEM images and particle size distributions of catalysts: (A) 1 wt % Pt/Al₂O₃ and (B) 2 wt % Pt/Al₂O₃

Table 4.2: Physicochemical properties of Pt, Pd and Pt-Pd catalysts vs. their catalytic performances for dehydrogenation of H18-DBT (99% doh; 20 ml), using 5 g of each catalyst at 320 °C

Catalyst	Metal dispersion (%) ^a	Metallic surface area (m ² .g ⁻¹ sample) ^a	Metal particle diameter (nm) ^a	H ₂ consumed (μmol.g ⁻¹) ^b	Productivity (gH ₂ .gPt ⁻¹ .min ⁻¹) ^c	Productivity (gH ₂ .m ⁻² .min ⁻¹) ^{§§}	Degree of dehydrogenation (%) ^c
0.5 wt % Pt/Al ₂ O ₃	19	0.23	6	29	0.61	0.065	51
1 wt % Pt/Al ₂ O ₃	17	0.42	7	75	0.55	0.067	82
2 wt % Pt/Al ₂ O ₃	13	0.64	9	134	0.43	0.067	96
1 wt % Pd/Al ₂ O ₃	9	0.38	13	5	<0.10	<0.013	11
1:1wt % Pt-Pd/Al ₂ O ₃	6	0.41	19	0.6	<0.01	<0.002	6

^a CO pulse chemisorption

^b Temperature-programmed reduction

^c Catalyst mass-based productivity

^{§§} In order to provide more data after the work was published, we added area-based productivity column to the Table 4.2. The productivity is calculated using the metallic surface area obtained from CO pulse chemisorption experiments. As shown in Table 4.2, the area-based productivity also increases with increasing metallic surface area but for only 0.5 and 1 wt % Pt.

4.3.4 The effect of Pt loading on turnover frequency ***

This subsection was prepared to address the effect of metal loading in terms of turnover frequency (TOF). Turnover frequency is defined as the number of molecules reacted at each available catalytic active site per unit time. Therefore, this will provide more accurate information regarding the effect of Pt loading on the catalytic activity for dehydrogenation of H18-DBT. TOF is calculated using the estimated 1st order rate constants and the initial concentration of the reactant used, as indicated by Eqs 6 and 7.

$$TOF = \frac{r \cdot M_{Pt}}{x_{Pt} \cdot D_{Pt}} \quad (6)$$

$$r = kC_0 \quad (7)$$

where, r is the reaction rate, k is the rate constant, C_0 is the initial concentration of H18-DBT, M_{Pt} is the molecular weight of Pt, x is the Pt loading and D_{Pt} is platinum dispersion determined by CO pulse chemisorption. Figure 4.10 shows the relation between TOF (number of molecules of H18-DBT converted per second per active site) and Pt loading, where TOF is found to be the highest for 1 wt % Pt/Al₂O₃. As shown in Figure 4.10, TOF is also found to increase with increasing reaction temperature because the reaction rate also increases with increasing reaction temperature. The decrease in TOF at 2 wt % loading is attributed to the larger particle size which contributed to lower Pt dispersion. Therefore, the TOF based activity indicate that the increase in metal loading is effective from 0.5 to 1 wt %, further increase to 2 wt % result in low TOF values. This is also justified in Table 4.2, where the area-based productivity increases with increasing metallic surface area but only for 0.5 and 1 wt % Pt. The area-based productivity remained the same for 1 and 2 wt % Pt metal loadings.

*** This subsection was not included in the original publication; reaction rate and rate constant values are in Table A3 of the appendix section.

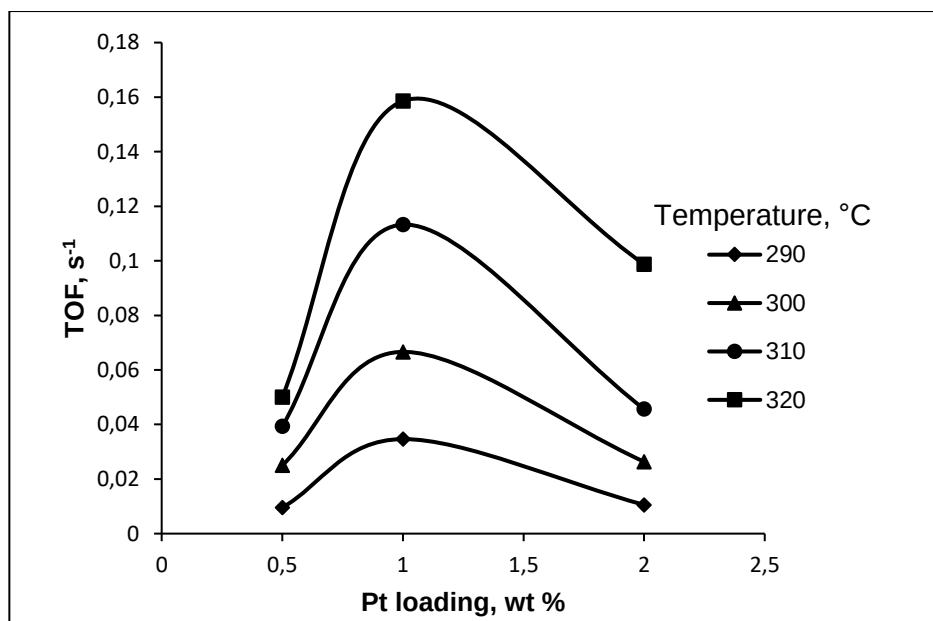


Figure 4.10: Turnover frequency vs. Pt metal loading for dehydrogenation of H18-DBT (99 % doh; 20 ml) using a batch reactor and 5 g of each catalyst at temperatures from 290–320 °C.

4.3.5 Theoretical insights on catalyst activity

In a further step, we used *ab initio* calculations to investigate the dehydrogenation of H18-DBT on Pt, Pd and bimetallic Pt-Pd catalyst surfaces. We hypothesized the arrangement of the metal atoms of the bimetallic catalyst, where the metal atoms are on the surface, at the bottom and sandwiched. See Figure 4.11. The activity of these catalysts towards H18-DBT dehydrogenation was estimated using the reaction energy for the removal of the first hydrogen atom (H) from an H18-DBT molecule (this is the first dehydrogenation step). Recently, *ab initio* DFT calculations have been used to investigate the adsorption characteristics of H18-DBT on different surfaces, including Pt, Pd and bimetallic Pt-Pd catalysts surfaces [45]. The 110 surface was found to be highly favoured for the adsorption of H18-DBT. DFT calculations have also been used to investigate the dehydrogenation of octahydroindole to indole [46]. Furthermore, Bachmann et al. reported that DFT results obtained for dehydrogenation of octahydroindole on Pt (111) surface were consistent with the experimental observations [47]. Due to the above, we endeavoured to employ DFT in this work as well.

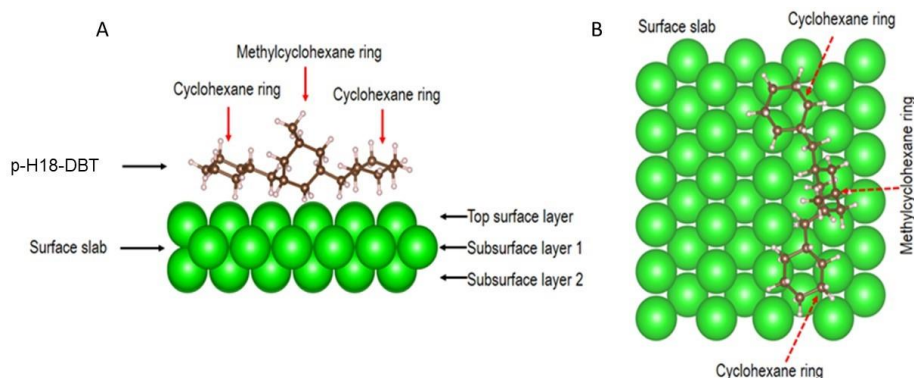


Figure 4.11: Surface–adsorbate model used in this study. A) Side view and B) Top view of the model. p-H18-DBT (para configuration of the H18-DBT molecule).

DFT studies are being increasingly adopted in investigations into how different surfaces give rise to different catalytic reactions [23,24,48,49]. The aim of these studies is usually to gather fundamental insight into the different processes and reactions that take place on/at the different catalysts' surfaces as well to screen for catalysts that could be suitable to achieve a particular reaction [23,24]. Using the surface favoured for H18-DBT adsorption, the 110 surface, the reaction for removal/abstraction of a H atom was calculated using dispersion-corrected DFT, as implemented in the plane wave code Quantum ESPRESSO [50]. The basis set was expanded in the form of plane waves and ultra-soft pseudopotentials were used to describe the valence electrons for all the atomic species. The surface was constructed using the approach reported by Ouma et al. [45], where one of the regioisomers of H18-DBT was used as the adsorbate molecule to be dehydrogenated. The surface–adsorbate model used is presented in Figure 4.11.

Studies have shown that it is easier to dehydrogenate the outer cyclohexane rings of H18-DBT hence they are likely to be dehydrogenated first, before the middle methylcyclohexane rings are dehydrogenated [51,52]. To this end, a H atom will thus be abstracted from one on the outer rings of the chosen H18-DBT. H abstraction has been used in this study to probe the onset of catalytic dehydrogenation of H18-DBT. This is because H abstraction has been found to be the rate-determining aromatization of tetrahydrocarbazole on Pd catalyst, where the first H abstraction was found to have the highest reaction barrier [53]. Hence, following the above observations [53,54], the reaction energy for the first H abstraction was then used to indicate

the onset of catalytic dehydrogenation in this study. The pristine and bimetallic surface–adsorbate systems considered are presented in Figure 4.12.

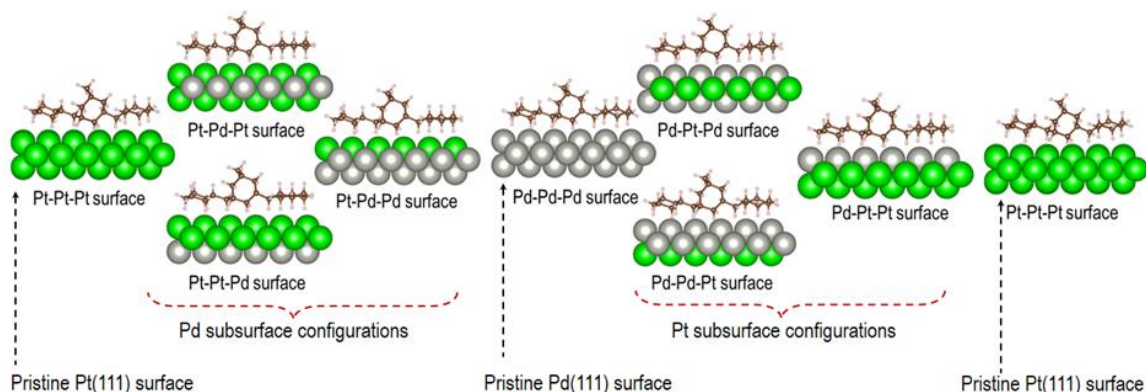


Figure 4.12: Pt and Pd pristine (110) surface slabs, and their respective subsurface configurations.

Computationally, there are two techniques that can be used to calculate the reaction energy for H abstraction on the different surfaces [55,56]. One of the techniques involves the co-adsorption of both products (H17-DBT and the abstracted H atom) on the same surface ($\text{H18-DBT}^* \rightarrow \text{H17-DBT}^* + \text{H}^*$) and the other involves the individual adsorption of each of the products on a surface ($\text{H18-DBT}^* + * \rightarrow \text{H17-DBT}^* + \text{H}^*$), where $*$ is an adsorption site on the surface. It has been shown that these two techniques give similar reaction energies, thus one can use any of the two techniques to calculate the reaction energy of any reaction [57].

Here, we elected to adopt the second approach, $\text{H18-DBT}^* + * \rightarrow \text{H17-DBT}^* + \text{H}^*$, from which the reaction energy (E_{RXN}) for abstraction of a single hydrogen atom (dehydrogenation) from adsorbed an adsorbed H18-DBT molecules. The E_{RXN} is defined as the difference between the total energies before and after the dissociation of one hydrogen atom and was obtained, as follows:

$$E_{\text{RXN}} = (E_{\text{H17-DBT}} + E_{\text{H}}) - (E_{\text{H18-DBT}} + E_{\text{S}}) \quad (8)$$

where, $E_{\text{H18-DBT}}$, $E_{\text{H17-DBT}}$, E_{S} and E_{H} are the calculated total energies of the surface–H18-DBT system, the surface–H17-DBT system, surface alone and a dissociated H adsorbed on the surface, respectively. The calculated E_{RXN} values on different surfaces are presented in Table 4.3. As defined by Eq. 8, positive and negative values of E_{RXN} indicate endothermic and

exothermic reactions, respectively. In this table, all the calculated reaction energies are positive, indicating that the reaction is endothermic in nature. This observation is consistent with other experimental observations, where dehydrogenation reactions have been found to be endothermic [58–60]. It is also consistent with other catalytic dehydrogenation processes predicted using *ab initio* DFT [61–63].

Table 4.3: Calculated reaction energies on different surfaces

	Adsorption energy (eV)		E_{RXN} (eV)
	p-H18-DBT	p-H17-DBT	
Pd-Pd-Pd	-2.62	-3.79	0.82
Pd-Pd-Pt	-2.73	-3.93	0.87
Pd-Pt-Pd	-2.52	-3.77	0.79
Pd-Pt-Pt	-2.56	-3.85	0.87
Pt-Pd-Pd	-2.36	-3.91	0.29
Pt-Pd-Pt	-2.47	-4.15	0.08
Pt-Pt-Pd	-2.12	-3.81	0.11
Pt-Pt-Pt	-2.23	-3.90	0.08

p-para, eV-electronvolt, E_{RXN} -reaction energy

The calculated reaction energies for H abstraction were found to be lower in the cases where Pt formed the top-most layer compared with where Pd was the top-most layer. This indicates that the Pt surfaces are more favorable for the dehydrogenation processes than Pt surfaces. This agrees with other experimental observations and reports that dehydrogenation reactions prefer Pt to Pd catalysts [54,38]. It was further observed that Pt-Pt-Pt and Pt-Pd-Pt surfaces had the lowest reaction energy (+0.08 eV or +7.72 kJ/mol), whereas Pd-Pd-Pt and Pd-Pt-Pt had the highest reaction energies. Assuming that the same reaction energy will be required each time a H atom is abstracted, then the estimated reaction energy for the complete dehydrogenation of H18-DBT to H0-DBT is approximated to be +69.47 kJ/mol- H_2 . The experimentally reported reaction energy for the dehydrogenation of H18-DBT is +65.4 kJ/mol [34].^{†††} We also noted that a Pd layer sandwiched between two Pt layers (Pt-Pd-Pt), can exhibit relatively similar activity towards H18-DBT dehydrogenation as the pristine Pt surface catalyst.

^{†††} The reaction enthalpy value (65.4 kJ/mol) reported in the cited reference [34] is valid for standard conditions. Since the reaction enthalpy has a small temperature dependence, the value (65.4 kJ/mol calculated at 298.15 K) will slightly be higher at elevated temperature.

4.4 Conclusions

For a fixed reaction time of 1h 20 min, the dod of Pt was five times higher than that of Pd alone and the catalytic activity of Pt-Pd was much lower than that of Pt and Pd alone. DFT calculations revealed that the reaction energy for H abstraction is lower for Pt than for Pd and Pt-Pd. Therefore, both experimental and theoretical observations indicate that Pd and bimetallic Pt-Pd catalysts are less active for the dehydrogenation of H18-DBT than Pt alone. The degree of dehydrogenation reached a maximum of 96% within a short reaction time of 1h 20 min when 2 wt % Pt/Al₂O₃ catalyst is used for dehydrogenation of H18-DBT at 320 °C. Moreover, 0.5 wt % Pt/Al₂O₃ catalyst took 7 h to reach a dod of 96%. In a reaction period of 1h 20 min, the dod of 1 wt % Pt/Al₂O₃ and 2 wt % Pt/Al₂O₃ differs by 16%. Therefore, 2 wt % Pt loading seems un-economical based on hydrogen produced per loading of Pt. The TOF based activity also indicated that the increase in metal loading is effective from 0.5 to 1 wt % Pt, further increase to 2 wt % Pt resulted in low TOF values. Using 1 wt % Pt/Al₂O₃, the low concentration of methane gas was only achieved at low dehydrogenation temperature (290 °C), hence high hydrogen purity (>99.99 %) was obtained. Furthermore, at high dehydrogenation temperature (320 °C), the hydrogen purity decreased to 99.96 % and the methane increased to >350 ppm. The hydrogen production rate increased from 5 to 23 NL/h at 290 and 320 °C, respectively.

Dehydrogenation of H18-DBT at 300 °C using 1 wt % Pt loading is optimum because the hydrogen purity remains at 99.99% and the hydrogen flow and dod is 10 NL/h and 60%, respectively. Furthermore, dehydrogenation of H18-DBT followed 1st order reaction kinetics and the activation energies for 1 wt % Pt/Al₂O₃, 1 wt % Pd/Al₂O₃ and 1:1 wt % Pt-Pd/Al₂O₃ catalysts were 205, 84 and 66 kJ/mol, respectively. Regarding the catalysts, the particle size and metallic surface area are inversely proportional to the metal dispersion—both increase with an increase in metal loading. Metal particle size, metallic surface area and the number of reducible species increased with an increase in metal loading, resulting in an improvement in the dod. Textural properties of the catalysts, obtained from BET analysis, revealed that the catalysts retained their mesoporous structure after metal loading.

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CHAPTER 5: STRESS TOLERANCE ASSESSMENT OF DIBENZYL TOLUENE-BASED LIQUID ORGANIC HYDROGEN CARRIERS

This chapter is a version of the article published in Sustainable Energy & Fuels, 4(9), 4662–4670. DOI: 10.1039/D0SE00625D, and no permission is required. “If you are the author of this article you do not need to formally request permission to reproduce figures, diagrams etc. contained in this article in third party publications or in a thesis or dissertation provided that the correct acknowledgement is given with the reproduced material”

OVERVIEW

Hydrogen production from charged liquid organic hydrogen carrier (LOHC) systems is always a trade-off between the molecule's storage capacity and the stability over the numerous charging/discharging cycles. This is because deep dehydrogenation induces cracking of the molecule and thus the storage capacity could be compromised by partial dehydrogenation. It is crucial to optimize a hydrogenation system in order to avoid possible excessive exothermic temperature whilst maintaining a high degree of hydrogenation (doh). Pure dibenzyltoluene (was hydrogenated up to 98% at a relatively low pressure of 15 barg (instead of at the frequently used 30–50 barg)). We determined the number of cycles that a LOHC molecule can tolerate from the amount of by-products produced during each hydrogen charging/discharging cycle. If toxic by-products are produced, the permissible amount of the by-products must be low to avoid harmful exposure. Therefore, the amount of hydrogenation and dehydrogenation cycles will be low (LOHC molecule duration of usage will be short). A higher limit for LOHC-based by-products suggests a long duration of usage. Furthermore, in the absence of any by-products, the LOHC molecule usage could be infinite. The infinite amount of hydrogenation and dehydrogenation cycles certainly depends on operational conditions, catalyst type and metal loading used. Accelerated stress tests were used to predict the time to failure of the LOHC molecule. In this tests, perhydro-dibenzyltoluene is dehydrogenated at extreme temperature. By-products were observed in both gaseous and liquid phase. Methane was obtained in the gas phase and in the liquid phase, the following by-products were obtained, benzene, C₂₁, xylene, C₁₃–C₁₅, toluene and benzyltoluene. Indications were that dibenzyltoluene is quite stable because the amount of liquid by-products obtained under stress conditions is 7.4 mol %.

5.1 Introduction

There is a need to expand the existing traditional hydrogen storage technologies by introducing alternative storage methods, such as the liquid organic hydrogen carrier (LOHC) technology. It is also important that the traditional and the new hydrogen storage technologies are specifically directed to their most suitable applications. LOHCs offer sustainable hydrogen economy due to their safe handling and efficient storage of hydrogen for long periods of time without self-discharge [1,2]. Moreover, a LOHC molecule operates like a rechargeable battery, where a hydrogen-lean carrier molecule is charged with hydrogen to become a hydrogen-rich molecule [3,4]. When required, hydrogen is discharged from a hydrogen-rich molecule by a dehydrogenation process. To date, dibenzyltoluene (H0-DBT) is considered the most preferred LOHC due to its attractive hydrogen storage properties [5,6]. H0-DBT meets most of the specifications required for hydrogen storage, for example, a high boiling point, low melting point, and high storage capacity: $1 \text{ m}^3 \text{ H18-DBT} = 57 \text{ kg-H}_2$ (1, 9 MWh) [7,8]. Hydrogen, produced by various methods, including the electrolysis of water, can be chemically bound to a LOHC. In this way, the handling of gaseous hydrogen is eliminated. LOHC technology lends itself to the linking of sites where hydrogen is produced with the sites where it is consumed—the so-called “sectoral integration”. Hydrogen produced from LOHCs can be used in various industries (chemical and petrochemical, food, glass manufacturing) [9–11], power generation (electricity generators, hydrogen fuel cells) [12,13] and sustainable emission-free mobility (cars, trains, heavy-duty trucks) [14–16].

To date, the only demonstration of LOHC technology in South Africa is at HySA Infrastructure CoC (North-West University, Potchefstroom). There, a pre-commercial-scale hydrogenation system for the hydrogenation of LOHCs was procured from an industrial partner, Framatome (previously Areva, Germany). The purpose of procuring this hydrogenation system is to demonstrate the production of hydrogenated LOHC, on a relatively large scale, through the solar-to-hydrogen pilot plant facility there.

A considerable amount of work on LOHCs has been carried out, worldwide, and interest therein is growing rapidly. For example, there are reports available describing LOHC catalyst development [17–19], reactor configurations [20–22], process optimization [23], techno-economic assessments [24], adoption of analytical methods [25,26], environmental considerations [27], thermodynamic evaluation [28] methods of heat integration [29], and many more. Results of all these efforts indicate the pros and cons of this technology, including the gaps in knowledge that still remain.

In this contribution, the main objective is to determine the number of LOHC H_2 charging/discharging cycles that a LOHC molecule can tolerate, using both hydrogenation and dehydrogenation systems, separately. The number of cycles that a LOHC molecule can

tolerate is determined by the amount of by-products produced during each charging/discharging cycle.

A further objective is to determine the LOHC molecule stability by performing accelerated stress tests (ASTs). In an AST, a high level of stress is applied to a product for a short period of time, to then predict its long-term failure under normal stress conditions. The types of stress can include temperature, voltage, humidity, vibration, or any other stress that directly affects the life of the product [30,31]. In this study, a high dehydrogenation temperature was used to stress the LOHC molecule. To the best of our knowledge, the hydrogenation of H0-DBT at a pressure of 3 barg has not been reported yet (in open literature). Estimation of the hydrogen charging/discharging cycles of H0-DBT based on the rate of formation of by-products has also not been explored yet. Here, for the first time, ASTs are used to predict LOHC molecule time of failure and the extent of decomposition under normal dehydrogenation stress operation.

5.2 Materials and methods

5.2.1 Chemicals

Dibenzyltoluene (H0-DBT) and monobenzyltoluene (H0-MBT) were purchased from Sasol (Germany) and Arkema (Germany), respectively. A mixture of H0-DBT isomers has ~0.5 mol % by-products (H0-MBT) (due to technical production processes). Extruded alumina pellets (computer designed shape; Clariant, South Africa) were used to prepare the dehydrogenation catalysts. Hexachloroplatinic acid hydrate (~38% Pt basis) and hexane (GC grade, >99.9% pure) were purchased from Sigma-Aldrich (Germany). The following gases were supplied by Afrox South Africa: 10% H₂/Ar, H₂ (99.999%), N₂ (99.999%) and He (99.999%).

5.2.2 Preparation of dehydrogenation catalyst

To produce 1 wt % Pt/Al₂O₃ catalyst, hexachloroplatinic acid solution (0.03 M) was prepared by adding 2.63 g of hexachloroplatinic acid powder to 200 ml of deionized water. This solution was then added to 100 g alumina pellets and the mixture allowed to settle for 1 h. Water was removed from the solid pellets by evaporation under reduced pressure using a Buchi R300 rotary evaporator, operated at 50 °C, 46 mbar and 40 rpm. The pellets were dried in a bench-top oven (Espec SU-221) at 120 °C for 4 h to immobilize the chloroplatinate ions. After drying, the pellets were calcined in a stream of air (150 ml/min) for 5 h, using a Carbolite furnace, ramped to 400 °C at 5 °C/min. The calcined pellets were reduced at 350 °C in a stream of 10% H₂/Ar (50 ml/min) over a period of 5 h.

5.2.3 Liquid and gas analysis

Analysis of the LOHC molecules was performed using a single quadrupole (SQ) mass spectrometry (MS) gas chromatography (GC) instrument (436-GC-SQ-MS; Scion, Netherlands). The system was equipped with a CP 8400 auto sampler (7683 D), a GS-Tek GsBP-50+MS column (30 m, 0.25 mm i.d., 0.25 mm d.f.) and a SQ mass spectrometer. Helium was used as carrier gas. Liquid analysis was carried out as follows: samples of a reaction mixture were drawn from the reactor, diluted with hexane (1:100 wt/wt), then aliquots of each diluted sample (1 ml) were injected at a split ratio of 1:100. The gaseous phase analysis was performed using a gas chromatograph (SRI8610C GC, USA) equipped with a 0.9 m molecular sieve column and a thermal conductivity detector. During dehydrogenation experiments, the gas samples were collected using 1 L sampling bags (Restek, USA).

5.2.4 Hydrogenation/dehydrogenation cycles

Hydrogenation of H0-DBT was performed using a fixed bed reactor (FBR) (downflow option) packed with a commercial Ni-based catalyst (NISAT 310, 50 wt % Ni). A double-walled FBR allowed heating by means of an external oil-based heating unit. A chiller was connected to the heating unit to reduce any temperature spike that may result from the exothermic nature of the reaction. During hydrogenation, the reactor was heated and pressurized with H₂. Thereafter, a pre-heated LOHC (H0-DBT) was fed into the reactor using a piston pump. For the dehydrogenation of perhydrodibenzyltoluene (H18-DBT), a 500 ml three-necked round bottom flask loaded with 1 wt % Pt/Al₂O₃ was used as batch reactor. The reactor was heated from the outside, using a heating mantle with a digital feedback controller. Furthermore, the reactor was connected to a cooling condenser and, in line with this, filters and a mass flow meter were also connected. Figure 5.1 shows a schematic representation of the experimental setup used for the hydrogenation and dehydrogenation cycling tests.

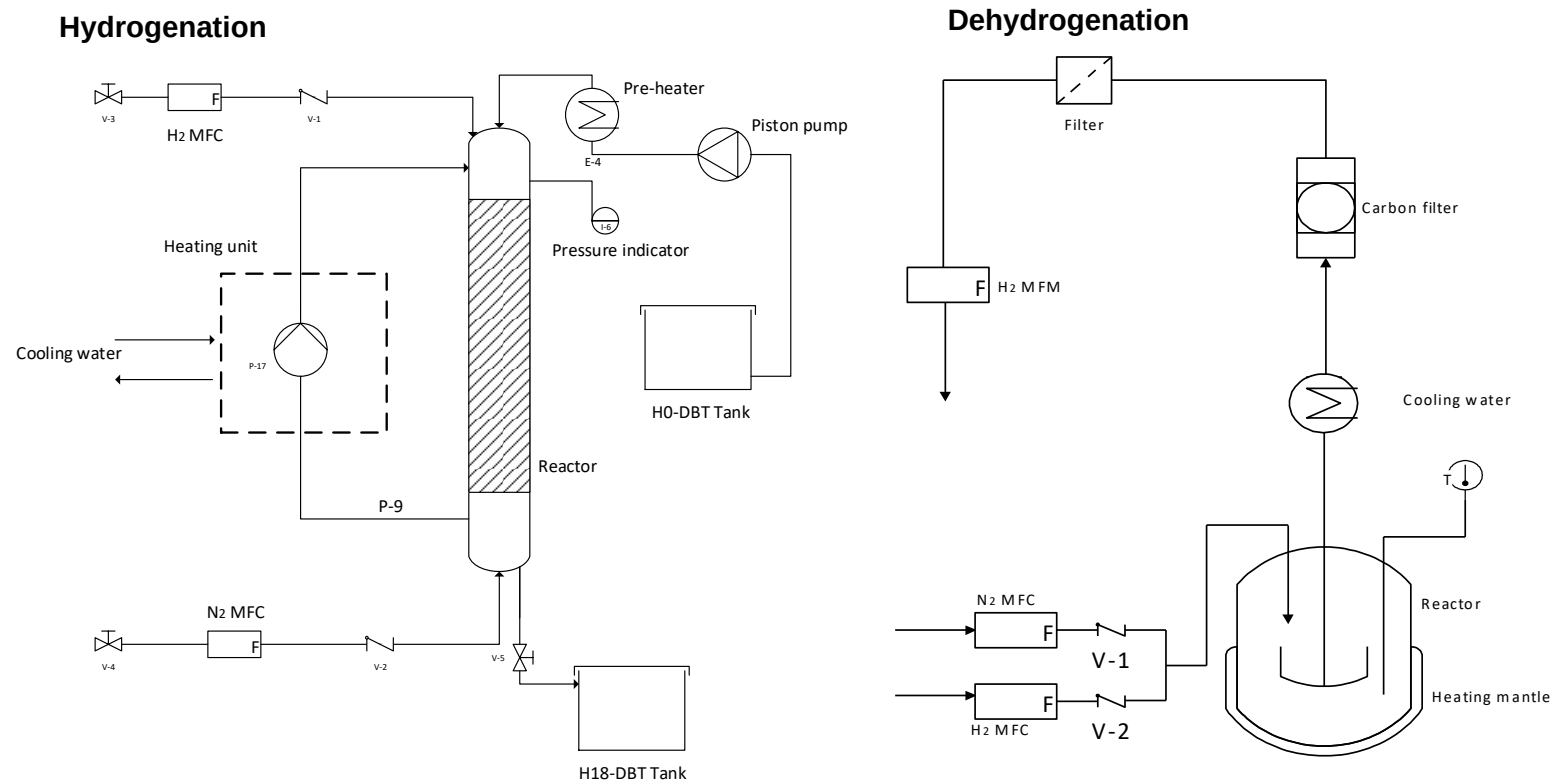


Figure 5.1: Schematic flow diagrams for hydrogenation and dehydrogenation systems used in this study.

5.3 Results and discussion

5.3.1 Hydrogenation of prepared LOHC mixtures and pure H0-DBT

The hydrogenation system described in this study was designed and built to hydrogenate H0-DBT. Various mixtures of H18-DBT/H0-DBT were prepared in this study to represent partially dehydrogenated LOHCs. This could be as a result of a scenario where deep dehydrogenation is not completed. In the event of the exothermic reaction temperature becoming high, the reaction rate can be slowed down by controlling operational parameters such as the hydrogen pressure, heating unit temperature and the feed flow rate. The effect of hydrogen pressure on the degree of hydrogenation (doh) of various LOHC mixtures and pure LOHC was determined. Figure 5.2 shows the doh vs. hydrogen pressure when using different H18-DBT:H0-DBT ratios and pure H0-DBT. The doh was >99% for the hydrogenation of 1:1 ratio (initial doh ~49%) at pressures in the range 3–20 barg. At hydrogenation pressures of 3–15 barg, the ratios 3:7 (initial doh ~29%) and 1:9 (initial doh ~9 %) showed an increase in the doh, from 87 to 99% and 85 to 98%, respectively. When pure H0-DBT was used, we were able to achieve 74% doh at 3 barg pressure. Increasing the pressure to 15 barg resulted in a further increase in doh to 98%. Ali and co-workers reported that 21% doh (1.33 wt %) was obtained when Raney Ni catalyst was used for the hydrogenation of H0-DBT at 8 barg [32]. Therefore, we were able to achieve high doh values at pressures lower than the typical range of 30–50 barg [20, 33–35].

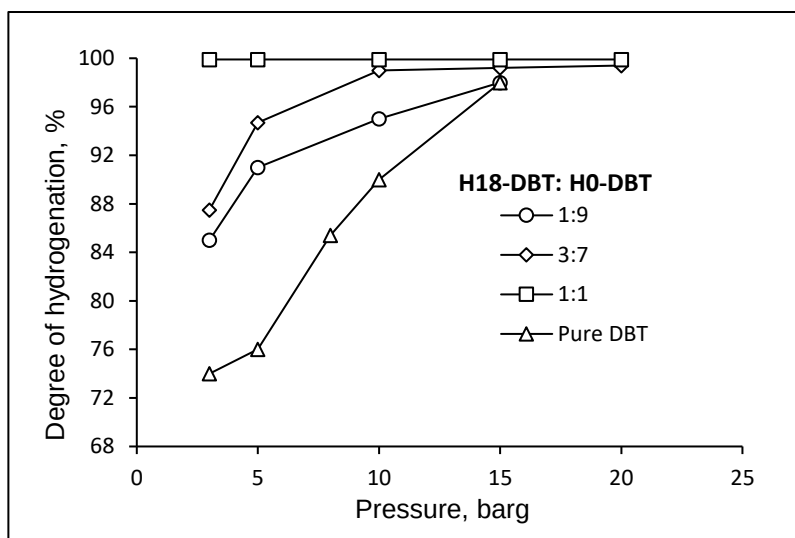


Figure 5.2: Hydrogenation of LOHC mixtures (H18-DBT:H0-DBT, various ratios) and pure H0-DBT at different pressures (3–20 barg). Reaction conditions: reaction temperature range 150–170 °C, liquid feed flow 1.3 ml/min, fixed bed catalyst packed with 50 wt % Ni-based catalyst.

5.3.2 Cycling tests

The application of separate hydrogenation and dehydrogenation systems for cycling tests is to mimic scenarios where a hydrogenation plant is used to store hydrogen and the charged LOHC is transported to a different site where the dehydrogenation plant is located (e.g., a hydrogen refuelling station). After dehydrogenation, discharged LOHC is transported back to the hydrogenation plant for the storage of hydrogen. The LOHC durability, or usage time, is determined by the amount of by-products produced during each charging/discharging cycle.

First, the hydrogenation reactor was heated to 120 °C and pressurized with hydrogen up to 15 barg. Thereafter, pure H0-DBT was fed, using a piston pump set at 1.3 ml/min. At this flow rate, it takes ~3 h to hydrogenate 300 ml of H0-DBT. Therefore, all 15 hydrogenation cycles made 45 h in total. Conditions for the hydrogenation cycles were kept constant to avoid exothermic temperature. For each dehydrogenation cycle, a 1 L batch reactor was loaded with 300 ml of H18-DBT (previously hydrogenated). About 40 g of 1 wt % Pt/Al₂O₃ was used. The dehydrogenation reaction temperature for the first five cycles was 300 °C (2 h for each cycle). For the second five cycles, the reaction temperature for each cycle was increased to 320 °C (3 h for each cycle). For the last five cycles, the temperature was increased to 340 °C (4 h for each cycle). All dehydrogenation cycles were (also) 45 h in total. The total time, for both hydrogenation and dehydrogenation, was therefore 90 h for 15 cycles.

Figure 5.3 shows the doh and the degree of dehydrogenation (dod) for, and the by-products formed in, each cycle. The average doh for all hydrogenation cycles was 98% and the by-products increased from 0.4 to 5.3 mol %. This suggests the possibility of hydrocracking side reactions, which could be an effect of the catalyst. Within the first five cycles of dehydrogenation at 300 °C, both the dod and the amount of by-products are high in cycle 1. This is ascribed to the highly active fresh catalyst. (This activity does decrease with time, however). A similar trend for the loss in activity during dehydrogenation has been reported in literature [5], [20]. The loss in activity is due to the product H0-DBT not completely diffusing out of the catalyst pores. However, when the temperature was increased from 320 to 340 °C (cycles 6–15), diffusion of H0-DBT increased and the activity was regained. The average dehydrogenation reaction by-products at 300 °C for cycles 1–5 was 4.7 mol % and, as the temperature was increased to 320 °C for cycles 6–10, and 340 °C for cycles 11–15, the by-products averaged 5.8 and 6.5 mol %, respectively. An increasing trend in the by-products is seen on the hydrogenation side, whereas for most dehydrogenation runs the by-products remain almost constant, except in the first run (with fresh catalyst). This occurs because some of the by-products from dehydrogenation are hydrogenated and others undergo side reactions to form new products. GC-SQ-MS chromatograms offered confirmation of this; some of the

corresponding (or derivatives of) dehydrogenation by-products are not present after hydrogenation (see Figure 5.4). Furthermore, the disappearance of corresponding by-products peaks after hydrogenation could mean that some of the dehydrogenation by-products are unstable. For example, perhydromethylfluorene type by-products do not appear after hydrogenation. This could be as a result of hydrocracking of the five-membered ring of methylfluorene and hydrogenation to produce perhydrobenzyltoluene. This hydrocracking is known to take place on the acidic sites of the catalyst support [18].

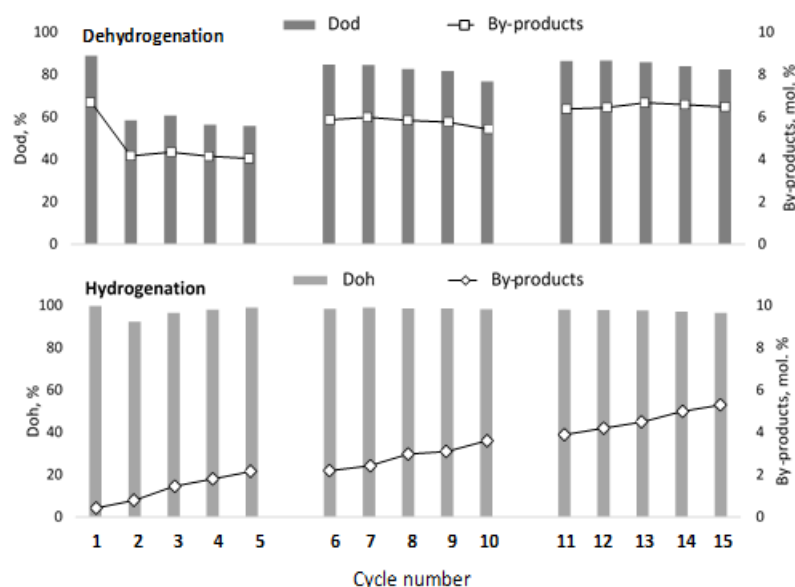


Figure 5.3: Degrees of hydrogenation and dehydrogenation from cycles 1–15 and the amount of by-products (mol %). Hydrogenation conditions: feed flow 1.3 ml/min, reaction temperature 150 °C, using 50 wt % Ni-based catalyst. Dehydrogenation conditions: batch reactor loaded with 40 g of 1 wt % Pt Al₂O₃ and 300 ml of LOHC. Cycles 1–5 at 300 °C for 2 h each, cycles 6–10 at 320 °C for 3 h each and cycles 11–15 at 340 °C for 4 h each.

Figure 5.4 shows GC-SQ-MS chromatograms of by-products obtained during cycle 10 dehydrogenation (A) and hydrogenation (B). The product identification was done using information from the NIST 17 library—the molecules with the highest probability match were selected. Chromatogram A shows the most intense peaks at *Rt* = 12.8 min, identified as isomers of H0-MBT. The qualification accuracy was confirmed by a sample of pure H0-MBT. After hydrogenation (Chromatogram B), perhydro monobenzyltoluene peaks shifted to low retention time. These isomers were also identified by Leinweber and Muller [36]. The high-boiling products were identified as isomers of benzyl-methylfluorene [26]. It is noteworthy that Ni catalysts also promote isomerism because more than 10 isomers can be identified after hydrogenation, whereas pure H0-DBT has about 6 isomers. Furthermore, the Ni catalyst could be a replacement for PGM catalysts for the hydrogenation of H0-DBT. However, the relatively

high amount of side product formation observed in hydrogenation is an effect of the applied Ni catalyst. The Pt-based hydrogenation reactions of H0-DBT have been shown to produce much fewer side products [37].

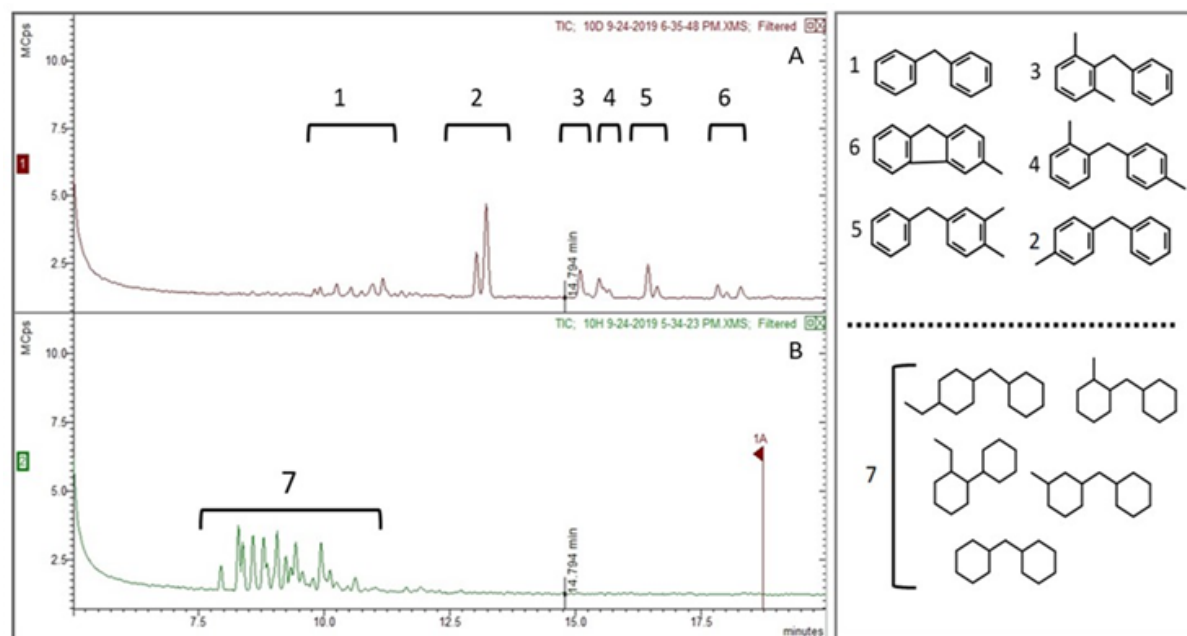


Figure 5.4: GC-SQ-MS chromatogram showing by-products of cycle 10 dehydrogenation (A) / hydrogenation (B) and examples of by-products, identified from the NIST 17 library. ^{†††}

One of the remarkable properties of H0-DBT is its high boiling point—this limits the escape of vapours with the hydrogen stream. However, this property may be affected by the amount and type of the by-products present. The by-products (low and high boilers) from the dehydrogenation reaction are also LOHCs and they can become hydrogenated. In this study, low and high boilers are defined as molecules that have low boiling points or short retention times (0–20 min) and high boiling points ^{†††} or long retention times (40–50 min), respectively. It is therefore important to direct some focus on the hydrogenation by-products. If the acceptable amount of by-products is known, then we can determine the duration of LOHC usage before its replacement with a new LOHC is required, or before purification is required. Here, as an example, we use the by-product limit in the range 0.5–35 mol %. A lower acceptable limit could be applied for by-products that are toxic to humans and a higher limit could be used for LOHC-based by-products (e.g., H0-MBT or benzomethylfluorene type).

The by-product formation equation, $y = 0.1106x + 0.2644$, is obtained from the plot of by-products vs. time for 45 h of hydrogenation cycles. Therefore, the rate of by-product formation

^{†††} Information regarding high boilers retention time window and M^+ peak can be found in Chapter 3 subsection 3.3.2.

over a total of 15 hydrogenation cycles is 0.1106 mol %/h (gradient of by-product formation equation). As has been reported by Jorschick et al. [37], if one cycle of hydrogenation and dehydrogenation takes 40 min (the R_t for typical reactors is 20 min), then for the by-product limits of 0.5, 5, 15, 25 and 35 mol % the permitted number of cycles would be 7, 130, 404, 678 and 951, respectively.

The following assumption is based on an application that requires 20 cycles per year [37]. If the limit of by-products is low (e.g., 0.5 mol %) then the LOHC duration of use will be <1 year, whereas if the limit is high (e.g., 35 mol %) then the LOHC duration of use could be up to 48 years. Table 5.1 shows the estimated duration of use of H0-DBT based on the above by-product formation equation. The permitted usage time (x) is obtained by replacing the (y) with the by-product limit (mol %).

Table 5.1: Estimated duration of LOHC use at different acceptable limits of hydrogenation by-products. Hydrogenation conditions: feed flow 1.3 ml/min, reaction temperature 150 °C, using 50 wt % Ni-based catalyst

By-product limit, mol %	0.5	5	15	25	35
Permitted usage time, h	2	42	133	223	314
Permitted number of cycles at $R_t = 0.33$ h	7	130	404	678	951
Duration of use, years*	0.3	6.5	20	34	48

*Assuming 20 cycles per year

5.3.3 Accelerated stress tests

Heat distribution in reactors can be uneven as a result of the overshooting of heaters or malfunctioning of the control unit. As this may well occur at some point, we proceeded to determine how the LOHC molecule could be affected should there be a sudden increase in temperature. In this test, the dehydrogenation of H18-DBT was performed at a higher temperature than used in the normal operation, to accelerate any form of negative effect, such as decomposition. Here, high amounts of by-products characterize H18-DBT decomposition. The normal dehydrogenation temperature for H18-DBT is ~300 °C. For the AST, the temperature was increased to 355 °C. Results of ASTs can also predict the time at which and the extent to which a molecule will decompose under normal dehydrogenation stress [38], [39]. In a constant temperature AST, the typical failure mode is dependent on chemical reactions. The Arrhenius equation relates reaction rates to temperature—this is used to compare the time in the field at normal temperature use [37,38]. Dehydrogenation of H18-DBT follows first-order reaction kinetics [17]. To determine the activation energy for this reaction, the rate constants were determined at reaction temperatures ranging from 300 to 355 °C. The

Arrhenius plot, in which the natural logarithm of k is plotted against these temperatures, was obtained for the dehydrogenation of H18-DBT, where 1 wt % Pt/Al₂O₃ was used as catalyst. Results are shown in Figure 5.5.

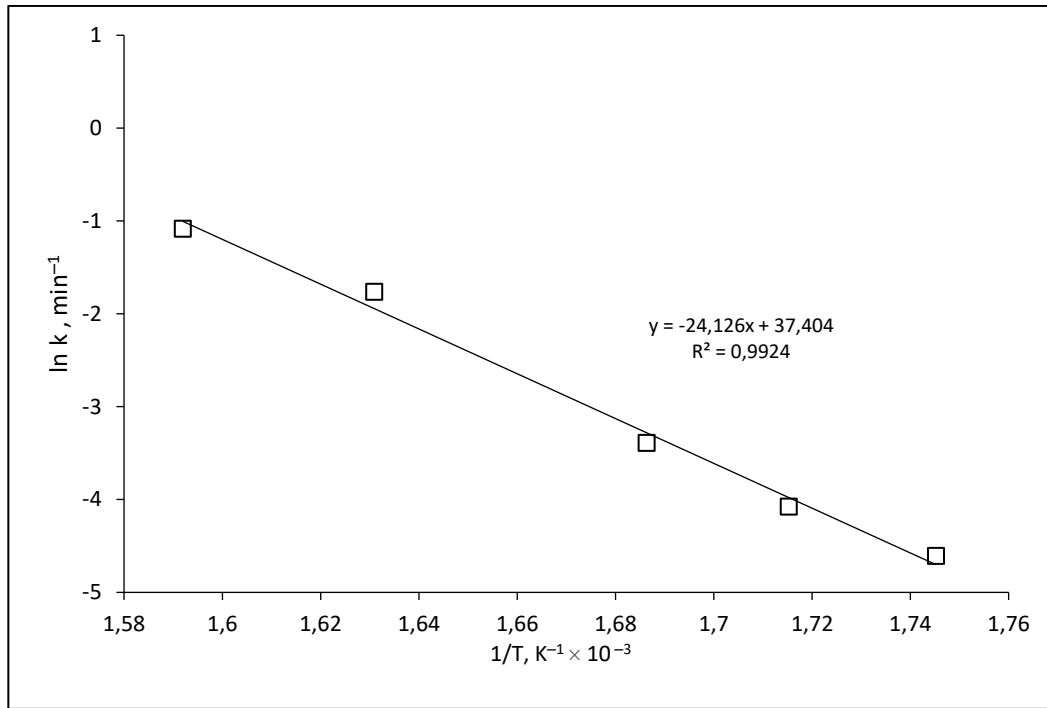


Figure 5.5: Arrhenius plot of the rate constant $\ln k$ vs. $1/T$ for dehydrogenation of H18-DBT. Dehydrogenation conditions: batch reactor loaded with 40 g of 1 wt % Pt Al₂O₃ and 300 ml of LOHC.

It is important to first determine the factor by which a test is accelerated, to obtain information about the effect at normal stress. The acceleration factor (A_F) is calculated from the activation energy E_A , the universal gas constant R , and the two temperatures T_{use} and T_{stress}

$$A_F = e^{\frac{E_A}{R} \cdot \left(\frac{1}{T_{use}} - \frac{1}{T_{stress}} \right)} \quad (1)$$

where T_{stress} is the temperature applied during the stress test and T_{use} is the temperature used during a normal dehydrogenation reaction. The acceleration factor A_F corresponds to the ratio of the operating time t_{opt} and the test period t_{test} , as follows

$$A_F = \frac{t_{opt}}{t_{test}} \quad (2)$$

The calculated acceleration factor was 38, given that the activation energy is 201 kJ/mol. This calculated activation energy is in agreement with the values reported in literature [17],[21]. Using Eq. 2, we calculated that a dehydrogenation test period of 2.2 h results in 89 h of normal operation. Therefore, the 2.2 h stress test suggests that after 89 h of normal dehydrogenation stress a total of 7.4 mol % of liquid phase by-products and 1.94 mol % of methane in the gas

phase should be expected. The liquid phase by-products are obtained from the reactor and also from the cold trap installed between the cooling condenser and the filters. This is because by-products with low boiling point (e.g., benzene, xylene, toluene, etc.) escape through the gas phase. In addition, a dod of >90% is achieved within 2.2 h under the stress temperature. See Figure 5.6. A higher dod indicates that more aromatic molecules are produced. These aromatic molecules are susceptible to the acid sites of the support material, which provides the cracking function. Hence, when there is an increase in the dod there is an increase in by-products.

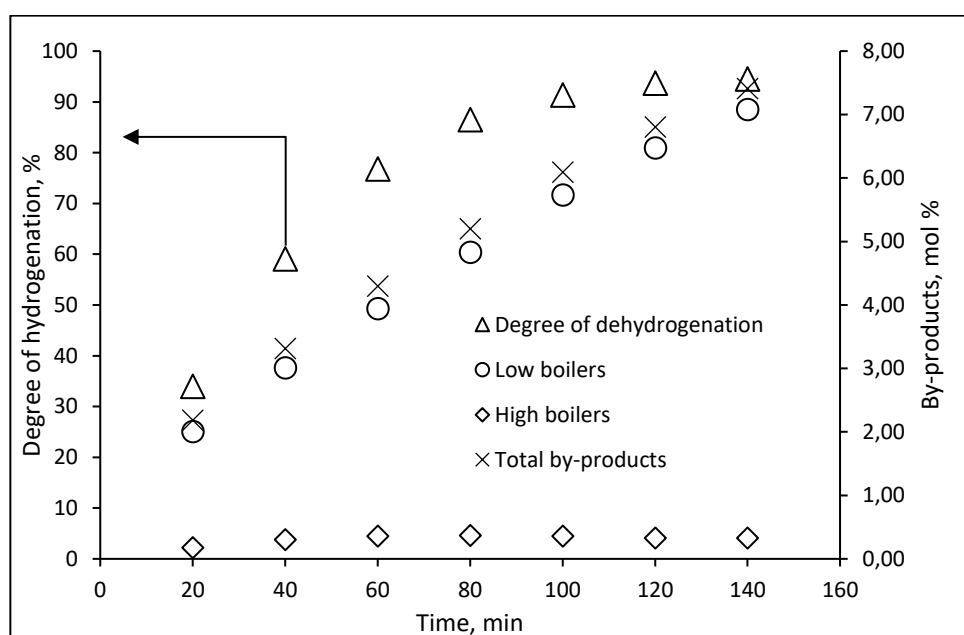


Figure 5.6: Low- and high-boiling by-products formed during dehydrogenation of H18-DBT under high stress temperature (355 °C).

Figure 5.7 included data on the quantities of by-products (low boilers, high boilers and methane) obtained under high-stress temperature, at 355 °C, and an image of two reaction mixtures, one dehydrogenated at 300 °C (A) and one at 355 °C (B). It is evident that the quantity of the low-boiler H0-MBT is higher than that of all other by-products. A reason for this is that H0-DBT from the supplier already contains H0-MBT (~0.5 mol %) During the hydrogenation of H0-DBT, H0-MBT is also hydrogenated; thereafter, it is dehydrogenated in the process and it will add to the H0-MBT produced as a by-product, resulting from cracking of the H0-DBT molecule. Furthermore, cracking resulting from hydrogenation could also lead to additional MBT. As is also evident in Figure 5.7, the liquid by-products follow the following increasing order: benzene < C21 (benzo methylfluorene) < xylene < C13–C15 (diphenyl

methane, methylfluorene, etc.) < toluene < H0-MBT. The probability of formation of these by-products will be explained later in this chapter

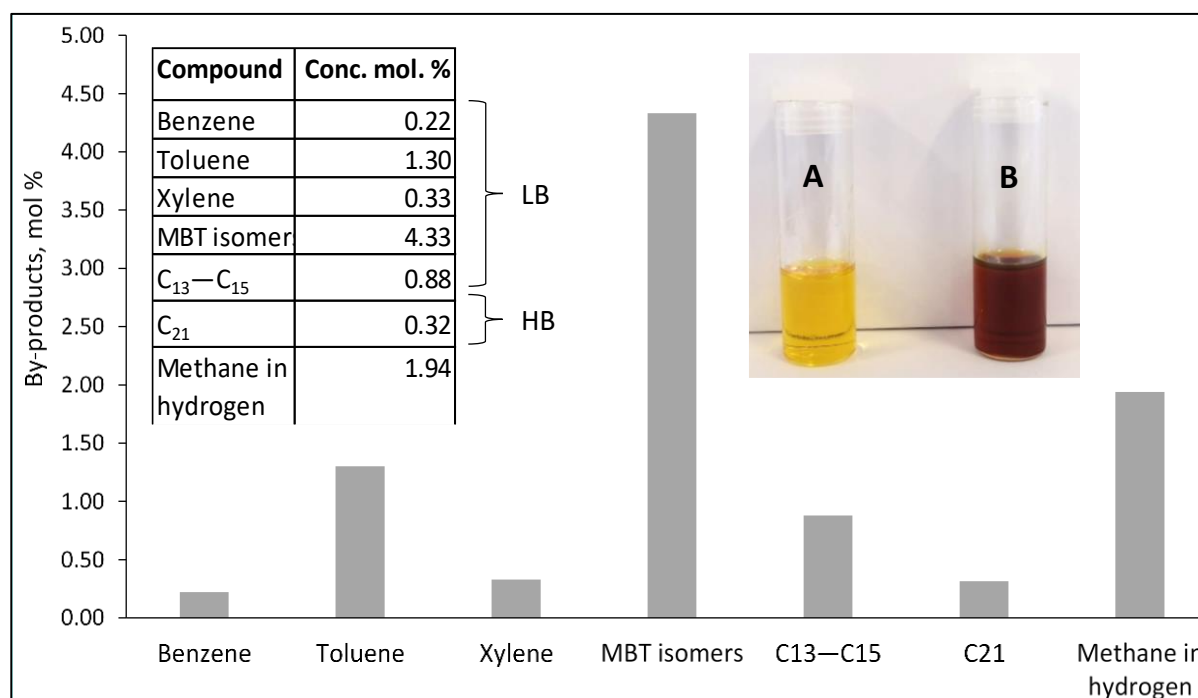


Figure 5.7: By-products formed during dehydrogenation of H18-DBT under high stress temperature (355 °C). Insert: Table of LB and HB quantities and a picture showing reaction mixtures dehydrogenated at 300 °C (A) and 355 °C (B).

Figure 5.8 shows a GC-SQ-MS chromatogram of by-products that escaped through the gas phase; after the reaction, ~1.8 ml of liquid was collected from the cold trap (installed between the cooling condenser and the filters). In the chromatogram, the highly volatile by-products (benzene, toluene and xylene) are to be seen between 3 and 6 min (the retention time window); only two isomers of xylene were observed, as indicated by two peaks. The presence of hydrogenated low boilers between 7 and 12.5 min indicate that these by-products result from cracking that occurred during the hydrogenation reaction. As mentioned earlier, the H0-MBT (dehydrogenated by-product of hydrogenation reaction) will add to the H0-MBT that results from H0-DBT cracking. Isomers of partially and fully dehydrogenated H18-DBT are also observed.

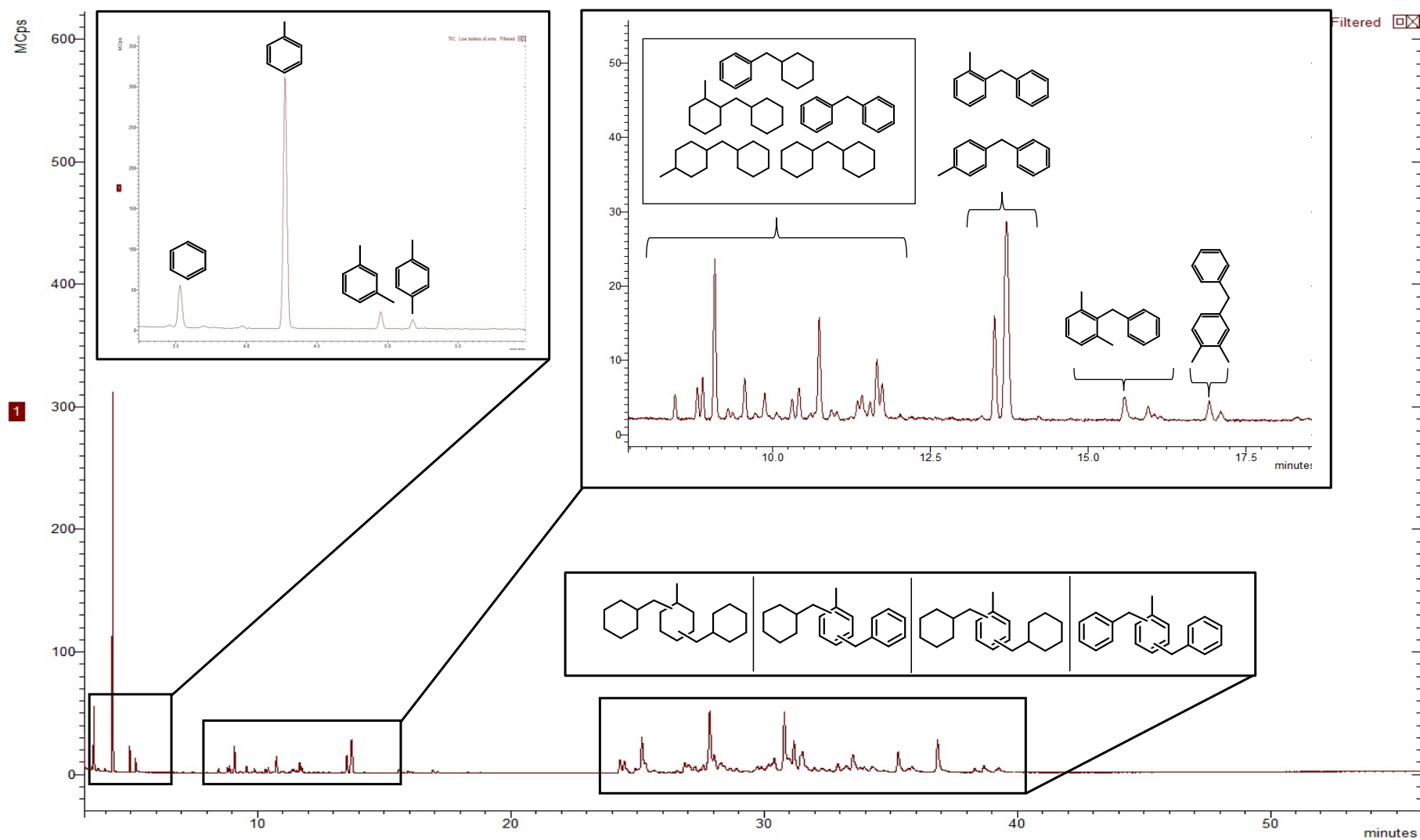


Figure 5.8: GC-SQ-MS chromatogram showing compounds obtained from a cold trap sample during dehydrogenation of H18-DBT at 355 °C.

The by-products formed indicate that there are side reactions that take place during dehydrogenation reactions, as confirmed by GC-SQ-MS and GC-TCD analyses. Figure 5.9 shows possible C–C breaking and cyclization during the dehydrogenation of H18-DBT. The presence of methane and other low-boiling-point aromatic by-products suggests the possibility of hydrogenolysis by a Pt catalyst. See Figure 5.9 (A–E). According to Blakely and Somorjai, the kinks in steps on the platinum surface structure are active sites responsible for C–C bond cleavage, besides also C–H and H–H bond cleavage [40]. Furthermore, isomers of H0-DBT could also result in different types of by-products, for example, isomers of xylene could result via routes C and D (Figure 5.9). The other possible side reaction is the dehydrogenative cyclization of 4-benzyltoluene to form methyfluorene, via route F. Moreover, a by-product with a high boiling point could be of the benzyl-methylfluorene type, also originating from a dehydrogenative cyclization of H0-DBT. On the other hand, hydrogenolysis side reactions can be expected to occur when a Ni catalyst is used [41], [42]. It is known that Ni-based catalysts can cause C–C bond cleavage [41].

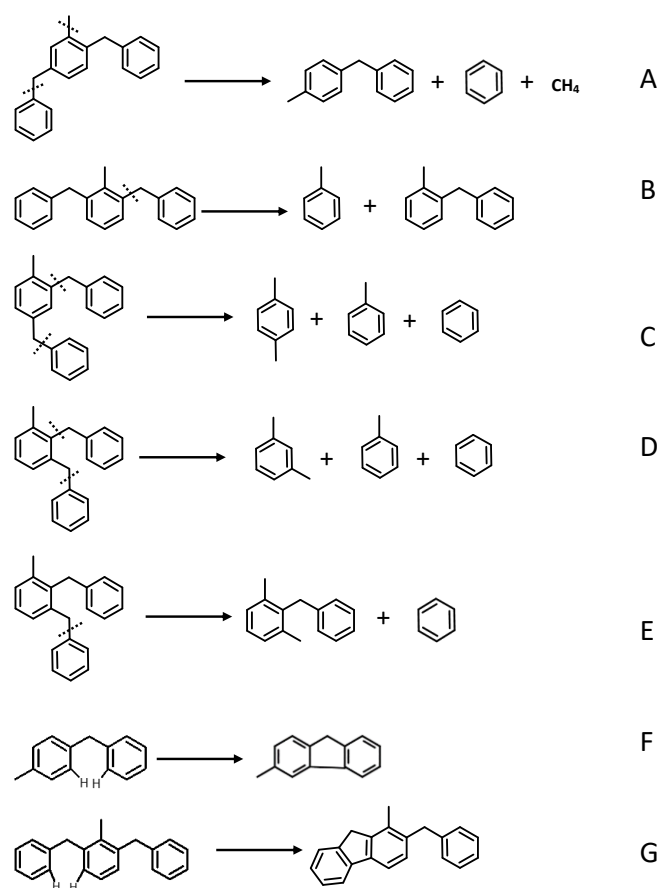


Figure 5.9: Possible C–C cleavage and dehydrogenative cyclization routes during dehydrogenation of H18-DBT.

5.4 Conclusions

The average d_{od} for 15 cycles of dehydrogenation is 77% and the by-products increased from 4.7 to 6.5 mol %. Fresh Pt/Al₂O₃ catalyst is usually high in activity, hence the initial by products is 4.7 mol %. By-products obtained from 15 hydrogenation cycles increased from 0.4 to 5.3 mol % and the average d_{oh} was 98%. The dehydrogenation by-products are also hydrogenated; however, some derivatives were not observed after hydrogenation. This is an indication of hydrocracking as an effect of the applied Ni catalyst. If toxic by-products are produced, the permissible amount must be low (e.g., 0.5 mol %) to avoid harmful exposure. In this instance, the hydrogenation and dehydrogenation cycles will be limited to 7. A higher permissible amount of by-products (e.g., 35 mol %) for LOHC-based compounds suggest up to 951 hydrogenation and dehydrogenation cycles. The accelerated stress test period of 2.2 h at 355 °C predicted that 7.4 mol % of liquid-phase by-products will be obtained after 89 h of normal stress operation (300 °C). Methane was obtained in the gas phase and in the liquid phase the by-products obtained follow the following increasing order: benzene < C₂₁ < xylene < C₁₃–C₁₅ < toluene < H₀-MBT. This confirms the stability and durability of H₀-DBT based LOHC, because the molecule did not fully decompose at high temperature.

5.5 Conflict of interest

There are no conflicts to declare.

5.6 Acknowledgements

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CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

I - To determine existing gaps in the LOHC technology, by reviewing the following, for example: (a) hydrogen storage properties of common aromatic and heteroaromatic LOHC molecules, (b) suitable catalytic materials for the the hydrogenation/dehydrogenation reactions (noble and non-noble metal catalysts supported on metal oxides and perovskites, (c) various reactor configurations, including the heating options used for dehydrogenation reactions. A goal, throughout, was also to ascertaining the maturity of LOHC technology, overall, and subsequently identify application scenarios and opportunities available within the South African hydrogen market.

Dibenzyltoluene (H0-DBT) is currently a benchmark liquid organic hydrogen carrier (LOHC) molecule due to its good availability, affordability, high hydrogen storage capacity, non-flammability and the fact that it can be stored for a long period of time without self-discharge at ambient conditions, using the existing infrastructure for fuels. To date, common dehydrogenation systems for H0-DBT-based LOHC involve the use of electrically heated horizontal fixed bed reactors packed with Pt/Al₂O₃ catalyst. This configuration allows better separation of hydrogen gas from the liquid phase. The current state-of-the-art LOHC catalysts, reactors and processes do, however, require further development towards achieving high conversion and effective hydrogen production, with minimal by-product formation. LOHC technology has reached the pre-commercial stage. Globally, the major industry players are Chiyoda Corporation (Japan) and Hydrogenious Technologies (Germany). Upon considering the potential future application of LOHC technology in South Africa, a market survey has indicated that there are numerous opportunities where the LOHC technology can be applied, for example, in mining, rural electrification and in hydrogen logistics companies.

II - To develop a suitable chromatographic method for the separation, identification, and quantitative analysis of isomeric reaction mixtures of dibenzyltoluene-based LOHCs and to determine the effect of reaction temperature on the distribution of isomer fractions and the doh.

A method for the analysis of H0-DBT-based LOHC molecules was successfully developed—all the isomer fractions of reaction mixtures could be separated and identified by the techniques of two-dimensional gas chromatography coupled with time of flight-mass spectrometry (2D-GC-TOF-MS) and one-dimensional gas chromatography coupled with mass spectrometry. Results indicated that the aliphatic rings of a H18-DBT molecule are not dehydrogenated

simultaneously. The H18-DBT dehydrogenation is a stepwise process. It affords intermediates and products following the reaction pathway $\text{H18-DBT}-3\text{H}_2 \rightarrow \text{dodecahydro-dibenzyltoluene (H12-DBT)}-3\text{H}_2 \rightarrow \text{hexahydro-dibenzyltoluene (H6-DBT)}-3\text{H}_2 \rightarrow \text{H0-DBT}$. Increasing of the reaction temperature from 270 to 300 °C resulted in a gradual decrease of the H18-DBT isomer fraction, coupled with the formation of the H6-DBT and H12-DBT isomer fractions, which also decrease, and the H0-DBT isomer fraction is formed. Therefore, the doh decreases with an increase in reaction temperature. Furthermore, 2D-GC-TOF-MS analysis revealed that at 300 °C all of the H18-DBT isomer fraction is converted: the H6-DBT and H12-DBT fractions contribute 37%, and the main product (H0-DBT) 63%. These findings are comparable with GC-SQ-MS results. The observed low- and high-boiling point by-products suggest disintegration, and cyclization of the molecule due to side reactions.

III - To reduce the turnaround time required for obtaining dehydrogenation results for the degree of dehydrogenation (dod) using chromatographic methods.

A refractometer was successfully calibrated using samples analysed by the state-of-the-art chromatography techniques employed earlier in the study. Indications were that it takes 30 s to measure the dod with a refractometer and 1 h when using chromatography techniques—results indicated that hereby the turnaround time is improved by 99%. The refractive index data is based on the optical properties of a molecule; it does not provide details about composition of the mixture.

IV -To evaluate (both experimentally and theoretically, by DFT calculations) Pt and Pd based catalysts, and then characterize monometallic catalysts $\text{Pt/Al}_2\text{O}_3$ and $\text{Pd/Al}_2\text{O}_3$, as well as the bimetallic counterparts ($\text{Pt-Pd/Al}_2\text{O}_3$), for the dehydrogenation of H18-DBT.

Experimental and theoretical evaluations indicated that Pd- and Pd–Pt-based catalysts are not preferred for the dehydrogenation of H18-DBT. Based on results of the H18-DBT dehydrogenation experiments, the dod achieved with catalysts with 0.5, 1 and 2 wt % Pt loading was 50, 80 and 96%, respectively. The dod of reactions carried out with 1 wt % and 2 wt % Pt differed by 16%. Therefore, based on the hydrogen produced according to the loading of Pt, the 2 wt % Pt loading appears to be uneconomical (based on hydrogen produced per loading of Pt). The TOF based activity also indicated that the increase in metal loading is effective for 0.5 and 1 wt % Pt, further increase to 2 wt % resulted in low TOF values. Furthermore, the metallic surface area-based productivity remained the same for 1 and 2 wt % Pt loading. The particle size and metallic surface area are inversely proportional to the metal dispersion and increase with an increase in metal loading. Metal particle size, metallic surface

area and the number of reducible species increase with an increase in metal loading, resulting in an improvement of the dod. Analysis of textural properties confirmed that the catalysts retained their mesoporous structure after metal loading.

V - To optimize the catalyst metal loading and reaction temperature towards achieving a reasonably high dod, with a minimum amount of by-products and a high purity of hydrogen.

Dehydrogenation of H18-DBT at 290 °C using 1 wt % Pt/Al₂O₃ resulted in fewer by-products being formed, thus resulting in high hydrogen purity (>99.99%). The hydrogen flow and dod values were low, 5 NL/h and 35%, respectively. Increasing the temperature to 320 °C resulted in high hydrogen flow (23 NL/h) and 90% dod. However, the hydrogen purity here was <99.99%, due to increased formation of by-products. Therefore, the dehydrogenation of H18-DBT at 300 °C using a catalyst with 1 wt % Pt loading could be considered optimum—the hydrogen purity remains at 99.99%, and the hydrogen flow and dod were 10 NL/h and 60%, respectively.

VI - To determine the durability of dibenzyltoluene-based LOHCs, by performing an increasing number of hydrogenation and dehydrogenation cycles, and then carrying out ASTs.

Remarkably, H0-DBT can be hydrogenated up to 98% (doh) at a relatively low pressure of 15 barg, rather than at the frequently used pressure range of 30–50 barg. If the desired limit of by-products is low (e.g., 0.5%), such as in the case of toxic compounds, the number of hydrogen charging/discharging cycles will be limited to 7. For a higher limit of LOHC-based by-products (e.g., 35%), up to 951 hydrogen charging/discharging cycles have been obtained. Overall, in the absence of any form of by-products, the H0-DBT molecule usage could be infinite. For an AST period of 2.2 h, at 355 °C, 7.4% of by-products was obtained after 89 h of normal stress operation (300 °C). This offers confirmation of the durability of H0-DBT-based LOHCs. During dehydrogenation at extremely high temperature (355 °C), methane (1.94%) was obtained in the gas phase and in the liquid phase. The following by-products were obtained: benzene (0.22%), C₂₁ (0.32%), xylene (0.33%), C₁₃–C₁₅ (0.88%), toluene (1.30%) and H0-MBT (4.33%). Results of both the cycling tests and AST tests confirmed the durability of H0-DBT. Indications are that this molecule can endure many years of hydrogenation and dehydrogenation cycles, provided that the by-products are non-toxic.

6.2 Recommendations for future work

Opportunities (in mining, hydrogen logistics companies and rural electrification) for the application of LOHC technology have been identified within the South African context. However, further detailed studies are required to determine the feasibility and techno-economics for potential applications—for example, costs associated with converting a diesel mining dozer to be powered by LOHC hydrogen, the cost of equipment flameproofing, the management of on-board hydrogen production and the safety of underground hydrogen. These aspects need to be addressed, taking the current technology into account. Some recommendations for future work in this regard include the following:

The application of elemental analysis to quantitatively determine the load and to check for carbon deposits or impurities on the catalyst surface should be explored—elemental analysis is also a very useful analytical tool—it provides rapid and precise quantitative results.

The synthesis of pure H0-DBT, without isomers, will go a long way to make analyses less complex, and thus kinetics studies much simpler and more accurate.

Further improvement of the catalyst is still required, in order to achieve more highly effective conversion at minimal by-product formation, hence reducing the costs associated with additional purification systems for hydrogen. Therefore, modification of chemical and textural properties of the catalyst supports (e.g., acidity, porosity and wetting), and the use of promoters (e.g., S, Sn, etc.) should offer rewarding approaches for ongoing and future research activities. Catalyst synthesis methods including, but not limited to, the use of supercritical CO₂ should be explored.

In the liquid phase reactions, the effective diffusivity is reduced when compared to molecular diffusion, and this is significant when the molecular diameter/pore diameter ratio is 1:10. The H18-DBT molecule has a maximum expansion of approximately 1.4 nm and the pore size of common alumina supported catalysts is about 10 nm. Therefore, this diffusion limitations could strongly affect the dehydrogenation reaction.

The use of pulsed-field gradient nuclear magnetic resonance measurements for diffusion-ordered spectroscopy mapping could be considered to study the diffusion properties of catalysts with different pore diameters. This should address issues pertaining to the catalyst stability, since it is assumed that the aromatic product does not diffuse completely out of the catalyst pore. Catalyst deactivation is therefore observed when the catalyst is recycled.

Ultimately, it is desirable to have the LOHC technology for on-board hydrogen production for passenger cars; however, in this regard, the high dehydrogenation temperatures required remain a drawback. LOHC molecules with low heat of reaction, but with other (favourable) properties similar to those of H0-DBT, will surely be advantageous for low-temperature

dehydrogenation (<200 °C). Other heating methods, such as induction and the application of heat-conductive catalyst support structures will provide more efficient dehydrogenation process. In addition, other methods that requires less heat, such as electrochemical dehydrogenation and direct LOHC fuel cells should attract further attention.

The aromatic molecules produced in the H18-DBT dehydrogenation reaction are susceptible to the acidic sites of the support, which has a molecule cracking function. Hence, by-products produced by the side reactions increase with an increase in the degree of dehydrogenation. Therefore, less acidic catalyst supports could surely suppress the side reactions, and consequently no (or fewer) by-products will be produced. A dehydrogenation reaction driven by a catalyst, without side reactions, could lead to excellent (potentially endless) recyclability of the LOHC H0-DBT.

APPENDIX A: SUPPLEMENTARY INFORMATION

Figure A1 and A2 shows calibration curves used for determination of degree of hydrogenation and purity of hydrogen, respectively.

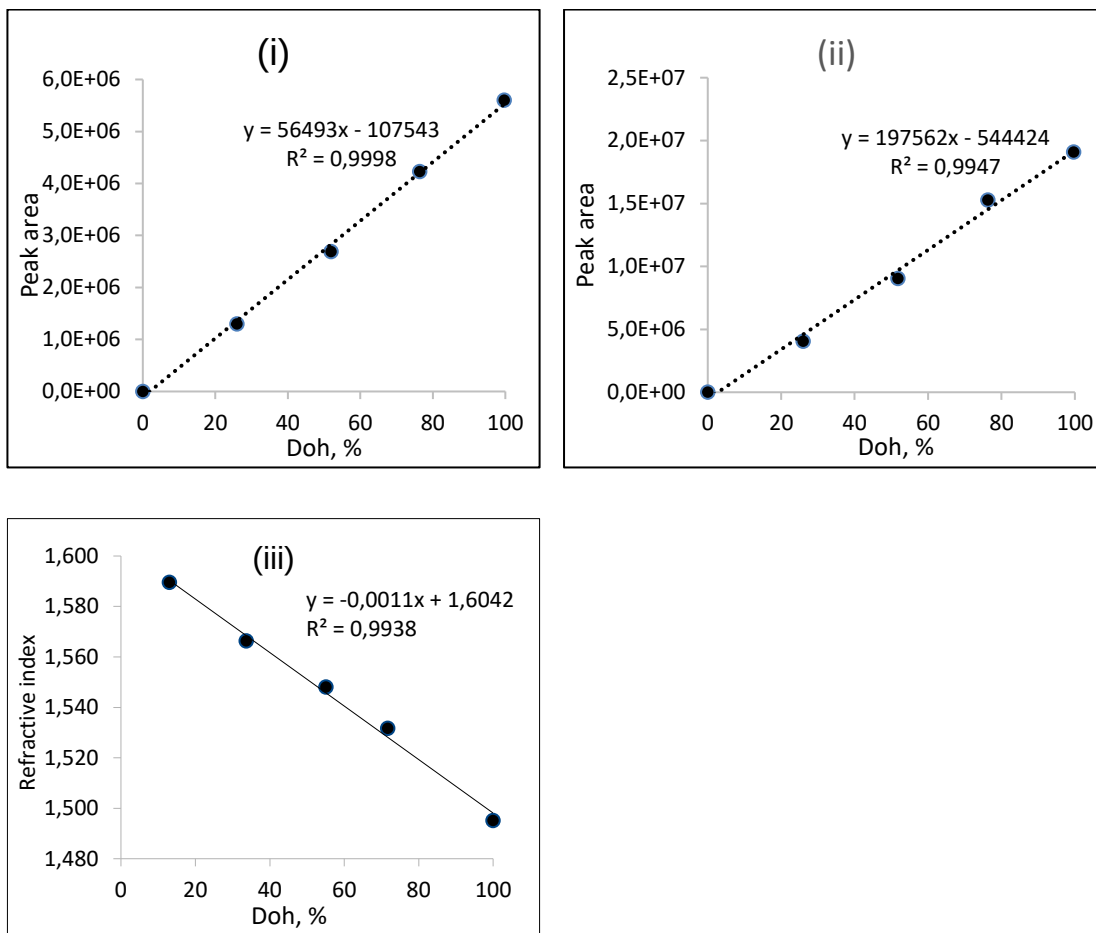


Figure A1: Calibration curves for analysis of the H0-DBT based LOHC using (i) 2D-GC-TOF-MS, (ii) GC-SQ-MS and (iii) refractometer.

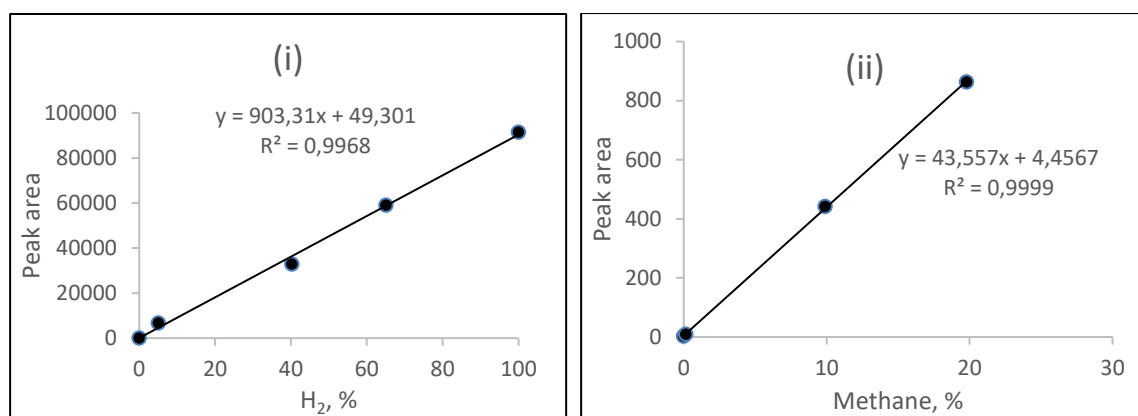


Figure A2: GC-TCD calibration curves for determination of the purity of (i) hydrogen and (ii) quantity of methane (ii) produced during dehydrogenation of H18-DBT.

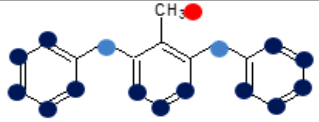
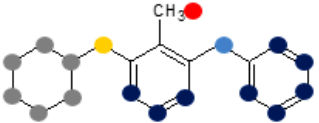
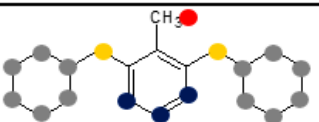
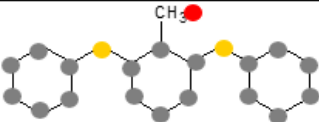
H0-DBT/H18-DBT	Proton Assignment
 H0-DBT	● Aromatic: 7-7.5 ● Methyl: 2.23 ● Methylene: 3.95
 H6-DBT	● Aromatic: 7-7.5 ● Methyl: 2.22 ● Methylene: 3.95 ● Aliphatic: 1.48-1.71
 H12-DBT	● Aromatic: 7-7.5 ● Methyl: 2.20 ● Methylene: 2.62 ● Aliphatic: 1.48-1.70
 H18-DBT	● Methyl: 0.97 ● Methylene: 1.36 ● Aliphatic:

Figure A3: ¹H-NMR spectra and proton assignment of un-hydrogenated, partially, and fully hydrogenated dibenzyltoluene based LOHC.

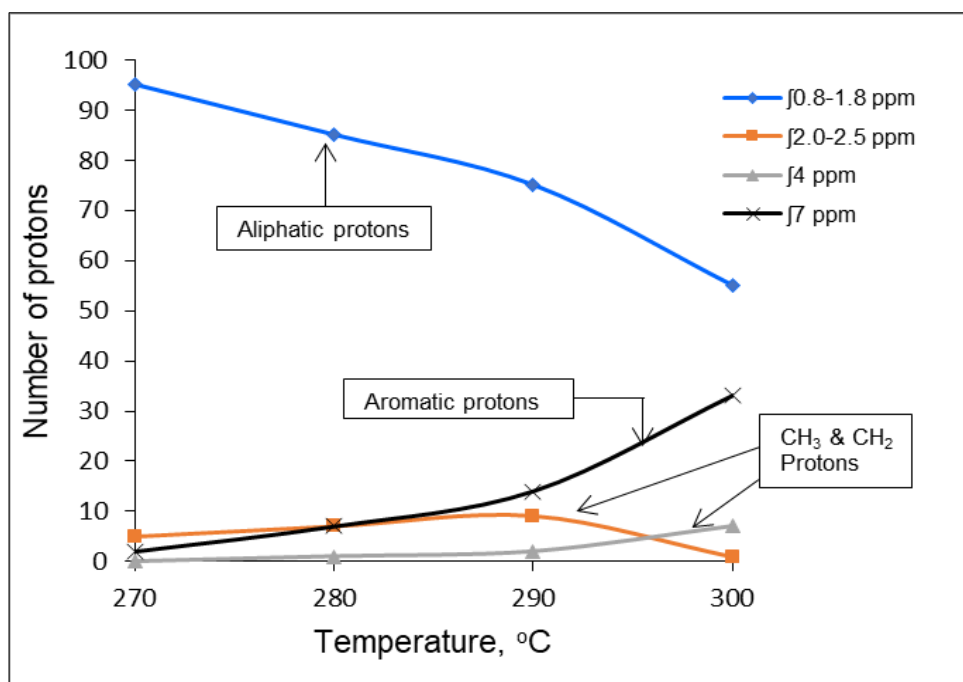


Figure A4: The effect of dehydrogenation temperature on the formation of aromatic protons and reduction of aliphatic protons.

Figure A5 shows the emergence of aromatic C=C (1608 cm^{-1} ; 1492 cm^{-1}), C–H (3027 cm^{-1}) and a decrease in intensity of the aliphatic C–H (2918 cm^{-1} ; 2849 cm^{-1}) upon dehydrogenation.

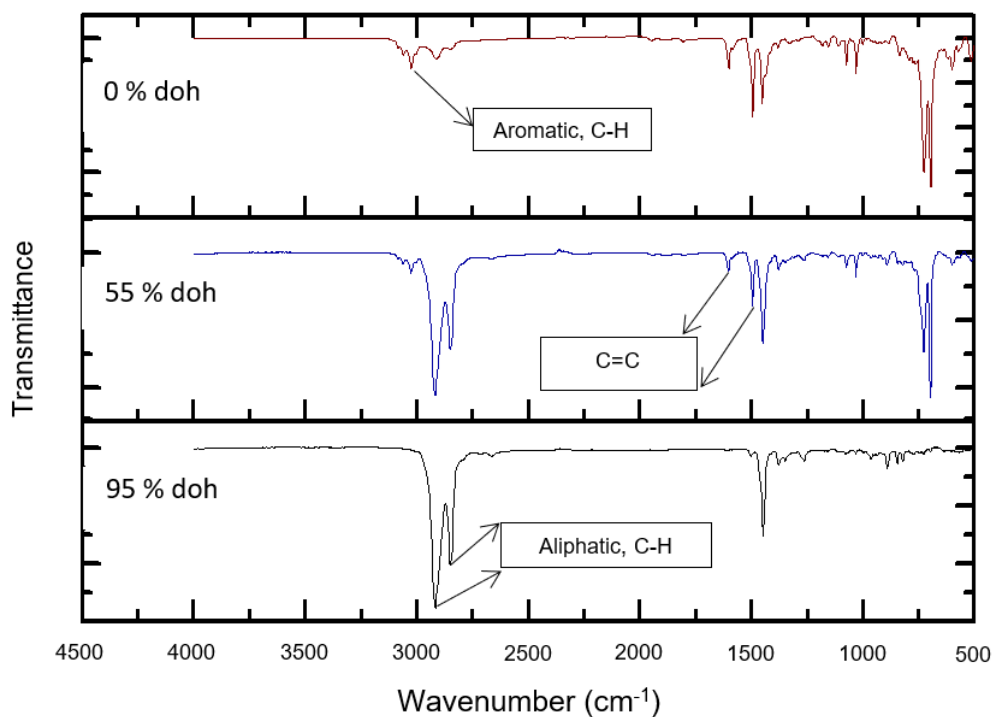


Figure A5: FTIR spectra of partially hydrogenated, partially dehydrogenated, and unhydrogenated dibenzyltoluene.

Figure A6 shows that 12.3 litres of hydrogen was produced from dehydrogenation of 20 ml H18-DBT. Therefore, 1ml of H18-DBT produced approximately 615 ml of hydrogen.

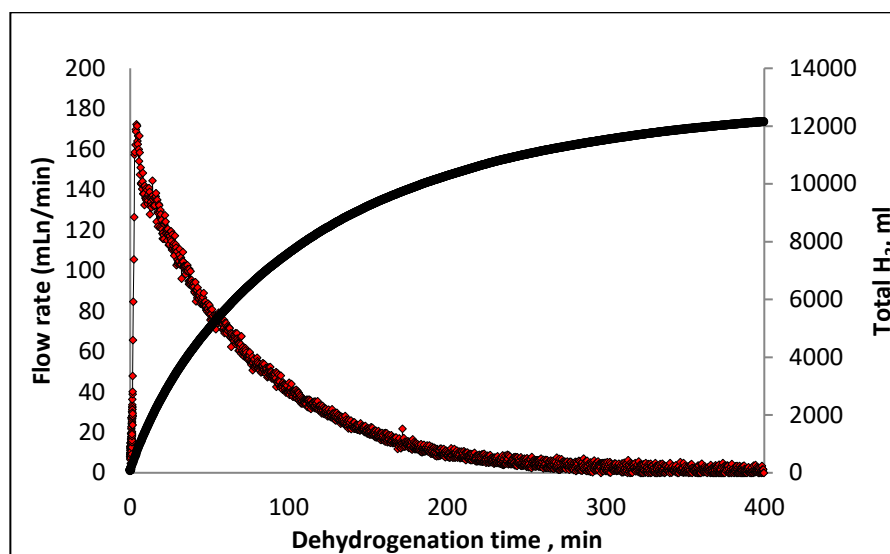


Figure A6: Hydrogen flow rate and total H₂ recovered vs. dehydrogenation time using batch reactor setup at 320 °C. Reaction conditions: H18-DBT (99% doh; 63 mmol (20 ml)) using 0.4 mol % of Pt as 5 g of 1 wt % Pt/Al₂O₃.

The catalyst metal loading was confirmed by inductively coupled plasma–optical emission spectrometry (ICP-OES), using an Agilent 5110 ICP-OES instrument and the ICP Expert software.

Table A1: Metal loadings and elemental compositions of the catalysts determined using ICP-OES.

Catalyst	Target loading (wt %)		Actual loading (wt %)	
	Pt	Pd	Pt	Pd
Pt/Al ₂ O ₃	0.5	—	0.48	—
Pt/Al ₂ O ₃	1	—	1.04	—
Pt/Al ₂ O ₃	2	—	2.23	—
Pd/Al ₂ O ₃	1	1	—	1.14
Pt-Pd/Al ₂ O ₃	1	1	1.2	0.95

Table A2: Textural properties of the catalysts

Cat. ID	Catalyst	Alumina Phase	BET surface area (m ² /g)	Total pore volume(cc/g) ^a	Pore diameter (nm) ^a
Gen 1	0.5 wt % Pt/Al ₂ O ₃	Gamma	218	0.5	7
Gen 2	0.5 wt % Pt/Al ₂ O ₃	Gamma	244	0.7	8
Gen 3	0.5 wt % Pt/Al ₂ O ₃	Transition	77	0.4	19
Gen 4	0.5 wt % Pt/Al ₂ O ₃	Gamma	279	0.7	7
Gen 5	0.5 wt % Pt/Al ₂ O ₃	Mixture	190	0.6	11
OEM 1 *	0.5 wt % Pt/Al ₂ O ₃	—	—	—	—
OEM 2 *	0.5 wt % Pt/Al ₂ O ₃	—	—	—	—

^a Determined using the Barrett–Joyner–Halenda (BJH) method

*Textural properties of the OEM catalysts are confidential

*Generation (Gen)

*Original equipment manufacturer (OEM)

The Pt/Al₂O₃ catalyst (fifth generation (Gen 5) in Figure A7) mentioned in Chapter 3 was selected after benchmarking of a series of catalysts including original equipment manufacturers (OEMs). Gen 5 is selected because, its activity is close to that of OEM 2 catalyst. The difference between Gen catalysts is the type of alumina support used, See Table A2.

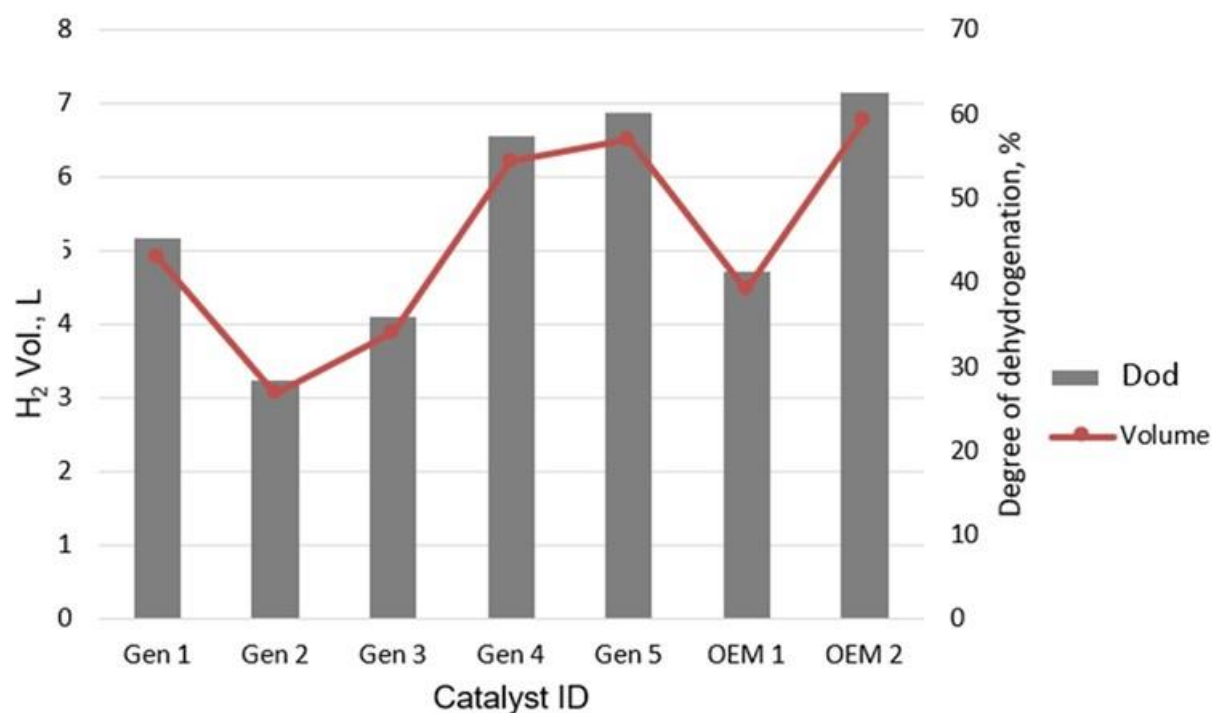


Figure A7: Screening of Pt/Al₂O₃ catalysts for dehydrogenation of H18-DBT at 320 °C for 90 min, using a batch reactor. Pt loading, 0.5 wt %; Catalyst mass, 5 g; LOHC volume, 20 ml of H18-DBT (99 % doh).

Table A3: Relation between Pt loading and TOF at different reaction temperatures for dehydrogenation of H18-DBT

Pt loading (wt %)	Pt dispersion (%) ^a	Reaction temperature (°C)	r (mol. g ⁻¹ .s ⁻¹)	k (s ⁻¹)	TOF (s ⁻¹)
0.5	19	290	2.78E-06	1,33E-05	0,009538
		300	7.29E-06	3,50E-05	0,025037
		310	1.15E-05	5,50E-05	0,039343
		320	1.46E-05	7,00E-05	0,050073
1	17	290	1.80E-05	8,67E-05	0,034644
		300	3.47E-05	1,67E-04	0,066624
		310	5.90E-05	2,83E-04	0,113261
		320	8.26E-05	3,97E-04	0,158565
2	13	290	8.33E-06	4,00E-05	0,010536
		300	2.08E-05	1,00E-04	0,02634
		310	3.61E-05	1,73E-04	0,045656
		320	7.81E-05	3,75E-04	0,098774

Pt molecular weight: 195.84 g.mol⁻¹, C₀: 3.47×10⁻³ mol.g⁻¹, ^a Determined using CO chemisorption

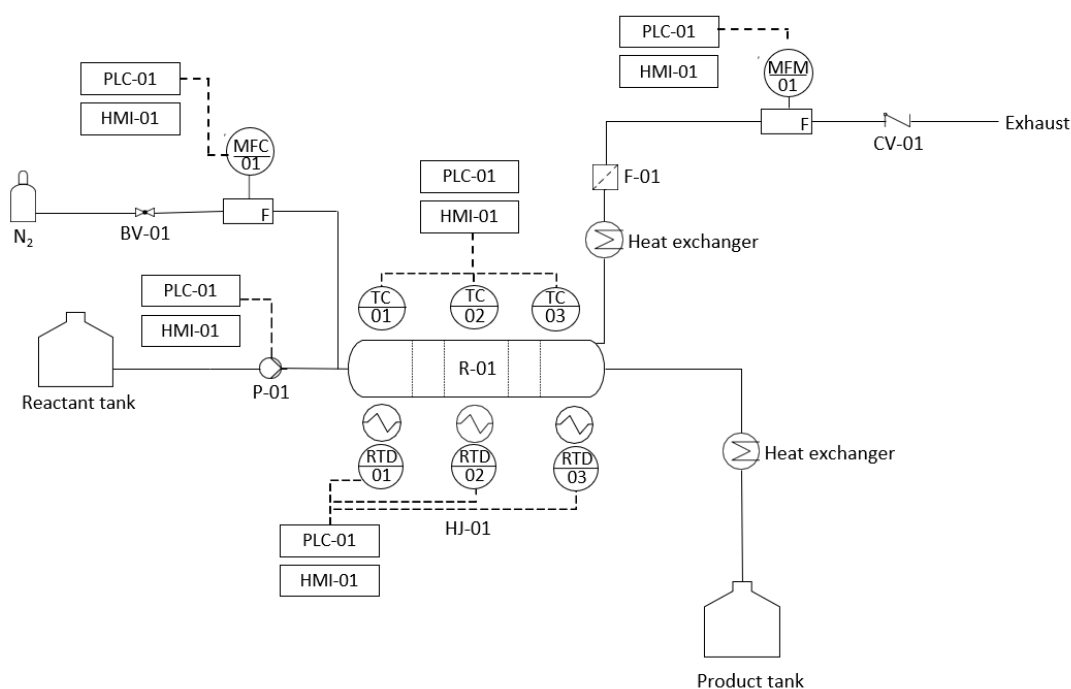


Figure A8: Piping and instrumentation diagram for LOHC dehydrogenation system.



Figure A9: Photograph of LOHC dehydrogenation setup at North West University, supplied by Hydrogenious Technologies GmbH.

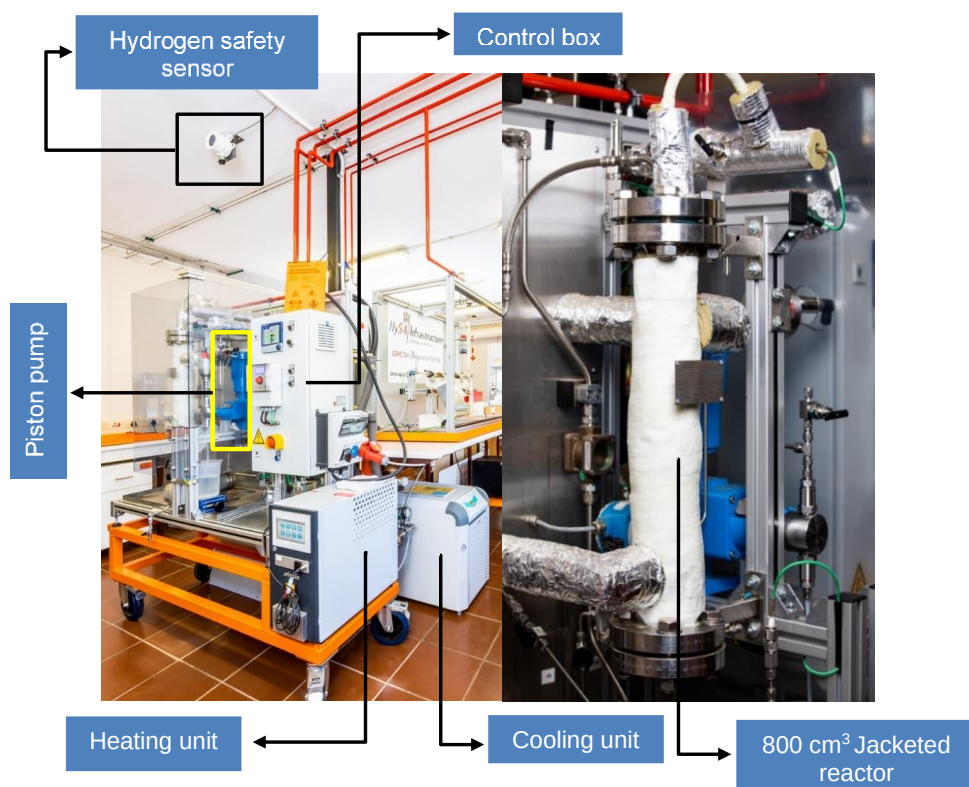


Figure A10: Photograph of LOHC hydrogenation system used for cycling tests at North West University, supplied by Framatome GmbH.

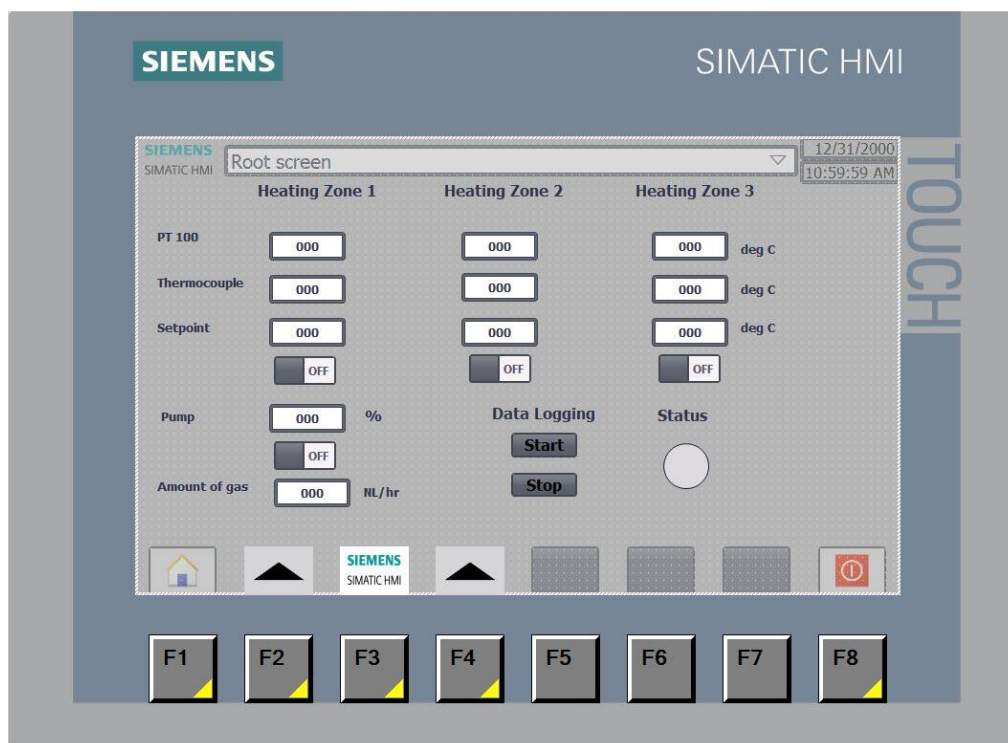


Figure A11: Front control panel of the plug flow reactor system for dehydrogenation

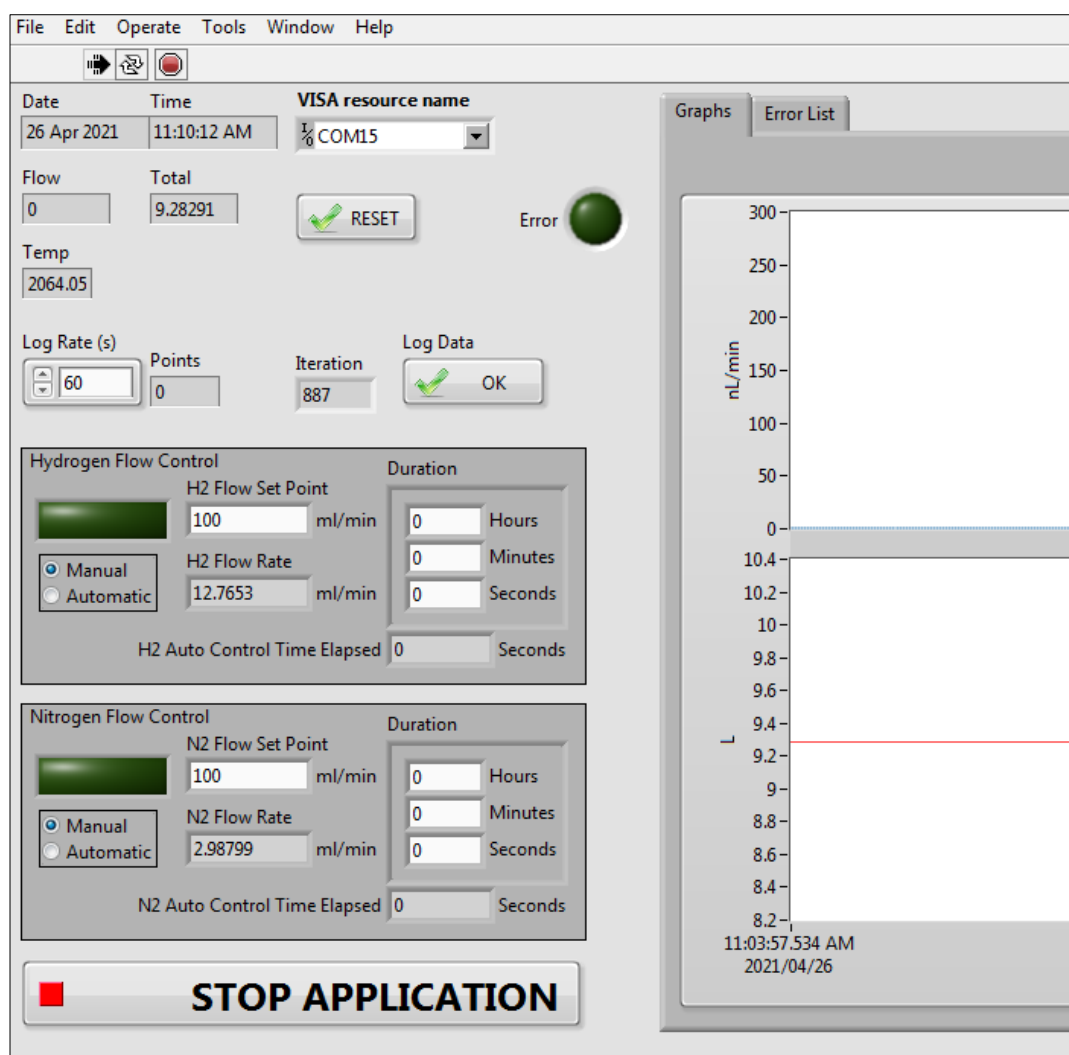


Figure A12: Front control panel of the batch dehydrogenation setup.

The Prospect of Hydrogen Storage Using Liquid Organic Hydrogen Carriers

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ABSTRACT: Reducing CO₂ emissions is an urgent global priority. The enforcement of a CO₂ tax, stringent regulations, and investment in renewables are some of the mitigation strategies currently in place. For a smooth transition to renewable energy, the energy storage issue must be addressed decisively. Hydrogen is regarded as a clean energy carrier; however, its low density at ambient conditions makes its storage challenging. The storage of hydrogen in liquid organic hydrogen carriers (LOHC) systems has numerous advantages over conventional storage systems. Most importantly, hydrogen storage and transport in the form of LOHC systems enables the use of the existing infrastructure for fuel. From a thermodynamic point of view, hydrogen storage in LOHC systems requires an exothermic hydrogenation step and an endothermic dehydrogenation step. Interestingly, hydrogenation and dehydrogenation can be carried out at the same temperature level. Under high hydrogen pressures (typically above 20 bar as provided from electrolysis or methane reforming), LOHC charging occurs and catalytic hydrogenation takes place. Under low hydrogen pressures (typically below 5 bar), hydrogen release from the LOHC system takes place. Hydrogen release from charged LOHC systems is always in conflict between highly power-dense hydrogen production and LOHC stability over many charging/discharging cycles. We therefore discuss the role of different catalyst materials on hydrogen productivity and LOHC stability. The use of density functional theory techniques to determine adsorption energies and to identify rate-determining steps in the LOHC conversion processes is also described. Furthermore, the performance of a LOHC dehydrogenation unit is strongly dependent on the applied reactor configuration. Industrial implementation of the LOHC technology has started but is still in an early stage. Related to this, we have identified promising application scenarios for the South African energy market.

INTRODUCTION

Renewable energy sources such as wind and solar energy are seen as alternatives to fossil-based fuels. However, wind and solar are not stable—they fluctuate; hence, there is a need for energy storage systems that can assist in stabilizing such fluctuations. There are various types of energy storage systems. These can be classified as electrochemical (batteries),¹ chemical (hydrogen systems: metal hydrides, metal organic frameworks, ammonia, etc.),² potential (pumped storage hydropower),³ kinetic (flywheels),⁴ magnetic (superconductors),⁵ and thermochemical (molten salt)⁶ (see Figure 1). These energy storage systems (under listed categories) generally have their own limitations.

Battery technology is mature and has been widely used for stationary and mobile power applications. However, the relatively short life cycle of batteries could lead to high replacement costs and requires recycling processes. Moreover, redox flow batteries use toxic electrolytes that could impose severe health hazards, coupled with large footprint and low power density.^{7,8} Chemical-based storage systems (e.g., metal hydrides, metal organic frameworks, etc.) have low gravimetric and volumetric storage densities. Pumped storage hydropower is also a mature technology; however, it is limited to specific

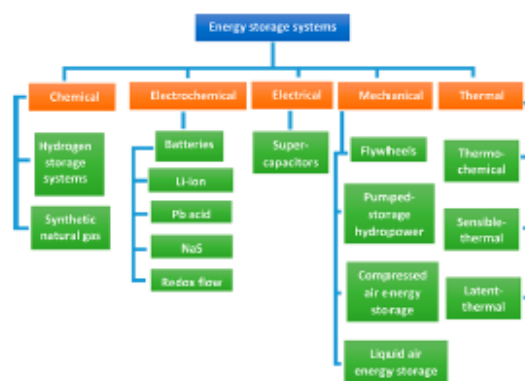


Figure 1. Classification of energy storage systems.¹⁵

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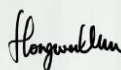
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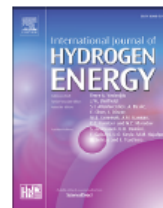
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Analysis of reaction mixtures of perhydro-dibenzyltoluene using two-dimensional gas chromatography and single quadrupole gas chromatography

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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. ¹H 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

* Corresponding author.

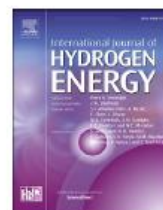
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Evaluation of catalyst activity for release of hydrogen from liquid organic hydrogen carriers

Phillimon Modisha^{a,*}, Pumeza Gqogqa^b, Rudaviro Garidzirai^a,
Cecil N.M. Ouma^a, Dmitri Bessarabov^{a,**}

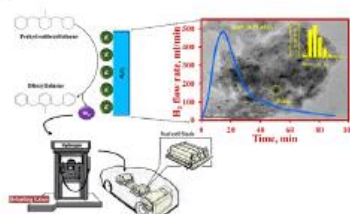
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HIGHLIGHTS

- The increase in Pt loading and temperature accelerated hydrogen production.
- High temperature lowered the hydrogen purity and increased the by-products.
- Palladium is not suitable for dehydrogenation of perhydrodibenzyltoluene.
- Dehydrogenation of perhydrodibenzyltoluene followed 1st order reaction kinetics.
- The calculated activation energy for 1 wt % Pt/Al₂O₃ is 205 kJ/mol.

GRAPHICAL ABSTRACT



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ABSTRACT

This contribution investigate the effect of parameters for production of hydrogen by catalytic dehydrogenation of perhydrodibenzyltoluene (H18-DBT). The sensitivity of the dehydrogenation reaction to temperature (290–320 °C) is justified by an increase in degree of dehydrogenation (DoD) from 40 to 90% when using 1 wt % Pt/Al₂O₃ catalyst. However, the increase in temperature increases the hydrogen production rate and decreases the hydrogen purity by increasing the formation of by-products. In addition, the DoD of 96% is obtained when 2 wt % Pt/Al₂O₃ is used at 320 °C. The DoD obtained for Pd, Pt, and Pt–Pd catalysts is 11, 82 and 6%, respectively. Therefore, Pd is not a metal of choice for dehydrogenation of H18-DBT, in both monometallic and bimetallic system. The ab-initio density functional theory (DFT) calculations are consistent with this observation. Furthermore, dehydrogenation of H18-DBT followed 1st order reaction kinetics and the activation

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Stress tolerance assessment of dibenzyltoluene-
based liquid organic hydrogen carriers

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Hydrogen production from charged liquid organic hydrogen carrier (LOHC) systems is always a trade-off between the molecule's storage capacity and the stability over the numerous charging/discharging cycles. This is because deep dehydrogenation induces cracking of the molecule and thus the storage capacity could be compromised by partial dehydrogenation. It is crucial to optimize a hydrogenation system in order to avoid possible excessive exothermic temperature whilst maintaining a high degree of hydrogenation (doh). Pure dibenzyltoluene (H0-DBT) was hydrogenated up to 98% at a relatively low pressure of 15 barg (instead of at the frequently used 30–50 barg). We determined the number of cycles that a LOHC molecule can tolerate from the amount of by-products produced during each hydrogen charge/discharge cycle. If a limit of by-products is low such as in the case of toxic compounds if available, the LOHC duration of use will be short. A higher limit for LOHC based by-products suggests a long duration of usage. Furthermore, in the absence of any by-products, the LOHC molecule usage could be endless. This certainly depends on operating conditions, catalyst type and metal loading used. Accelerated stress tests were used to predict the time to failure of the LOHC molecule. Methane was obtained in the gas phase and the liquid by-products follow the increasing order: benzene < C21 < xylene < C13–C15 < toluene < H0-MBT. Indications were that the dibenzyltoluene based LOHC is quite stable because the amount of liquid by-products obtained under stress conditions is 7.4 mol%.

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Introduction

There is a need to expand the existing traditional hydrogen storage technologies by introducing alternative storage methods, such as liquid organic hydrogen carrier (LOHC) technology. It is also important that the traditional and the new hydrogen storage technologies are specifically directed to their most suitable applications. LOHCs offer sustainable hydrogen economy due to their safe handling and efficient storage of hydrogen for long periods of time without self-discharge.^{1,2} Moreover, a LOHC molecule operates like a rechargeable battery, where a hydrogen-lean carrier molecule is charged with hydrogen to become a hydrogen-rich molecule.^{3,4} When required, hydrogen is discharged from a hydrogen-rich molecule by a dehydrogenation process.

To date, dibenzyltoluene (H0-DBT) has been the most preferred LOHC due to its attractive hydrogen storage properties, as reported elsewhere.^{5,6} Dibenzyltoluene meets most of the specifications required for hydrogen storage, e.g., a high boiling point, low melting point, and high storage capacity: 1 m³ H18-DBT = 57 kg H₂ (1, 9 MW h).^{7,8}

Hydrogen, produced by various methods, including the electrolysis of water, can be chemically bound to a LOHC. In this way, the handling of gaseous hydrogen is eliminated. LOHC technology lends itself to the linking of sites where hydrogen is produced with the sites where it is consumed—so-called sectoral integration. Hydrogen produced from LOHCs can be used in various industries (chemicals and petrochemicals, food, and glass manufacturing),^{9–11} power generation (electricity generators and hydrogen fuel cells)^{12,13} and sustainable emission-free mobility (cars, trains, and heavy-duty trucks).^{14–16}

To date, the only demonstration of LOHC technology in South Africa has occurred at the HySA Infrastructure CoC (North-West University, Potchefstroom). A pre-commercial-scale hydrogenation system for the hydrogenation of LOHCs was procured from an industrial partner, Framatome (previously Areva, Germany). The purpose of this hydrogenation system is to demonstrate the production, on a relatively large scale, of hydrogenated LOHCs through our solar-to-hydrogen pilot plant facility.

A considerable amount of work on LOHCs has been carried out worldwide, and interest therein is growing rapidly. For example, there are reports available describing LOHC catalyst development,^{17–19} reactor configurations,^{20–22} process optimization,²³ techno-economic assessments,²⁴ adoption of analytical methods,^{25,26} environmental considerations,²⁷ thermodynamic evaluation,²⁸ methods of heat integration,²⁹ and many more.

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APPENDIX C: AUTHORS CONSENT FORM

Statement of consent: Prof. Peter Wasserscheid

To whom it may concern

I, PETER WASSERSCHIED, hereby give PHILLIMON MOKANNE MODISHA consent to use the publication listed below, of which I am co-author, in the thesis entitled "Evaluation of perhydro-dibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production". The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Modisha, P., Jordaan, J. H., Bösmann, A., Wasserscheid, P., & Bessarabov, D. (2018). Analysis of reaction mixtures of perhydro-dibenzyltoluene using two-dimensional gas chromatography and single quadrupole gas chromatography. *International journal of hydrogen energy*, 43(11), 5620–5636.
2. Modisha, P., Ouma, C. N., Garidzirai, R., Wasserscheid, P., & Bessarabov, D. (2019). The prospect of hydrogen storage using liquid organic hydrogen carriers. *Energy & fuels*, 33(4), 2778–2796.

As the professor for chemical reaction engineering at the Friedrich-Alexander-University of Erlangen-Nuremberg located in Germany, I responsible for manuscript reviewing, revising, and editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Erlangen on the 29th day of April 2021

Signature: _____

Statement of consent: Dr Andreas Bösmann

To whom it may concern

I, ANDREAS BÖSMANN, hereby give PHILLIMON MOKANNE MODISHA consent to use the publication listed below, of which I am co-author, in the thesis entitled "Evaluation of perhydro-dibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production". The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Modisha, P., Jordaan, J. H., Bösmann, A., Wasserscheid, P., & Bessarabov, D. (2018). Analysis of reaction mixtures of perhydro-dibenzyltoluene using two-dimensional gas chromatography and single quadrupole gas chromatography. *International journal of hydrogen energy*, 43(11), 5620–5636.

As the group leader for hydrogen and energy at the Friedrich-Alexander-University of Erlangen-Nuremberg located in Germany, I was responsible for manuscript reviewing, revising, and DART-MS data acquisition and interpreting.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Eckental on 31. March 2021

Signature:



Statement of consent: Ms Rudaviro Garidzirai

To whom it may concern

I, RUDAVIRO GARIDZIRAI, hereby give PHILLIMON MOKANNE MODISHA consent to use the publication listed below, of which I am co-author, in the thesis entitled "Evaluation of perhydro-dibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production". The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Modisha, P., Ouma, C. N., Garidzirai, R., Wasserscheid, P., & Bessarabov, D. (2019). The prospect of hydrogen storage using liquid organic hydrogen carriers. *Energy & fuels*, 33(4), 2778–2796.
2. Modisha, P., Gqogqa, P., Garidzirai, R., Ouma, C. N., & Bessarabov, D. (2019). Evaluation of catalyst activity for release of hydrogen from liquid organic hydrogen carriers. *International Journal of Hydrogen Energy*, 44(39), 21926–21935.

As the Research Technician of HySA Infrastructure Center of Competence located at North West University (Potchefstroom Campus), I was responsible for manuscript editing.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Potchefstroom on 26th day of March 2021

Signature: Rudaviro
Garidzirai

Digitally signed by Rudaviro
Garidzirai
Date: 2021.03.26 13:57:57
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Statement of consent: Dr Johan Jordaan

To whom it may concern

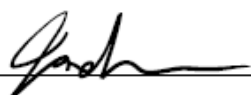
I, JOHAN JORDAAN, hereby give PHILLIMON MOKANNE MODISHA consent to use the publication listed below, of which I am co-author, in the thesis entitled "Evaluation of perhydro-dibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production". The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Modisha, P., Jordaan, J. H., Bösmann, A., Wasserscheid, P., & Bessarabov, D. (2018).
Analysis of reaction mixtures of perhydro-dibenzyltoluene using two-dimensional gas chromatography and single quadrupole gas chromatography. *International journal of hydrogen energy*, 43(11), 5620–5636.

As the Chief Subject Specialist in the Laboratory for analytical Services in the Focus Area Chemical Resource Beneficiation at the North West University (Potchefstroom Campus), I was responsible for 2D-GC-MS-TOF data acquisition.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Potchefstroom on 26 day of March 2021

Signature:  _____

Statement of consent: Ms Pumeza Gqogqa

To whom it may concern

I, PUMEZA GQOGQA, hereby give PHILLIMON MOKANNE MODISHA consent to use the publication listed below, of which I am co-author, in the thesis entitled "Evaluation of perhydro-dibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production". The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Modisha, P., Gqogqa, P., Garidzirai, R., Ouma, C. N., & Bessarabov, D. (2019). Evaluation of catalyst activity for release of hydrogen from liquid organic hydrogen carriers. *International Journal of Hydrogen Energy*, 44(39), 21926–21935.

As a former researcher of MINTEK located in Randburg South Africa, I was responsible for catalyst characterization by BET methods (data acquisition only).

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at Boskop on 06 day of May 2021

Signature:  _____

Statement of consent: Dr Cecil Moro Ouma

To whom it may concern

I, CECIL MORO OUMA, hereby give PHILLIMON MOKANNE MODISHA consent to use the publication listed below, of which I am co-author, in the thesis entitled "Evaluation of perhydro-dibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production". The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa:

1. Modisha, P., Ouma, C. N., Garidzirai, R., Wasserscheid, P., & Bessarabov, D. (2019). The prospect of hydrogen storage using liquid organic hydrogen carriers. *Energy & fuels*, 33(4), 2778–2796.
2. Modisha, P., Gqogqa, P., Garidzirai, R., Ouma, C. N., & Bessarabov, D. (2019). Evaluation of catalyst activity for release of hydrogen from liquid organic hydrogen carriers. *International Journal of Hydrogen Energy*, 44(39), 21926–21935.

As the Postdoctoral researcher of HySA Infrastructure Center of Competence located at North West University (Potchefstroom Campus), I was responsible for manuscript editing, providing modelling expertise for this project.

This statement satisfies Rule 5.4.2.8 and Rule 5.4.2.9 of the General Academic Rules 2015 of the North-West University.

Signed at POTCHEFSTROOM on 29th day of April 2021

Signature: 

APPENDIX D: RESEARCH ETHICS



Private Bag X1290, Potchefstroom
South Africa 2520

North-West University Engineering Research
Ethics Committee (NWU-ENG-REC)

Tel: 018 299-2645
Email: ENG-REC@nwu.ac.za

9/5/2019

RESEARCH ETHICS COMMITTEE LETTER OF DECISION: NO RISK

Based on the review by the North-West University Engineering Research Ethics Committee (NWU-ENG-REC) on 8/23/2019, the NWU-ENG-REC hereby clears your study as a No risk study. This implies that the NWU-ENG-REC grants its permission that, provided the general conditions specified below are met, the study may be initiated, using the ethics number below.

Study title:			
Evaluation of perhydrodibenzyltoluene dehydrogenation parameters and durability using noble metal catalysts for hydrogen production			
Principal Investigator/Study Supervisor/Researcher: DG Bessarabov			
Student: Phillimon Mokanne Modisha (25816268@nwu.ac.za)			
Ethics number:	NWU-01678-19-A1		
	Institution	Study Number	Year
Status: S = Submission; R = Re-Submission; P = Provisional Authorisation; A = Authorisation			
Application Type: Single	Risk: No		
Commencement date: 8/23/2019			

General conditions:

The following general terms and conditions will apply:

- The commencement date indicates the first date that the study may be started.
- In the interest of ethical responsibility, the NWU-ENG-REC reserves the right to:
 - request access to any information or data at any time during the course or after completion of the study;
 - to ask further questions, seek additional information, require further modification or monitor the conduct of your research;
 - withdraw or postpone clearance if:
 - any unethical principles or practices of the study are revealed or suspected;
 - it becomes apparent that any relevant information was withheld from the NWU-ENG-REC or that information has been false or misrepresented;
 - submission of the required amendments, or reporting of adverse events or incidents was not done in a timely manner and accurately; and/or
 - new institutional rules, national legislation or international conventions deem it necessary.
- NWU-ENG-REC can be contacted for further information via ENG-REC@nwu.ac.za or 018 299 2645

The NWU-ENG-REC would like to remain at your service and wishes you well with your study. Please do not hesitate to contact the NWU-ENG-REC for any further enquiries or requests for assistance.

Yours sincerely,

A handwritten signature in cursive script, reading "R. Coetzee".

Dr Rojanette Coetzee
Chairperson NWU-ENG-REC

Current details: (25767984) \NWUNextCloud\ENG-REC\Letters sent\([Date])9.1.5.4.3_NWU-ENG-REC_REC_LOD_NR_[student surname_name]

File Reference: 9.1.5.4.3