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Liquid Organic Hydrogen Carriers as an efficient vector for the transport and storage of renewable energy

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ABSTRACT

This contribution proposes the usage of Liquid Organic Hydrogen Carriers (LOHC) for the storage and subsequently the transport of renewable energy. It is expected that a significant share of future energy consumption will be satisfied with the import of energy coming from regions with high potential for renewable generation, e.g. the import of solar power from Northern Africa to Europe. In this context the transport of energy in form of chemical carriers is proposed supplementary to electrical transmission. Because of their high storage density and good manageability under ambient conditions Diesel-like LOHC substances could be transported within the infrastructure that already exists for the handling of liquid fossil fuels (e.g. oil tankers, tank trucks, pipelines, etc.). A detailed assessment of energy consumption as well as of transport costs is conducted that confirms the feasibility of the concept.

1. Introduction

In many countries around the world there exist ambitious goals to reduce mankind's dependency on fossil fuels like coal, oil and gas in favor of an increasing share of renewable energies like solar energy or wind power [1,2]. The hitherto existing vast use of the aforementioned fossil fuels in very different sectors has been a consequence not only of their good availability and comparably low costs, but also of their very beneficial physical handling characteristics. Especially liquid fossil fuels like crude oil have a high energy density and are therefore good energy carriers which can be transported and stored very efficiently – both in regard to technological and economic aspects.

With the transition of the energy system toward a higher share of renewable energy, hydrogen is often considered a very capable future energy vector [3]. It can be produced from renewable wind or solar power via electrolysis and has a wide range of potential applications in all important fields of energy supply.

The gravimetric energy storage density of hydrogen is excellent. One kilogram carries about 33 kWh of energy. Being the chemical element with the lowest density, the volumetric storage density of hydrogen is a huge problem though. Under ambient conditions 1 l of gaseous hydrogen stores about 3 Wh of energy only. In existing technical applications hydrogen is therefore either stored in its gaseous state under very high pressures up to 700 bar (called "Compressed Gaseous

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Hydrogen" or CGH2) or in its liquid state which requires temperatures below −253 °C (called "Liquid Hydrogen" or LH2). This very low temperature allows for an ambient pressure storage of hydrogen but still with the extremely low liquid density of 71.2 kg/m^3.

In addition to the technological complexity of these storage concepts, the huge investment costs that are necessary to establish a nation-wide distribution infrastructure for hydrogen are a big challenge. The handling of CGH2 for example is very well known in the chemical industry and a few hydrogen pipelines already exist. But to make hydrogen available in the same way like natural gas or electricity, a complete new hydrogen distribution system would have to be installed in addition to the already existing grids for electricity and natural gas.

Due to these limitations, researchers work on alternative concepts for the storage and transport of hydrogen in chemically bound forms [4].

One particularly attractive concept in this context is Energy Carrying Compounds (ETS, from the German name "Energie-Tragende Stoffe") [5,7]. Here the energy is stored in form of chemical compounds with a high energy content, which opens a chance to store big quantities over a longer period of time. The compound under consideration travels from the spot of energy delivery to the spot of energy demand and back. It is being charged with energy if the latter is available and it vice versa releases energy on demand. Like a catalyst the ETS is not consumed but undergoes a cyclic process of hydrogen loading and hydrogen releasing steps. This route of energy storage and distribution is virtually carbon free, so no CO_2 is released in the utilization of the stored energy.

One example for ETS is "Liquid Organic Hydrogen Carriers" (LOHC) where hydrogen does not exist in its molecular form but is covalently bound to a liquid carrier substance via hydrogenation [6–8]. At the time and place of energy demand, hydrogen can be released via dehydrogenation. The hydrogen carrying liquid itself is not consumed but can be reloaded and used in further cycles. Various substances have been discussed as potential ETS candidates, e.g. methylcyclohexane–toluene by [6], a variety of cycloalkanes [9] and ammonia-borane-based systems [8,10]. The focus of this contribution lies on heterocyclic aromatic hydrocarbons like N-ethylcarbazole [11], which – due to extensive research – are currently among the best understood LOHC systems with convenient material properties for the application as an energy carrier.

As hydrocarbazoles have many physico-chemical similarities to Diesel fuel, the complexity of handling, transporting and storing gaseous hydrogen is basically reduced to the handling of a liquid diesel-like substance. The fundamentals of the hydrogenation and dehydrogenation reactions of N-ethylcarbazole are illustrated in Fig. 1. For a detailed description there exist various publications [12–14].

The melting point of fully dehydrogenated N-ethylcarbazole is 69.1 °C and it is therefore a solid at ambient temperature. Perhydro-N-ethylcarbazole and the partially hydrogenated intermediates in contrast are liquids. To guarantee full liquid handling of the LOHC substance, the dehydrogenation process can be restricted to around 90% discharging by limiting the residence time within the catalytic reaction system. While the theoretical storage density of N-ethylcarbazole – perhydro-N-ethylcarbazole would be 5.8 wt-%, only 5.3 wt-% materials energy density can be achieved following this approach.

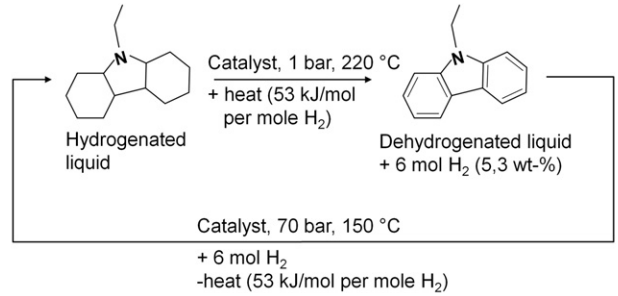

Fig. 1 – Energy storage via hydrogenation and dehydrogenation of N-ethylcarbazole.

Existing safety data sheets show that the toxicity of N-ethylcarbazole is rather uncritical, see Table 1 [15].

Because of its very low vapor pressure there is no detectable vapor phase under ambient conditions which further facilitates handling and safety issues of the carbazole LOHC system.

Under the assumption that the return and reloading of the unloaded carrier material is made possible, the existing, very well established infrastructure for the distribution of mineral oil based fuels could be used for LOHC. Because of its high energy storage density and good handling characteristics a variety of applications for mobility, heating, long distance energy transport or long-term energy storage (for example for energy coming from intermittent producing renewable energies) can be envisaged [16].

The local potential for the installation of renewable energies is geographically not evenly distributed and therefore there often is a local mismatch between the level of energy consumption (strongly depending on population and industrialization density) and the potential for renewable energy. Therefore, it is foreseeable that with the transition toward a higher share of renewable energies like wind or solar, more and more power must be transported over long distances in the future. The 'Desertec Industrial Initiative' [17] for instance planned to produce electricity on a grand scale in Northern Africa and to import it to Europe either by HVDC-lines under

Table 1 – Material safety information N-ethylcarbazole.

CAS number	86-28-2
Toxicity data	
LD50 (oral)	>5000 mg/kg = non-toxic
Skin	Not irritating (OECD 404)
Eye	Not irritating (OECD 405)
LC50 (96 h)	<10 mg/l (Golden Orfe)
Globally Harmonized System of Classification and Labeling of Chemicals	Aquatic chronic 2, H411, no signal word
Transport information	UN 3077 environmentally hazardous substance, solid, n.o.s., Class 9, PG III, Label 9