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### **Analysis of Liquid Organic Hydrogen Carrier Systems**

Properties of liquid organic hydrogen carriers, operation conditions and catalytic materials employed

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#### **<ABSTRACT>**

Liquid organic hydrogen carriers (LOHCs) provide attractive opportunities for hydrogen storage and transportation. In this study, a detailed examination of the most prominent LOHCs is performed, with a focus on their properties and scope for successful process implementation, as well as catalytic materials used for the hydrogenation and dehydrogenation steps. Different properties of each potential LOHC offer significant flexibility within the technology, allowing bespoke hydrogen storage and transportation solutions to be provided. Among different LOHC systems, dibenzyltoluene/perhydro-dibenzyltoluene has been identified as one of the most promising candidates for future deployment in commercial LOHC-based hydrogen

storage and transport settings, based on its physical and toxicological properties, process conditions requirements, availability and its moderate cost. PGM-based catalysts have been proven to catalyse both the hydrogenation and dehydrogenation steps for various LOHC systems, though base metal catalysts might have a potential for the technology.

## 1. Introduction

The Liquid Organic Hydrogen Carrier (LOHC) technology could be an attractive solution for storing and transporting green hydrogen, facilitating the transition to the hydrogen economy.<sup>1-16</sup> To better assess the implementation potential of the technology, it is necessary to review the most promising LOHC candidates, their respective catalysts, and system operating conditions in further detail.

Early investigations into the LOHC technology were conducted in the 1980s and were focussed around using benzene/cyclohexane or toluene/methylcyclohexane systems.<sup>2, 17-20</sup> Such systems were chosen for their high energy storage capacities and thus were predicted to allow the development of an efficient technology.<sup>10</sup> Interestingly, even at the very outset of these experiments, the efficiency of the technology was evaluated in a combined scheme with water electrolysis.<sup>17</sup> In terms of toxicity, a toluene/methylcyclohexane system was considered preferable, but the benzene/cyclohexane system was also studied further; in 2000 it was reported that 100% conversion of cyclohexane to benzene could be achieved at 175 °C if a palladium membrane reactor was used.<sup>17</sup> In the time since, numerous LOHC molecules have been investigated and assessed in terms of their techno-economic and environmental

impacts, with several carriers being noted to have a great potential for the LOHC technology.

Once established that a benzene/cyclohexane system facilitated the storage of hydrogen, substitutes to the known carcinogen, benzene, have been sought to reduce the hazards associated with the technology and facilitate its deployment (**Table 1**). In addition, alternative systems which reduce the thermodynamic limitations associated with benzene (i.e., high temperature requirement for cyclohexane dehydrogenation) have been studied.<sup>21</sup> This is important, given high temperatures increase the energy intensity, and thus the total costs of the LOHC technology.

A very common alternative to benzene is *N*-ethylcarbazole and more generally, *N*-containing aromatic heterocycles.<sup>2</sup> This class of compounds is recognised for their lower dehydrogenation enthalpy when compared against other LOHCs. For example, the dehydrogenation enthalpy of perhydro-*N*-ethylcarbazole (53.2 kJ/mol H<sub>2</sub>) is significantly lower than that of methylcyclohexane (68.3 kJ/mol H<sub>2</sub>), and hence hydrogen release from perhydro-*N*-ethylcarbazole is possible at lower temperatures.<sup>22</sup> This reduces energy costs and increases system efficiency. However, *N*-ethylcarbazole is significantly more expensive than toluene (40.00 €/kg and 0.30 €/kg, respectively), which could hinder the large-scale commercial implementation of this particular LOHC.<sup>1-2</sup> Additionally, the solid state of the fully dehydrogenated *N*-ethylcarbazole at room temperature complicates its handling and transport and can thus require dilution, which significantly reduces the efficiency of the system.<sup>1</sup> Solidification of a carrier also diminishes the key liquid-nature advantage of using LOHCs as storage materials. As a result, several subsequent studies have since concentrated on seeking alternatives

with higher boiling points and lower melting points, ensuring the carrier remains a liquid at ambient conditions throughout the cycle. A higher boiling point of the storage/transport medium also reduces the likelihood of atmospheric pollution *via* evaporation, and inhalatory exposure to potentially hazardous vapours, as well as lowering LOHC flammability.<sup>23</sup>

The heterocycle quinaldine (with a lower melting point than *N*-ethylcarbazole) has recently gained research interest. Decahydroquinaldine (H10-QLD) is reported to require a lower minimum temperature to achieve a dehydrogenation equilibrium corresponding to 99.99% hydrogen recovery when compared to alternative LOHC candidates, such as methylcyclohexane and dibenzyltoluene.<sup>24</sup> Although a quinaldine system has an ecotoxicity approximately equivalent to diesel oil, it is less biodegradable.<sup>23</sup> Of a series of quinaldine compounds tested, only 2-methylquinoline was noted to be biodegradable: thus, a spillage of an alternative, non-biodegradable quinaldine (as is occasionally reported for fossil fuels) could persist for several years.<sup>23</sup> In this regard, traditional fossil fuels could be considered superior over LOHCs: diesel oils primarily consist of chains of linear hydrocarbons of which the majority can decompose. Yet, for the diesel fraction of more complex structures this is not the case.<sup>23</sup>

The potential of many more carriers has been assessed and reported in the literature, each focussing on a favourable property which would be beneficial for LOHC technology. For instance, amine boranes have been reported to have high gravimetric storage densities and comparable overall efficiencies to other LOHC candidates, although regeneration of such a carrier presents a challenge.<sup>21</sup> Nevertheless, amine

boranes have previously been employed as a disposable hydrogen source in fuel cell based applications.<sup>25</sup>

Nevertheless, it is evident that some LOHC systems are emerging as favourites.<sup>1-2, 26</sup> One of the most well-studied LOHC candidates is the dibenzyltoluene/perhydro-dibenzyltoluene system. A well-known and commercially available heat transfer oil, dibenzyltoluene (DBT) has a much lower melting point than *N*-ethylcarbazole and can thus be considered like a more traditional liquid fuel (such as gasoline) with the advantage of low flammability. Yet, important differences between gasoline and DBT are the higher viscosity and lower volatility of DBT. The cost of DBT (4 €/kg) is also significantly lower than *N*-ethylcarbazole (40 €/kg).<sup>1</sup> Moreover, DBT is commonly regarded to have a good thermal stability, low toxicity and reasonable hydrogen storage capacity (6.2 wt%), highlighting the potential of this compound for the LOHC technology.<sup>27-28</sup> However, possible factors impeding commercial implementation of the LOHC technology with DBT as a carrier could comprise the relatively high dehydrogenation temperature and high cost (e.g., compared to toluene).<sup>23</sup>

**TABLE I**

**Comparison of the properties for selected LOHC candidates (NEC: N-ethylcarbazole, DBT: dibenzyltoluene, NAP: naphthalene, TOL: toluene, AB: 1,2-dihydro-1,2-azaborine, n.d.: no data available).<sup>1, 6</sup>**

<b>LOHC Candidate</b>	<b>NEC H<sub>0</sub>/H<sub>12</sub></b>	<b>DBT H<sub>0</sub>/H<sub>18</sub></b>	<b>NAP H<sub>0</sub>/H<sub>10</sub></b>	<b>TOL H<sub>0</sub>/H<sub>6</sub></b>	<b>AB H<sub>0</sub>/H<sub>6</sub></b>
<b>H<sub>2</sub> wt%</b>	5.8 <sup>a</sup>	6.2	7.3 <sup>b</sup>	6.2	7.1
<b>Energy Density (kWh/L)</b>	2.5	1.9	2.2 <sup>c</sup>	1.6	2.4
<b>Cost (€/kg)</b>	40	4	0.6	0.3	n.d.
<b>Liquid Range (°C)</b>	68–270 / 20–280	-39–390 / -45–354	80–218 / -43–185	-95–111 / -127–101	-45–87 / 63–87
<b>Dehydrogenation Temperature (°C)</b>	180–270	270–310	210–300	250–450	80
<b>Hydrogenation Temperature (°C)</b>	80–180	150–200	80–160	90–150	80
<b>Reaction Enthalpy (kJ/mol<sub>H<sub>2</sub></sub>)</b>	-53.2	-65.4	-66.3	-68.3	-35.9

<b>Hazard Information</b>	-	H305	H228, H302, H351, H400, H410	H225, H304, H315, H361d, H336, H373, H412	n.d.
<b>Flash point (°C)</b>	186	212	78	4	22

(a) N-ethylcarbazole is a solid at room temperature, severely restricting dehydrogenation and thus H<sub>2</sub> wt%; (b) naphthalene is also a solid at room temperature, dilution with toluene reduces H<sub>2</sub> storage to 3.8 wt% and energy density to (c) 1.1 kWh/L.

The evaluation of each LOHC medium also requires the implicit assessment of hydrogenation and dehydrogenation catalysts. The study of the hydrogenation and dehydrogenation steps of a LOHC cycle are typically performed independently, employing different catalysts. Where the dehydrogenation and hydrogenation plants are found at different locations, this allows for optimisation of the separate reactions and catalysts. However, if the LOHC technology were to be focussed more around the on-site hydrogen storage function, rather than transportation ability, a catalyst which is suitable for both reactions would be most favourable, with the interchanging of hydrogenation and dehydrogenation reactions driven by a change in pressure and a moderate change in temperature in the same reactor.<sup>29-31</sup> Clearly, the requirement for only one catalyst and one reactor for both hydrogenation and dehydrogenation reduces the costs associated with this application.<sup>10</sup>

As the dehydrogenation process is an endothermic reaction, this part of the LOHC cycle presents greater challenges than that of hydrogenation. Thus, a greater

proportion of studies have focussed their efforts towards evaluating effective catalysts for the dehydrogenation process. Several literature sources state that the dehydrogenation process contributes significantly to the overall cost of the LOHC technology.<sup>32-33</sup> In particular, it has been suggested that improvements to catalytic performance could lower the cost of the dehydrogenation reaction by almost 40%.<sup>32</sup>

PGM-based catalysts are commonly used for hydrogenation and dehydrogenation processes of the LOHC technology.<sup>10, 34</sup> Nevertheless, Ni-based catalysts have shown promise for the use within the LOHC technology, but further catalyst development is required to address the selectivity issues. Monometallic Ni catalysts are so active in hydrogenation reactions that unwanted reactions, such as carbon-carbon cleavage, can occur.<sup>35</sup> Additionally, it has been reported that Ni-based catalysts could be problematic if employed for feedstocks comprising oxygen or nitrogen functionalities. This is because Ni catalysts are also very active in hydrogenolysis side-reactions.<sup>35</sup> For example, it has been reported that aryl ethers can be converted into arenes and alcohols without any ring hydrogenation.<sup>36</sup> This would be an extremely unfavourable reaction for the LOHC technology, as no hydrogen storage is facilitated. Such issues might be overcome by the development of bimetallic Ni-based catalytic systems. In addition to their high activity, the addition of a second metal to a Ni-based catalyst, such as NiCu on activated carbon cloth, has been suggested to suppress unfavourable side reactions (e.g., hydrogenolysis) by electronic modification of Ni. This improves selectivity and overall efficiency of the LOHC technology.<sup>37</sup> Another example of improved selectivity for the ring hydrogenation when using Ni-based catalysts, is an addition of Zn which blocks sites for C-C dissociation.<sup>38-</sup>

<sup>39</sup> The comparatively high reducibility of several bimetallic catalysts (including NiCu and NiCo), further highlights their potential for implementation within the LOHC technology.<sup>40</sup>

Although the development of novel catalysts (PGM-free or with reduced PGM content) might lower the costs associated with the LOHC technology, as well as risks associated with reliance on highly fluctuating costs of PGMs, the key to this technology is catalyst performance (space-time yield, selectivity, lifetime). This is essential to reduce energy intensity during loading and particularly unloading of the LOHCs.<sup>32-33</sup> Catalyst stability is a particular issue in the dehydrogenation step of the LOHC cycle, where reaction temperatures are typically higher than those required for the hydrogenation step.<sup>41</sup> It is expected that over time, catalyst degradation from carbonization will occur, although the exact identity of such residues remains largely unknown.<sup>42</sup> Catalyst reactivation could be achieved by implementing a regular cleaning procedure, which for noble metal catalysts often involves thermal treatment with oxidative substances (e.g., air, oxygen).<sup>42</sup> However, this process is highly dependent on the catalyst and reactor used. For 0.5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> core shell pellets exposed to dynamic DBT experiments for 3 months (dehydrogenation temperatures between 280 °C and 320 °C), major regeneration was achieved between 200 °C and 300 °C, although complete regeneration could not be attained. Oxygenates and CO<sub>2</sub> were also produced during catalyst regeneration, which were suggested to contribute to catalyst restructuring.<sup>42</sup> The study of Oh *et al.* highlighted that a Pd catalyst supported on carbon-coated alumina was more stable than Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/C catalysts as the carbon-coated alumina support prevented the sintering of Pd nanoparticles into larger

particles.<sup>43</sup> Here, perhydro-2-(n-methylbenzyl)pyridine was deployed as the LOHC.<sup>43</sup> However, most literature studies discuss the stability of the catalyst over only a limited number of hydrogenation/dehydrogenation cycles. Thus, further work is required to assess catalyst stability over longer time periods.

## 2. Analysis of Liquid Organic Hydrogen Carrier Systems

### 2.1 Benzene/Cyclohexane

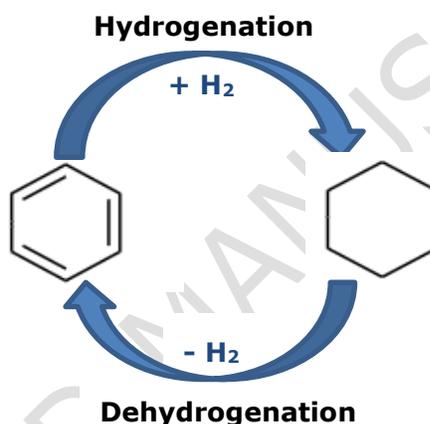


Fig.1. Benzene/Cyclohexane LOHC system.

Although benzene, which is the hydrogen-lean form of the benzene/cyclohexane LOHC system (**Figure 1**), is a known carcinogen (the most significant drawback of this specific system), several studies have been conducted into the properties of effective hydrogenation/dehydrogenation catalysts for this model feedstock.

Hydrogenation is generally accepted to occur *via* associative adsorption of benzene onto the catalytic surface. During the hydrogenation step, it is believed the carrier molecules are arranged as  $\pi$ -complexes and are hydrogenated in a stepwise

fashion, through a series of cycloolefins (**Figure 2**).<sup>44</sup> This is supported with the detection of cyclohexene.<sup>44</sup>

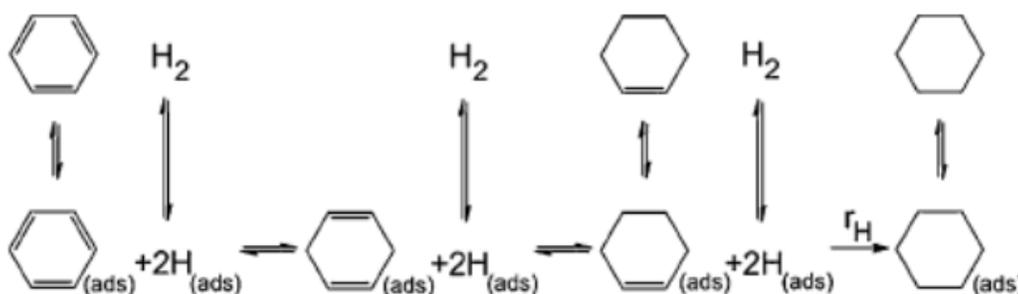


Fig. 2. The stepwise hydrogenation of benzene.<sup>44</sup>

Early research concluded that monometallic Fe-catalysts with body-centred structures were essentially inactive for the hydrogenation of benzene, while the activity of a mixed Fe-Co catalyst decreased with increasing Fe content.<sup>45</sup> Since Co and Ni, both with face-centred cubic structures, were found to be active for the reaction, it was assumed the body-centred structure of Fe was responsible for its inactivity.<sup>45</sup> However, a monometallic, face-centred Cu catalyst was deemed to be completely inactive unless in the presence of a suitable promoter, such as Ni.<sup>45</sup> The inactivity of the Cu catalyst has since been attributed to difficulties in obtaining a suitably high dispersion on the catalyst support, while the mechanism of the promotional effect observed with the addition of Ni remains a topic for debate.<sup>35</sup> Several hypotheses for this have arisen, including a changing in Cu crystal structure, or an alteration in surface concentration as a consequence of Ni collection.<sup>45</sup> Interestingly, even in the very early studies, it was clear that Pd has a high activity for the reaction, but only on the condition that the surface area was sufficiently high, while the conversion is also reported to be catalysed by rhodium (I) complexes.<sup>45-46</sup>

Ni-based catalysts are frequently considered for ring-hydrogenation reactions, with several detailed studies revealing key information for future catalyst development. For example, the hydrogenation of benzene using Ni catalysts has been suggested to be a structure insensitive reaction, while an unexpectedly low activity at low Ni loadings (less than 5 wt%) is the result of a nickel aluminate spinel formation, when an alumina support is used.<sup>47</sup> More commonly however, this spinel structure is formed at high reaction temperatures. Although expected, these findings are important, signifying not only the choice of metal, but also the properties of the support (such as acidity, interaction with the metal) and reaction conditions play a role in determining catalytic performance. The move from PGM-based catalysts to base metal catalysts could also lower the cost associated with the LOHC technology as well as reliance on highly fluctuating costs of PGMs.<sup>48-49</sup> This is provided that comparable or even improved catalytic performance can be achieved.

Ni is also widely referenced for its activity in catalysing the dehydrogenation reaction of cyclohexane. Given the low boiling point of cyclohexane (81 °C), this reaction is often performed in the gaseous phase. The studies have shown that when using a cyclohexane feedstock, a bimetallic Ni/Pt combination (20 wt% Ni and 0.5 wt% Pt) can improve catalytic dehydrogenation activity 60-fold when compared to using a monometallic Pt catalyst (0.5 wt% Pt on activated carbon cloth), or 1.5-fold when compared to a monometallic Ni catalyst (20 wt% Ni on activated carbon cloth).<sup>34</sup> In addition, selectivity in the dehydrogenation reaction was improved using various monometallic Ni catalysts with the addition of Pt.<sup>50</sup> For these cyclohexane

dehydrogenation studies, a spray-pulsed reactor was used at a temperature of 300 °C.<sup>34</sup>

The concept of improved catalytic performance through the use of bimetallic combinations has also been reported for Ag-based catalysts, employed for the benzene hydrogenation reaction.<sup>34</sup> Here, the same spray-pulse reactor and reaction temperature (300 °C) as discussed for the Pt catalyst above was used. For the most significant catalytic enhancement, it was concluded that the secondary promoter must be classified as a platinum group metal.<sup>34</sup> As an example, the hydrogen production rate was doubled when using a Pt-promoted Ag catalyst on activated carbon cloth (1 wt% Pt + 10 wt% Ag) compared to the non-promoted 10 wt% Ag equivalent.<sup>34</sup> This was suggested to be the result of a synergistic effect between the two metals for breaking C-H bonds, high hydrogen reverse-spillover, or hydrogen recombination abilities of the catalyst.<sup>51</sup> The improvement in catalytic activity of the Ag catalysts promoted with 1 wt% of a PGM were found to follow the trend: Pt > Rh > Pd, although catalyst stability improved in the order Pt > Pd > Rh.<sup>51</sup> The study did not comment on expected lifetime of the catalysts, highlighting the need for further research regarding key performance indicators (activity, selectivity, lifetime).

## 2.2 Toluene/Methylcyclohexane

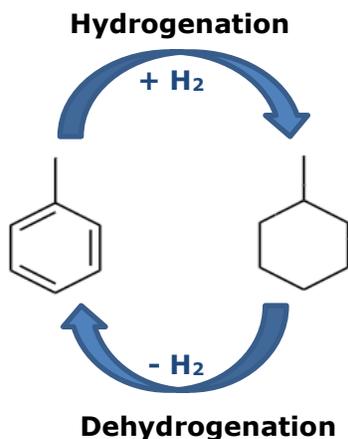


Fig. 3. Toluene/methylcyclohexane LOHC system.

To catalyse the hydrogenation of toluene to methylcyclohexane, Pd-based catalysts have been reported to be effective. For example, in one hour a 10 wt% Pd/C catalyst can achieve a 90% toluene conversion at 80 °C and 15 bar hydrogen pressure, when the hydrogenation reaction is performed in a batch reactor.<sup>52</sup> Interestingly, when this Pd/C catalyst was coated with a liquid coordination complex (LCC), the conversion of toluene increased to 99.9%, under otherwise identical reaction conditions.<sup>52</sup> Liquid coordination complexes are described as 'ionic liquid-like' Lewis acid species, with their equilibrium composition containing cations, anions and neutral components.<sup>52</sup> In this experiment, the LCC was synthesised from AlCl<sub>3</sub> and urea.<sup>52</sup> It was concluded that only a thin film of the liquid (ionic liquid coating at 13 wt%) was required to improve the catalytic performance; when larger quantities were applied to the catalyst a decrease in activity was observed as a result of pore blocking and mass diffusion limitations.<sup>52</sup>

As for benzene hydrogenation, Pt-based catalysts have also been found to be successful in catalysing the hydrogenation of toluene to methylcyclohexane. For

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example, a 0.3 wt% Pt catalyst supported on zeolite CBV-780 (Si/Al ratio of 40), is capable of achieving full hydrogenation at just 120 °C, with a hydrogen pressure of 30 bar.<sup>53</sup> The activity of the catalyst notably decreased when alloyed with Pd. A trimetallic combination of Ni, Co and Mo on a zeolite support was also found to effectively catalyse this hydrogenation reaction.<sup>54</sup> In a batch reactor, with a reaction temperature of 200 °C and a hydrogen pressure of 20 bar, it was found that a HY support (Si/Al ratio of 5.1) allowed for superior catalytic activity after 30 minutes on-stream, when compared to using mordenite, HY (Si/Al ratio of 80) or ZSM-5 alternatives. In explanation, the authors propose the larger pore volume and pore diameter of the HY support (Si/Al ratio of 5.1) reduces pore diffusion limitations.<sup>54</sup>

Moreover, monometallic, Ni-based catalysts are effective for toluene hydrogenation.<sup>55</sup> For example, one study highlighted the increase in catalytic activity observed for a 20 wt% Ni catalyst, compared to a 5 wt% Ni catalyst, both supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>55</sup> Since it is generally accepted that an increase in the number of metallic active sites increases catalytic activity, this result is unsurprising.<sup>55</sup> However, it was also found that employing supports of different alumina phases ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>) has different effects on catalytic activity when different Ni loadings are used. For instance, a significantly higher catalytic activity was reported for a 5 wt% Ni/ $\kappa$ -Al<sub>2</sub>O<sub>3</sub> catalyst than for a 5 wt% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (toluene conversions of 98% and 28%, respectively), under the same reaction conditions.<sup>55</sup> Yet at higher Ni loadings an opposite trend was observed: a 20 wt% Ni/ $\kappa$ -Al<sub>2</sub>O<sub>3</sub> catalyst resulted in a lower toluene conversion than that of a 20 wt% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, although the difference in activities between the catalysts is smaller at this higher Ni loading.<sup>55</sup> In explanation, it

was concluded that changes in reducibility of the surface Ni sites has a larger effect on the observed activity than simply the number of active sites present.<sup>55</sup> These reactions were performed in a plug-flow reactor, using 0.1 g of catalyst.<sup>55</sup>

Ni/kaolinite catalysts have also been considered for the hydrogenation of toluene.<sup>56</sup> Using a flow-type system at ambient pressures, it was found modification of the catalyst with a small amount (2 wt%) of either K or Zn ( $\text{KNO}_3$  or  $\text{Zn}(\text{NO}_3)_2$ ) increased catalytic activity, which was attributed to a decrease in interaction strength between the Ni and kaolinite. Yet, a larger modification (3 wt% – 7 wt%) resulted in a significant decrease in activity.<sup>56</sup> This was proposed to be a result of K covering the Ni active sites, or an unfavourable Zn-Ni interaction.<sup>56</sup>

The dehydrogenation reaction (methylcyclohexane to toluene, **Figure 3**) typically employs a Pt or Ni-based catalyst, supported on aluminium oxide.<sup>1</sup> Reaction temperatures for such catalysts often vary between 350 °C and 450 °C (with a general increase in temperature increasing the conversion of methylcyclohexane to toluene before equilibrium is reached).<sup>57-58</sup> Another study highlighted the influence of process conditions on increasing conversion of methylcyclohexane and lowering operating temperatures by using efficient Pd or Pd-alloy membranes in catalytic membrane reactors. Such reactors combine the catalytic dehydrogenation reaction with the extraction of hydrogen in a single unit.<sup>58</sup>

Interestingly, a K-Pt/ $\text{Al}_2\text{O}_3$  catalyst was reported to achieve a hydrogen yield of 95%, when employed at 320 °C in a fixed-bed reactor, which is slightly above the typical yield range given above.<sup>1</sup> Moreover, an excellent selectivity (>99.9%) was reported for this reaction.<sup>1</sup> A Raney-Ni catalyst has also been reported to achieve a

65% yield after 30 minutes on-stream, under multiphase reaction conditions.<sup>59</sup> Although this reaction was performed at the lower reaction temperature of 250 °C, the Raney-Ni catalyst is not a suitable candidate to catalyse the reactions of the LOHC technology.<sup>1</sup> This is in view of the accompanying isomerization and disproportionation reactions which would ultimately necessitate the need for more frequent LOHC replacement.<sup>1</sup> It should be noted that from a thermodynamic viewpoint, the dehydrogenation of methylcyclohexane, like all LOHC candidates, should be performed at the lowest possible pressure as this facilitates the use of the lowest possible temperature for full conversion to toluene.<sup>34</sup> However, in practice, it has been found that such conditions may not be compatible with the catalyst, potentially resulting in side reactions and catalyst deactivation.<sup>34</sup>

As has already been stated, the catalyst support materials can be modified to increase catalytic performance.<sup>34</sup> For the toluene/methylcyclohexane system, it was concluded that the hybrid composite support Al<sub>2</sub>O<sub>3</sub> – TiO<sub>2</sub> was responsible for a huge increase in catalytic dehydrogenation activity, when compared to Al<sub>2</sub>O<sub>3</sub> (99% and 16.5% methylcyclohexane conversion, respectively, where Ni is the active site).<sup>34</sup> In addition, properties of the perovskite La<sub>0.7</sub>Y<sub>0.3</sub>NiO<sub>3</sub>, and metal oxides including La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and MnO<sub>2</sub> have been evaluated in terms of their suitability as catalyst supports for the dehydrogenation of methylcyclohexane.<sup>34, 60</sup> Most notably, it was found the hydrogen production rate more than doubled when comparing the Pt/La<sub>2</sub>O<sub>3</sub> and Pt/La<sub>0.7</sub>Y<sub>0.3</sub>NiO<sub>3</sub> catalysts (21.1 mmol/g<sub>met</sub>/min and 45 mmol/g<sub>met</sub>/min, respectively).<sup>60</sup> These reactions were conducted in a spray-pulsed reactor.

This particular LOHC system has also been studied alongside a palladium membrane reactor, which allows for purification of the hydrogen released from the LOHC.<sup>34</sup> Contaminants of the hydrogen can include CO, CO<sub>2</sub>, methane and cyclic hydrocarbons and have been reported to be present in quantities between 100 ppm and 1000 ppm, depending upon the operating conditions of the LOHC system.<sup>61</sup> The exact origins of the impurities remain unknown, but it is believed a combination of atmospheric oxygen and residual moisture in the LOHC is responsible for the formation of CO and CO<sub>2</sub>, while partial decomposition of the LOHC at high reaction temperatures, or contaminants from the production of the LOHC, can explain the hydrocarbon presence.<sup>61</sup> The quality of the hydrogen released depends upon the intended application, for example several fuel cells have specific regulations on compatible hydrogen purity.<sup>61</sup> Despite this, only a few examples of hydrogen purification processes exist in the literature, most of which employ palladium membranes. This is not surprising, considering palladium has a high hydrogen solubility, permitting effective separation of hydrogen and contaminants at high temperatures (typically above 300 °C).<sup>61</sup>

A palladium membrane reactor has been reported to have a dual functionality, acting both as a dehydrogenation reactor and a hydrogen purification system.<sup>34</sup> The dehydrogenation of methylcyclohexane using such a reactor and a 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, permitted the use of a 20 °C decrease in temperature than would otherwise be required to achieve the same conversion (70%) without employing the membrane (225 °C and 245 °C, respectively).<sup>34</sup> In addition, the Pt catalyst demonstrated good stability and selectivity within the temperature range 150 °C – 325 °C, with no

significant deactivation for approximately 600 h time on stream.<sup>62</sup> A 5  $\mu\text{m}$  PdAg-membrane, coupled with a microstructured system, has also been reported to effectively purify the hydrogen released.<sup>61</sup>

### 2.3 Naphthalene/Decalin

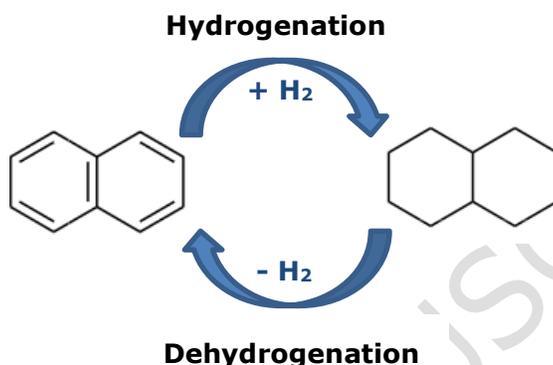


Fig. 4. Naphthalene/decalin LOHC system.

Boasting a high theoretical hydrogen storage capacity of up to 7.4 wt%, a naphthalene/decalin LOHC system has been considered (**Figure 4**). However, in practice, dilution with a solvent such as toluene is necessary to keep the LOHC cycle within the liquid phase (melting point of naphthalene: 80 °C). This lowers the overall hydrogen capacity to 3.8 wt%.<sup>1</sup> For this reason, the naphthalene/decalin system is less widely studied than other possible carriers, although important learnings have been gained, which can be transferred to other LOHC systems. It is worth noting that decalin exists as structural isomers, and thus an approximately equimolar mixture of the *cis*- and *trans*- isomers are produced upon hydrogenation of naphthalene, despite the thermodynamic favourability of the *trans*- isomer.<sup>1</sup> The exact *cis*- : *trans*- ratio is naturally dependent on reaction conditions, in addition to the catalyst itself.<sup>1</sup>

Much like other LOHC systems, Pt-based catalysts have also been the focus of most studies on the hydrogenation of naphthalene.<sup>1, 63</sup> Yet, in contrast to other systems discussed, an Al-MCM-41 (aluminium Mobil Composition of Matter) support was investigated.<sup>63</sup> Harsher reaction conditions (temperatures of 300 °C and pressures of 69 bar) than employed for alternative systems were required to achieve full hydrogenation to decalin in 150 min, in a batch reactor.<sup>1</sup> It was found that the reaction temperature could be lowered to 200 °C under the same reaction pressure, but this imposed the requirement of a drastically increased reaction time (480 min).<sup>1</sup> Generally, conclusions from this study are similar to those of others systems: hydrogenation activity and selectivity are both strongly dependent on support properties.<sup>63</sup>

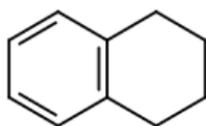


Fig. 5. Structure of tetralin, a probable naphthalene dehydrogenation intermediate.

Although the hydrogenation process presents its relative challenges, it is the dehydrogenation step which confirms the incompatibility of this system with the LOHC technology. For instance, this step is likely to produce intermediates including tetralin (**Figure 5**). Although tetralin itself can be dehydrogenated and become part of the LOHC process, it is unlikely that no tetralin molecules will remain following the dehydrogenation reaction. As tetralin is still partially hydrogenated, the hydrogen storage capacity of the LOHC is lowered in subsequent cycles. Thus, regular replacement of the carrier material would be required to ensure a constant hydrogen storage capacity, which is sufficiently high as to ensure economic viability, could be

achieved.<sup>34</sup> This would increase the operating expenditure of the technology (more LOHC required) in the case of naphthalene. In light of these challenges, a pilot scale demonstration is yet to be achieved.<sup>1</sup>

Research into the dehydrogenation reaction of naphthalene has, however, produced some interesting results. Typically, when employing a Pt catalyst supported on carbon at conditions slightly milder than those used for the hydrogenation reaction (280 °C for 150 min at atmospheric pressure), almost full conversion of decalin to naphthalene can be achieved in a batch reactor system. Furthermore, adding Re to the catalyst (Pt-Re/C) can decrease the reaction time from 150 min to 120 min under otherwise identical conditions.<sup>1, 64</sup>

A 3 wt% Pt/C catalyst was also used to investigate the effect of varying the catalyst preparation method on catalytic performance for the dehydrogenation of decalin.<sup>34</sup> It was found that advanced methods of preparation, including ion-exchange and polyol-assisted synthesis (in which ethylene glycol was used as a solvent and reducing agent), resulted in a greater dispersion of Pt (19.6% and 14%, respectively) than the more conventional precipitation and impregnation methods (10% and 5.4% Pt dispersion, respectively).<sup>34, 65</sup> Increasing the Pt dispersion increases the surface area of the metal over which the reaction can occur, consequently resulting in a greater rate of hydrogen release from decalin.<sup>34, 65</sup> Again, optimisation of the support must also be considered. Several carbon-based possibilities including nanofibers, carbon black, carbon xerogel and ordered mesoporous carbon have been evaluated, with the high surface area of ordered mesoporous carbon believed to be responsible for demonstrating the highest activity for the dehydrogenation of decalin.<sup>34</sup> Yet, over

longer operation times catalyst deactivation was observed as a result of pore blockages with the bulky LOHC feedstock.<sup>34</sup> Thus, it can be argued that as carbon black has wider pores than the ordered mesoporous carbon, this would be the most suitable support, despite a lower activity. These experiments were performed at 260 °C, in a batch reactor.<sup>34</sup>

Catalytic activity, in addition to selectivity, has also been reported to be improved with the addition of Sn to Pt/activated carbon.<sup>66</sup> The effect is two-fold: (1) the electronic modification of Pt by Sn prevents the cleavage of C-C bonds on the catalyst surface, facilitating the adsorption and desorption of reactant and product molecules; (2) the addition of Sn as a catalytic promoter improves catalyst stability by preventing the sintering and agglomeration of Pt at high temperatures.<sup>34</sup>

#### 2.4 *N*-Ethylcarbazole/Perhydro-*N*-Ethylcarbazole

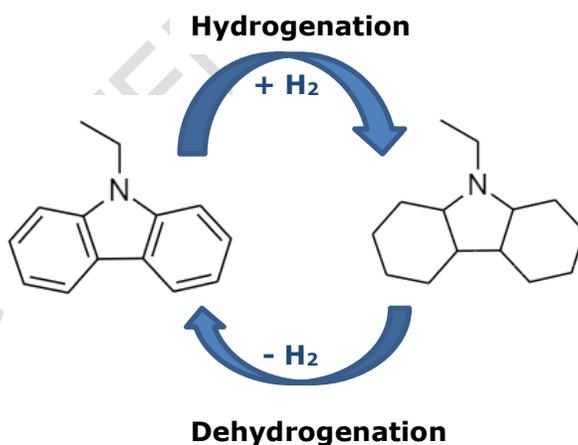


Fig. 6. *N*-ethylcarbazole/perhydro-*N*-ethylcarbazole LOHC system.

The most significant advantage of this LOHC system is the relatively low energy required for dehydrogenation (53.2 kJ/mol H<sub>2</sub>, **Table 1**).<sup>1</sup> This lower reaction enthalpy

facilitates a lower temperature for the dehydrogenation reaction and consequently improves the overall efficiency of the system. As such, interest into the potential applications of NEC has significantly grown in recent years, culminating in its use as a feedstock for the LOHC technology. However, like other LOHC candidates discussed thus far, *N*-ethylcarbazole (NEC) also possesses unfavourable properties for its employment within LOHC technology. Arguably the most significant of these is the solid nature of NEC at ambient temperatures. To ensure the key liquid property of the LOHC technology is not lost, employing NEC would thus require NEC dilution.<sup>1</sup> This reduces the efficiency of the LOHC technology.<sup>1</sup> Moreover, NEC is significantly more expensive than alternative LOHCs, such as toluene (40.00 €/kg and 0.30 €/kg, respectively).<sup>1</sup>

The dehydrogenation reaction is again most commonly performed with PGM-based catalysts, particularly Pd/Al<sub>2</sub>O<sub>3</sub> or Pt/Al<sub>2</sub>O<sub>3</sub>, at metal loadings of around 5 wt%. These catalysts have been reported to have the highest catalytic activities, when compared to Ru and Rh equivalents.<sup>67</sup> Specifically, catalyst dehydrogenation activity follows the trend Pd > Pt > Ru > Rh under atmospheric pressure and at 180 °C.<sup>67</sup> Full dehydrogenation to NEC was observed for Pd and Pt catalysts, after reaction times of 240 min and 300 min, respectively, while employment of a Ru catalyst over the same time frame produced a mixture of both the fully dehydrogenated NEC (71.28%) and the partially hydrogenated species, 4H-NEC (28.54%).<sup>67</sup> Using the catalyst with the lowest dehydrogenation activity (Rh/Al<sub>2</sub>O<sub>3</sub>), even less of the fully dehydrogenated NEC is obtained (10.64%).<sup>67</sup> Important to note, all reactions are carried out below 270 °C.

Beyond this temperature, NEC becomes susceptible to dealkylation reactions, producing the by-product carbazole.<sup>1, 68</sup>

Like the dehydrogenation reaction, the hydrogenation of NEC is frequently catalysed by a PGM. However, given the comparative ease of the hydrogenation reaction (in comparison to the dehydrogenation reaction), a Pd or Ru-based catalyst is more frequently employed than for the dehydrogenation reaction. For example, full hydrogen loading onto NEC has been achieved in 3 h at 150 °C and 50 bar hydrogen pressure using a 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst in a batch reactor.<sup>68</sup> The molar ratio of LOHC:Ru used in these experiments was 400:1.<sup>68</sup> The catalyst Pd<sub>2</sub>Ru on silicon carbonitride has also been reported to successfully catalyse the hydrogenation of NEC.<sup>69</sup> In comparison to the 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst discussed previously, a milder reaction temperature (110 °C) and hydrogen pressure (20 bar) can be employed.<sup>69</sup> However, a significantly longer reaction time (36 h) is required for full hydrogenation of NEC to perhydro-NEC, and a greater amount of active metal is also required, compared to the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst described above (0.52 mol% and 0.25 mol%, respectively).<sup>68-69</sup> The same Pd<sub>2</sub>Ru@SiCN catalyst has also been reported to successfully catalyse the dehydrogenation of perhydro-NEC at 180 °C in a reaction time of 7 h, in a batch reactor.<sup>69</sup>

More recently, full hydrogenation has also been attained using Ru supported on a rare earth hydride catalyst, Ru/YH<sub>3</sub>.<sup>70</sup> Reporting both the mildest conditions (100 °C, 10 bar) and the highest catalytic activity for the hydrogenation of NEC to date, it is clear that such rare earth supported catalysts have potential for LOHC applications.<sup>70</sup> This was highlighted by concluding the high stereoselectivity of the Ru/YH<sub>3</sub> catalyst for

the all-*cis* product would be advantageous for any subsequent dehydrogenation reactions, since the *cis*- product is more easily dehydrogenated than the *trans*-equivalent. In explanation, the authors propose the *cis*- product is less sterically hindered on the catalyst surface.<sup>70</sup> However, despite an excellent catalytic performance and satisfactory stability, a high hydrogen pressure is required to achieve high selectivity.<sup>70</sup> Manufacturing costs, handling and scale-up considerations were not discussed and may present challenges for such a material.

The Ru/YH<sub>3</sub> catalyst has also been reported to effectively catalyse the hydrogenation of another *N*-heterocycle: 2-methylindole, which has been suggested as a suitable LOHC candidate.<sup>70-71</sup> However, much like NEC, 2-methylindole is a solid at ambient temperatures and possesses a slightly lower hydrogen storage capacity than NEC (5.7 wt% and 5.8 wt%, respectively).<sup>71</sup>

## 2.5 Dibenzyltoluene/Perhydro-dibenzyltoluene

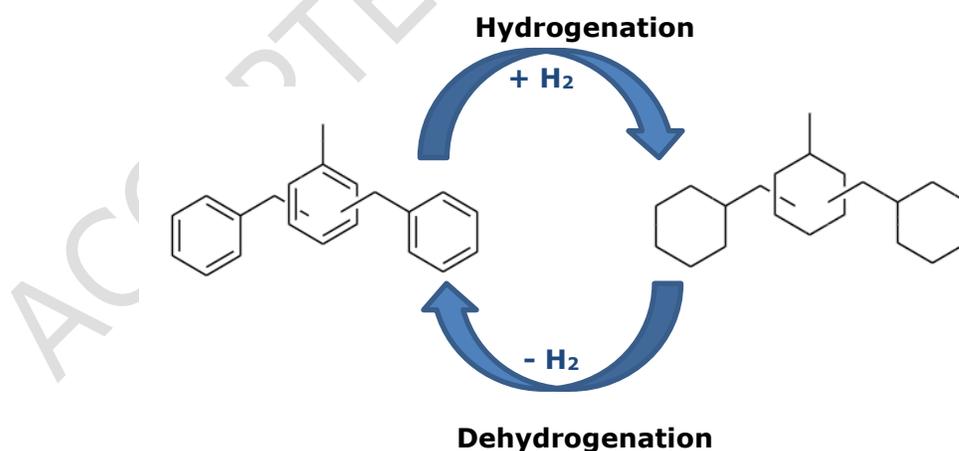


Fig. 7. Dibenzyltoluene/Perhydro-Dibenzyltoluene LOHC system.

To achieve an effective and efficient hydrogen storage and transportation system, the choice of LOHC is of critical importance. For commercial implementation of the LOHC technology, dibenzyltoluene (DBT) can be seen as the most suitable candidate, considering its key advantages: relatively low-cost, low toxicity and high hydrogen storage capacity (6.2 wt%, **Table 1**). In addition, DBT is already mass produced as it is used as a heat transfer agent. As a result, there is a vast exploration of DBT as a potential carrier molecule in the literature.

Several catalysts have been evaluated for the hydrogenation and dehydrogenation reactions of the dibenzyltoluene/perhydro-dibenzyltoluene system (**Figure 7**). Much like NEC, DBT hydrogenation is also typically catalysed with an alumina-supported PGM, namely Pt or Ru.<sup>1</sup> As an example, in a batch reaction, a Ru/Al<sub>2</sub>O<sub>3</sub> catalyst can achieve full hydrogen loading of DBT in 4 h at 150 °C with a 50 bar hydrogen pressure, which is longer than that of NEC (3 h) under the same conditions.<sup>68</sup>

The more in-depth studies on this feedstock have also revealed that the catalytic hydrogen-loading does not have to be performed with pure hydrogen. As DBT hydrogenation is selective, and provided the catalyst is not negatively affected by the presence of other components, a mixed gas stream (e.g., including methane, CO<sub>2</sub>) can be used.<sup>34</sup> From an industrial perspective this is very attractive, enabling otherwise low-value hydrogen present in waste gas streams, from processes including reforming and gasification reactions, to be stored and transported. The first example of such a process was reported in 2017 by Dürr *et al.*, in which a mixture of hydrogen and methane from the decomposition of methane (obtained from off-shore drilling) was

fed directly to the hydrogenation unit containing the DBT feedstock.<sup>72</sup> Separation of the loaded (hydrogenated) LOHC and gaseous methane can then be facilitated. It has also been reported that the presence of methane does not negatively affect the hydrogenation or dehydrogenation of DBT/perhydro-DBT.<sup>30</sup> In contrast, methane was remarkably found to slightly improve the hydrogenation rate, postulated to be a result of a lower DBT viscosity and thus improved hydrogen mass transport.<sup>34</sup>

In a similar vein, hydrogenation of DBT has been investigated using a hydrogen/CO<sub>2</sub> stream (up to 30% CO<sub>2</sub>).<sup>73</sup> However, with such a hydrogenating mixture, both methanation (CO<sub>2</sub> to methane) and reverse water gas shift (CO<sub>2</sub> to CO) processes were found to occur, with the extent of such side-reactions being strongly dependent on the catalyst employed.<sup>34</sup> Even with the most promising Pd/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, the degree of hydrogenation in a batch reactor reached only 0.8 and required elevated temperatures (210 °C and 270 °C for the Rh and Pd catalysts, respectively) when compared to using a pure hydrogen stream.<sup>34</sup> For the Rh catalyst, moderate methane formation (methane/CO<sub>2</sub> ratio of less than 0.1) can be achieved at temperatures between 120 °C and 150 °C (Rh/Al<sub>2</sub>O<sub>3</sub>), while the Pd catalyst showed a lower selectivity for methane formation, with a methane/CO<sub>2</sub> ratio of less than 0.1 between 120 °C and 270 °C (Pd/Al<sub>2</sub>O<sub>3</sub>).<sup>34, 73</sup>

Despite the frequent employment of Pt and Ru catalysts with pure hydrogen streams, these catalysts were found to be ineffective for the selective hydrogenation of DBT using a hydrogen/CO<sub>2</sub> stream.<sup>34</sup> Their respective unsuitability was concluded to be a result of Pt catalyst poisoning from the reduction product CO formed *via* reverse water gas shift of CO<sub>2</sub> and facilitation of CO<sub>2</sub> methanation by Ru.

Pd-based catalysts have low activities for the dehydrogenation reaction of perhydro-dibenzyltoluene, and have thus been identified as catalysts to avoid.<sup>34</sup> Under the same reaction conditions (270 °C, 3.5 h, batch reactor), a stark difference in the degree of dehydrogenation between a Pd/C (5 wt%) catalyst and its Pt equivalent has been observed (16% and 55%, respectively).<sup>68</sup> In a different study, a lower metal loading has proven to be advantageous (lowering the metal content of the Pt/C catalyst to 1 wt% from 5 wt% increased the degree of dehydrogenation from 55% to 71%), while the support preference for this particular dehydrogenation reaction was found to follow C > Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>.<sup>34, 68</sup> For these experiments, the Pt/C catalysts were both supplied by Hydrogenious Technologies and used in batch reactions, in quantities of 0.15 mol% with respect to perhydro-DBT.<sup>68</sup>

Interestingly, the wider research around the use of DBT as a LOHC has included a study in which the same Pt/Al<sub>2</sub>O<sub>3</sub> (0.3 wt%) catalyst has been used for both hydrogenation and dehydrogenation reactions.<sup>34</sup> Under the same reaction temperature (291 °C), Jorschick *et al.* reported that the two reactions could be interchanged by varying the pressure between 1.05 bar (dehydrogenation) and 30 bar (hydrogenation) in a hot pressure swing reactor.<sup>30</sup> However, the use of a non-optimised catalyst for the dehydrogenation process resulted in a lengthy reaction time (20 h), when compared to the examples discussed previously. In addition, it must be noted that the productivity of the dehydrogenation (and thus catalyst activity) decreased significantly over the first cycle, before stabilising for the following 3 cycles. This was concluded to be a consequence of bulky, high boiling point by-product formation *via* thermal cracking of DBT. Such molecules, including diphenylmethane and 2,6-

dimethyldiphenylmethane, were found to increase per cycle and can be expected to block active sites of the catalyst.<sup>34, 74</sup> It has also been suggested that some of the possible by-products of the dehydrogenation reaction are unstable and thus undergo cracking during a subsequent hydrogenation reaction. Such an example would be the conversion of perhydromethylfluorene to perhydrobenzyltoluene.<sup>74</sup>

DBT exists as structural isomers and consequently, more than 24 stable intermediates can be found in a partially hydrogenated solution. These can be categorised into four main groups: dibenzyltoluene (H0-DBT), hexahydro-dibenzyltoluene (H6-DBT), dodecahydro-dibenzyltoluene (H12-DBT) and octadecahydro-dibenzyltoluene (H18-DBT).<sup>75</sup> Laboratory studies regarding selectivity would require advanced analytical detection methods. DBT conversion can be studied using ultraviolet-visible spectroscopy (i.e., the degree of ring hydrogenation, providing information about conversion levels only), but detailed studies probing catalyst selectivity would be challenging, requiring either a complex HPLC method or <sup>1</sup>H NMR analysis.<sup>29, 76-77</sup>

As such, alternative model carriers are often sought for fundamental academic studies aimed at deepening the chemical understanding of how to improve the performance of catalytic materials for the LOHC technology. In addition to being easily characterizable, the ideal carrier would have high boiling points and low melting points of both hydrogen-rich and hydrogen-lean molecules. This enables the whole cyclic process to be carried out in the liquid phase. A high melting point would result in the formation of a solid at ambient temperatures, with a dissolving process or incomplete hydrogen-unloading significantly lowering storage efficiency. Whereas a low boiling

point would require extra economic expense in gas condensation equipment. Frequently, toluene is employed as such a model compound. Given its structural similarities to the central motif of dibenzyltoluene, this is a logical choice. Yet, the environmental health and safety hazards associated with its usage are quite significant, being noted for serious concern regarding both human and aquatic toxicity.<sup>23</sup> Thus, to lower the hazards associated with the feedstock, other aromatic compounds similar in structure to toluene might be chosen.

### 3. Summary and Perspectives

In this study, the most prominent carriers for the LOHC technology are discussed in terms of their properties, typical reaction conditions, and catalytic materials employed in the respective hydrogenation and dehydrogenation reactions. The following LOHC systems are reviewed: benzene/cyclohexane, toluene/methylcyclohexane, naphthalene/decalin, *N*-ethylcarbazole/perhydro-*N*-ethylcarbazole, dibenzyltoluene/perhydro-dibenzyltoluene. Each LOHC candidate has properties which are advantageous for use within the LOHC technology, but also has disadvantages associated with its use. Among these LOHC systems, *N*-ethylcarbazole/perhydro-*N*-ethylcarbazole and dibenzyltoluene/perhydro-dibenzyltoluene were found to be the most attractive for commercial deployment, given their favourable physical properties and demands on process conditions. For example, employment of *N*-ethylcarbazole lowers the dehydrogenation temperature, yet at ambient conditions the fully dehydrogenated NEC is a solid. Dibenzyltoluene on the other hand, is a more cost-effective LOHC option than *N*-ethylcarbazole, given its relatively moderate price, and has lower toxicity compared to toluene which results in

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fewer regulatory restrictions to its use. However, higher temperatures for the dehydrogenation process are required to release the hydrogen. Typically, to achieve such temperatures, a portion of the hydrogen released from the LOHC is burned, which clearly reduces the efficiency of the technology. Using the waste heat from fuel cells (e.g., in a LOHC – fuel cell coupled system) to provide the heat for the dehydrogenation reaction, can diminish this effect and increase the overall efficiency of the technology. These competing advantages and disadvantages of each LOHC candidate arguably increase the complexity of the LOHC technology but provide an opportunity to develop bespoke hydrogen storage and transportation solutions.

According to the literature, PGM-based catalysts have been proven to catalyse both the hydrogenation and dehydrogenation steps for various LOHC systems, though base metal catalysts might have a potential for the LOHC technology. Given the lack of information currently available in the literature and understanding of key performance indicators, such as catalyst lifetime, selectivity, and activity under truly industrial conditions (TRL 6 and above), further research into the LOHC technology is still required. Specifically, developments should attempt to reduce the energy intensity associated with the hydrogenation and dehydrogenation reactions, while increasing catalyst lifetime and cycle efficiency. This might be achieved either through the catalyst or reactor technology development.

In summary, to improve economic viability and enable widespread commercial deployment of the LOHC technology, further work might be required, focusing on: development of novel cost-effective catalysts with improved space-time yield, activity, selectivity and lifetime; increased lifetime of the LOHC (i.e., number of cycles before

a replacement is required); reduction of total costs for transporting the LOHC, including the cost of transporting the unloaded LOHC back to the hydrogenation plant; high purity of the hydrogen released in the dehydrogenation reaction; deployment and system integration of LOHCs with different industries. Furthermore, the selection of a suitable LOHC candidate must also be considered: it should remain a liquid throughout the LOHC cycle, have a low toxicity and low cost, and a high hydrogen loading capacity.

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#### 5. References

1. Niermann, M.; Beckendorff, A.; Kaltschmitt, M.; Bonhoff, K., Liquid Organic Hydrogen Carrier (LOHC) – Assessment based on chemical and economic properties. *International Journal of Hydrogen Energy* **2019**, *44* (13), 6631-6654.
2. Niermann, M.; Drünert, S.; Kaltschmitt, M.; Bonhoff, K., Liquid organic hydrogen carriers (LOHCs) – techno-economic analysis of LOHCs in a defined process chain. *Energy & Environmental Science* **2019**, *12* (1), 290-307.
3. Niermann, M.; Timmerberg, S.; Drünert, S.; Kaltschmitt, M., Liquid Organic Hydrogen Carriers and alternatives for international transport of renewable hydrogen. *Renewable and Sustainable Energy Reviews* **2021**, *135*, 110171.
4. Teichmann, D.; Arlt, W.; Wasserscheid, P., Liquid Organic Hydrogen Carriers as an efficient vector for the transport and storage of renewable energy. *International Journal of Hydrogen Energy* **2012**, *37* (23), 18118-18132.

5. Teichmann, D.; Arlt, W.; Wasserscheid, P.; Freymann, R., A future energy supply based on Liquid Organic Hydrogen Carriers (LOHC). *Energy & Environmental Science* **2011**, 4 (8), 2767-2773.
6. Aakko-Saksa, P. T.; Cook, C.; Kiviaho, J.; Repo, T., Liquid organic hydrogen carriers for transportation and storing of renewable energy – Review and discussion. *Journal of Power Sources* **2018**, 396, 803-823.
7. Knosala, K.; Kotzur, L.; Röben, F. T. C.; Stenzel, P.; Blum, L.; Robinius, M.; Stolten, D., Hybrid Hydrogen Home Storage for Decentralized Energy Autonomy. *International Journal of Hydrogen Energy* **2021**, 46 (42), 21748-21763.
8. Hurskainen, M., *Liquid organic hydrogen carriers (LOHC): Concept evaluation and techno-economics*. VTT Technical Research Centre of Finland: 2019.
9. Hurskainen, M.; Ihonen, J., Techno-economic feasibility of road transport of hydrogen using liquid organic hydrogen carriers. *International Journal of Hydrogen Energy* **2020**, 45 (56), 32098-32112.
10. Preuster, P.; Papp, C.; Wasserscheid, P., Liquid Organic Hydrogen Carriers (LOHCs): Toward a Hydrogen-free Hydrogen Economy. *Accounts of Chemical Research* **2017**, 50 (1), 74-85.
11. Ahluwalia, R. K.; Hua, T. Q.; Peng, J.-K.; Kromer, M.; Lasher, S.; McKenney, K.; Law, K.; Sinha, J. Technical Assessment of Organic Liquid Carrier Hydrogen Storage Systems for Automotive Applications , United States, <https://doi.org/10.2172/1219358>.
12. Teichmann, D.; Stark, K.; Müller, K.; Zöttl, G.; Wasserscheid, P.; Arlt, W., Energy storage in residential and commercial buildings via Liquid Organic Hydrogen Carriers (LOHC). *Energy & Environmental Science* **2012**, 5 (10), 9044-9054.
13. Wild, J.; Friedrich, T.; Cooper, A.; Toseland, B.; Muraro, G.; Tegrotenhuis, W.; Wang, Y.; Humble, P.; Karim, A., Liquid Organic Hydrogen Carriers (LOHC): An Auspicious Alternative to Conventional Hydrogen Storage Technologies. *Energy Environ* **2010**, 78.
14. Raab, M.; Maier, S.; Dietrich, R.-U., Comparative techno-economic assessment of a large-scale hydrogen transport via liquid transport media. *International Journal of Hydrogen Energy* **2021**, 46 (21), 11956-11968.
15. Southall, E.; Lukashuk, L., Hydrogen Storage and Transportation Technologies to Enable the Hydrogen Economy: Liquid Organic Hydrogen Carriers. *Johnson Matthey Technology Review* **2021**, submitted.

16. Southall, E.; Lukashuk, L., Potential Deployment and Integration of Liquid Organic Hydrogen Carrier Technology within Different Industries. *Johnson Matthey Technology Review* **2021**, submitted.
17. Itoh, N.; Xu, W. C.; Hara, S.; Sakaki, K., Electrochemical coupling of benzene hydrogenation and water electrolysis. *Catalysis Today* **2000**, *56* (1), 307-314.
18. Kariya, N.; Fukuoka, A.; Ichikawa, M., Efficient evolution of hydrogen from liquid cycloalkanes over Pt-containing catalysts supported on active carbons under "wet-dry multiphase conditions". *Applied Catalysis A: General* **2002**, *233* (1), 91-102.
19. Taube, M.; Rippin, D. W. T.; Cresswell, D. L.; Knecht, W., A system of hydrogen-powered vehicles with liquid organic hydrides. *International Journal of Hydrogen Energy* **1983**, *8* (3), 213-225.
20. Giordano, N.; Cacciola, G.; Parmaliana, A., Energy Storage and Transmission. *Platinum Metals Review* **1986**, *30* (4), 174-182.
21. Müller, K.; Stark, K.; Müller, B.; Arlt, W., Amine Borane Based Hydrogen Carriers: An Evaluation. *Energy & Fuels* **2012**, *26* (6), 3691-3696.
22. Müller, K.; Völkl, J.; Arlt, W., Thermodynamic Evaluation of Potential Organic Hydrogen Carriers. *Energy Technology* **2013**, *1* (1), 20-24.
23. Markiewicz, M.; Zhang, Y.-Q.; Empl, M. T.; Lykaki, M.; Thöming, J.; Steinberg, P.; Stolte, S., Hazard assessment of quinaldine-, alkylcarbazole-, benzene- and toluene-based liquid organic hydrogen carrier (LOHCs) systems. *Energy & Environmental Science* **2019**, *12* (1), 366-383.
24. Naseem, M.; Usman, M.; Lee, S., A parametric study of dehydrogenation of various Liquid Organic Hydrogen Carrier (LOHC) materials and its application to methanation process. *International Journal of Hydrogen Energy* **2021**, *46* (5), 4100-4115.
25. Mohajeri, N.; T-Raissi, A., Regeneration of Ammonia-Borane Complex for Hydrogen Storage. *MRS Online Proceedings Library* **2006**, *884* (1), 14.
26. Uhrig, F.; Kadar, J.; Müller, K., Reliability of liquid organic hydrogen carrier-based energy storage in a mobility application. *Energy Science & Engineering* **2020**, *8* (6), 2044-2053.
27. Wunsch, A.; Mohr, M.; Pfeifer, P., Intensified LOHC-Dehydrogenation Using Multi-Stage Microstructures and Pd-Based Membranes. *Membranes (Basel)* **2018**, *8* (4).
28. Rivard, E.; Trudeau, M.; Zaghbi, K., Hydrogen Storage for Mobility: A Review. *Materials* **2019**, *12*, 1973.

29. Shi, L.; Qi, S.; Qu, J.; Che, T.; Yi, C.; Yang, B., Integration of hydrogenation and dehydrogenation based on dibenzyltoluene as liquid organic hydrogen energy carrier. *International Journal of Hydrogen Energy* **2019**, *44* (11), 5345-5354.
30. Jorschick, H.; Preuster, P.; Dürr, S.; Seidel, A.; Müller, K.; Bösmann, A.; Wasserscheid, P., Hydrogen storage using a hot pressure swing reactor. *Energy & Environmental Science* **2017**, *10* (7), 1652-1659.
31. Jorschick, H.; Dürr, S.; Preuster, P.; Bösmann, A.; Wasserscheid, P., Operational Stability of a LOHC-Based Hot Pressure Swing Reactor for Hydrogen Storage. *Energy Technology* **2019**, *7* (1), 146-152.
32. ERIA (2020), 'Review of Hydrogen Transport Cost and its Perspective (Liquid Organic Hydrogen Carrier)', in Kimura, S., I. Kutani, O. Ikeda, and R. Chihiro (eds.), *Demand and Supply Potential of Hydrogen Energy in East Asia – Phase 2*. ERIA Research Project Report FY2020 no. 16, Jakarta: ERIA, pp.52-59.
33. VTT WP8 Business Development and sustainability – Concept Studies, Economic Analysis, Life Cycle Assessment, D8.3, A preliminary feasibility study; 2019.
34. Modisha, P. M.; Ouma, C. N. M.; Garidzirai, R.; Wasserscheid, P.; Bessarabov, D., The Prospect of Hydrogen Storage Using Liquid Organic Hydrogen Carriers. *Energy & Fuels* **2019**, *33* (4), 2778-2796.
35. Shi, D.; Wojcieszak, R.; Paul, S.; Marceau, E., Ni Promotion by Fe: What Benefits for Catalytic Hydrogenation? *Catalysts* **2019**, *9* (5), 451.
36. Sergeev, A. G.; Webb, J. D.; Hartwig, J. F., A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation. *Journal of the American Chemical Society* **2012**, *134* (50), 20226-20229.
37. Gulyaeva, Y. K.; Alekseeva, M. V.; Ermakov, D. Y.; Bulavchenko, O. A.; Zaikina, O. O.; Yakovlev, V. A., High-Loaded Nickel Based Sol-Gel Catalysts for Methylcyclohexane Dehydrogenation. *Catalysts* **2020**, *10* (10), 1198.
38. Al-ShaikhAli, A. H.; Jedidi, A.; Cavallo, L.; Takanebe, K., Non-precious bimetallic catalysts for selective dehydrogenation of an organic chemical hydride system. *Chemical Communications* **2015**, *51* (65), 12931-12934.
39. Al-ShaikhAli, A. H.; Jedidi, A.; Anjum, D. H.; Cavallo, L.; Takanebe, K., Kinetics on NiZn Bimetallic Catalysts for Hydrogen Evolution via Selective Dehydrogenation of Methylcyclohexane to Toluene. *ACS Catalysis* **2017**, *7* (3), 1592-1600.
40. De, S.; Zhang, J.; Luque, R.; Yan, N., Ni-based bimetallic heterogeneous catalysts for energy and environmental applications. *Energy & Environmental Science* **2016**, *9* (11), 3314-3347.

41. Oh, J.; Bathula, H. B.; Park, J. H.; Suh, Y.-W., A sustainable mesoporous palladium-alumina catalyst for efficient hydrogen release from N-heterocyclic liquid organic hydrogen carriers. *Communications Chemistry* **2019**, *2* (1), 68.
42. Amende, M.; Kaftan, A.; Bachmann, P.; Brehmer, R.; Preuster, P.; Koch, M.; Wasserscheid, P.; Libuda, J., Regeneration of LOHC dehydrogenation catalysts: In-situ IR spectroscopy on single crystals, model catalysts, and real catalysts from UHV to near ambient pressure. *Applied Surface Science* **2016**, *360*, 671-683.
43. Oh, J.; Kim, T. W.; Jeong, K.; Park, J. H.; Suh, Y.-W., Enhanced Activity and Stability of a Carbon-Coated Alumina-Supported Pd Catalyst in the Dehydrogenation of a Liquid Organic Hydrogen Carrier, Perhydro 2-(n-methylbenzyl)Pyridine. *ChemCatChem* **2018**, *10* (17), 3892-3900.
44. Leinweber, A.; Müller, K., Hydrogenation of the Liquid Organic Hydrogen Carrier Compound Monobenzyl Toluene: Reaction Pathway and Kinetic Effects. *Energy Technology* **2018**, *6* (3), 513-520.
45. Emmett, P. H.; Skau, N., The Catalytic Hydrogenation of Benzene over Metal Catalysts. *Journal of the American Chemical Society* **1943**, *65* (6), 1029-1035.
46. Halligudi, S. B.; Bajaj, H. C.; Bhatt, K. N.; Krishnaratnam, M., Hydrogenation of benzene to cyclohexane catalyzed by rhodium(I) complex supported on montmorillonite clay. *Reaction Kinetics and Catalysis Letters* **1992**, *48* (2), 547-552.
47. Peyrovi, M. H.; Toosi, M. R., Study of benzene hydrogenation catalyzed by nickel supported on alumina in a fixed bed reactor. *Reaction Kinetics and Catalysis Letters* **2008**, *94* (1), 115-119.
48. Price pressures on metals. *Nature Catalysis* **2019**, *2* (9), 735-735.
49. Maes, J.; Mitchell, E. A.; Maes, B. U. W., Chapter 16 Base Metals in Catalysis: From Zero to Hero. In *Green and Sustainable Medicinal Chemistry: Methods, Tools and Strategies for the 21st Century Pharmaceutical Industry*, The Royal Society of Chemistry: 2016; pp 192-202.
50. Biniwale, R. B.; Kariya, N.; Ichikawa, M., Dehydrogenation of Cyclohexane Over Ni Based Catalysts Supported on Activated Carbon using Spray-pulsed Reactor and Enhancement in Activity by Addition of a Small Amount of Pt. *Catalysis Letters* **2005**, *105* (1), 83-87.
51. Pande, J. V.; Shukla, A.; Biniwale, R. B., Catalytic dehydrogenation of cyclohexane over Ag-M/ACC catalysts for hydrogen supply. *International Journal of Hydrogen Energy* **2012**, *37* (8), 6756-6763.

52. Lijewski, M.; Hogg, J. M.; Swadźba-Kwaśny, M.; Wasserscheid, P.; Haumann, M., Coating of Pd/C catalysts with Lewis-acidic ionic liquids and liquid coordination complexes – SCILL induced activity enhancement in arene hydrogenation. *RSC Advances* **2017**, *7* (44), 27558-27563.
53. Thomas, K.; Binet, C.; Chevreau, T.; Cornet, D.; Gilson, J. P., Hydrogenation of Toluene over Supported Pt and Pd Catalysts: Influence of Structural Factors on the Sulfur Tolerance. *Journal of Catalysis* **2002**, *212* (1), 63-75.
54. Shuwa, S. M.; Jibril, B. Y.; Al-Hajri, R. S., Hydrogenation of toluene on Ni-Co-Mo supported zeolite catalysts. *Nigerian Journal of Technology* **2017**, *36*, 1114-1123.
55. Choi, J.; Zhang, S.; Hill, J. M., Reducibility and toluene hydrogenation activity of nickel catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>. *Catalysis Science & Technology* **2012**, *2* (1), 179-186.
56. ElShafei, G. M. S.; Zaki, T.; Eshaq, G.; Riad, M., Studies of Ni/Kaolinite Catalysts for the Hydrogenation of Toluene. *Adsorption Science & Technology* **2006**, *24* (10), 833-849.
57. Yolcular, S.; Olgun, Ö., Ni/Al<sub>2</sub>O<sub>3</sub> catalysts and their activity in dehydrogenation of methylcyclohexane for hydrogen production. *Catalysis Today* **2008**, *138* (3), 198-202.
58. Hatim, M. D. I.; Fazara, M. A. U.; Syarhabil, A. M.; Riduwan, F., Catalytic Dehydrogenation of Methylcyclohexane (MCH) to Toluene in a Palladium/Alumina Hollow Fibre Membrane Reactor. *Procedia Engineering* **2013**, *53*, 71-80.
59. Zhang, L.; Xu, G.; An, Y.; Chen, C.; Wang, Q., Dehydrogenation of methylcyclohexane under multiphase reaction conditions. *International Journal of Hydrogen Energy* **2006**, *31* (15), 2250-2255.
60. Shukla, A. A.; Gosavi, P. V.; Pande, J. V.; Kumar, V. P.; Chary, K. V. R.; Biniwale, R. B., Efficient hydrogen supply through catalytic dehydrogenation of methylcyclohexane over Pt/metal oxide catalysts. *International Journal of Hydrogen Energy* **2010**, *35* (9), 4020-4026.
61. Wunsch, A.; Berg, T.; Pfeifer, P., Hydrogen Production from the LOHC Perhydro-Dibenzyl-Toluene and Purification Using a 5  $\mu$ m PdAg-Membrane in a Coupled Microstructured System. *Materials (Basel)* **2020**, *13* (2), 277.
62. Artur, G.; Tanaka, D. A. P.; Mizukami, F.; Suzuki, T. M., Lower Temperature Dehydrogenation of Methylcyclohexane by Membrane-assisted Equilibrium Shift. *Chemistry Letters* **2006**, *35* (12), 1372-1373.

63. Park, K.-C.; Yim, D.-J.; Ihm, S.-K., Characteristics of Al-MCM-41 supported Pt catalysts: effect of Al distribution in Al-MCM-41 on its catalytic activity in naphthalene hydrogenation. *Catalysis Today* **2002**, *74* (3), 281-290.
64. Hodoshima, S.; Takaiwa, S.; Shono, A.; Satoh, K.; Saito, Y., Hydrogen storage by decalin/naphthalene pair and hydrogen supply to fuel cells by use of superheated liquid-film-type catalysis. *Applied Catalysis A: General* **2005**, *283* (1), 235-242.
65. Lee, G.; Jeong, Y.; Kim, B.-G.; Han, J. S.; Jeong, H.; Na, H. B.; Jung, J. C., Hydrogen production by catalytic decalin dehydrogenation over carbon-supported platinum catalyst: Effect of catalyst preparation method. *Catalysis Communications* **2015**, *67*, 40-44.
66. Suttisawat, Y.; Sakai, H.; Abe, M.; Rangsunvigit, P.; Horikoshi, S., Microwave effect in the dehydrogenation of tetralin and decalin with a fixed-bed reactor. *International Journal of Hydrogen Energy* **2012**, *37* (4), 3242-3250.
67. Yang, M.; Dong, Y.; Fei, S.; Ke, H.; Cheng, H., A comparative study of catalytic dehydrogenation of perhydro-N-ethylcarbazole over noble metal catalysts. *International Journal of Hydrogen Energy* **2014**, *39* (33), 18976-18983.
68. Brückner, N.; Obesser, K.; Bösmann, A.; Teichmann, D.; Arlt, W.; Dungs, J.; Wasserscheid, P., Evaluation of Industrially Applied Heat-Transfer Fluids as Liquid Organic Hydrogen Carrier Systems. *ChemSusChem* **2014**, *7* (1), 229-235.
69. Forberg, D.; Schwob, T.; Zaheer, M.; Friedrich, M.; Miyajima, N.; Kempe, R., Single-catalyst high-weight% hydrogen storage in an N-heterocycle synthesized from lignin hydrogenolysis products and ammonia. *Nature Communications* **2016**, *7* (1), 13201.
70. Wu, Y.; Yu, H.; Guo, Y.; Jiang, X.; Qi, Y.; Sun, B.; Li, H.; Zheng, J.; Li, X., A rare earth hydride supported ruthenium catalyst for the hydrogenation of N-heterocycles: boosting the activity via a new hydrogen transfer path and controlling the stereoselectivity. *Chemical Science* **2019**, *10* (45), 10459-10465.
71. Li, L.; Yang, M.; Dong, Y.; Mei, P.; Cheng, H., Hydrogen storage and release from a new promising Liquid Organic Hydrogen Storage Carrier (LOHC): 2-methylindole. *International Journal of Hydrogen Energy* **2016**, *41* (36), 16129-16134.
72. Dürr, S.; Müller, M.; Jorschick, H.; Helmin, M.; Bösmann, A.; Palkovits, R.; Wasserscheid, P., Carbon Dioxide-Free Hydrogen Production with Integrated Hydrogen Separation and Storage. *ChemSusChem* **2017**, *10* (1), 42-47.

73. Jorschick, H.; Bösmann, A.; Preuster, P.; Wasserscheid, P., Charging a Liquid Organic Hydrogen Carrier System with H<sub>2</sub>/CO<sub>2</sub> Gas Mixtures. *ChemCatChem* **2018**, *10* (19), 4329-4337.
74. Modisha, P.; Bessarabov, D., Stress tolerance assessment of dibenzyltoluene-based liquid organic hydrogen carriers. *Sustainable Energy & Fuels* **2020**, *4* (9), 4662-4670.
75. Aslam, R.; Khan, M. H.; Ishaq, M.; Müller, K., Thermophysical Studies of Dibenzyltoluene and Its Partially and Fully Hydrogenated Derivatives. *Journal of Chemical & Engineering Data* **2018**, *63* (12), 4580-4587.
76. Aslam, R.; Minceva, M.; Müller, K.; Arlt, W., Development of a liquid chromatographic method for the separation of a liquid organic hydrogen carrier mixture. *Separation and Purification Technology* **2016**, *163*, 140-144.
77. Müller, K.; Stark, K.; Emel'yanenko, V. N.; Varfolomeev, M. A.; Zaitsau, D. H.; Shoifet, E.; Schick, C.; Verevkin, S. P.; Arlt, W., Liquid Organic Hydrogen Carriers: Thermophysical and Thermochemical Studies of Benzyl- and Dibenzyl-toluene Derivatives. *Industrial & Engineering Chemistry Research* **2015**, *54* (32), 7967-7976.

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