



Review article

Liquid organic hydrogen carriers for transportation and storing of renewable energy – Review and discussion

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HIGHLIGHTS

- Solutions are needed for storing and transporting the renewable energy.
- Hydrogen storage options are reviewed and discussed.
- Some end-use sectors are more demanding than the others.
- Liquid organic hydrogen carriers are promising hydrogen storages.
- The “circular” methanol and hydrocarbons or are also promising hydrogen storages.

ARTICLE INFO

Keywords:

Hydrogen
Liquid organic hydrogen carriers
Energy storage
Dibenzyl toluene
Methanol

ABSTRACT

Transition to renewable energy systems is essential to achieve the climate change mitigation targets. However, the timing and the regions of the production and consumption of the renewable energy do not always match, and different energy storage technologies are needed to secure the uninterrupted energy supply. Liquid organic hydrogen carriers (LOHCs) offer a flexible media for the storage and transportation of renewable energy. These “liquid hydrogen batteries” are reversibly hydrogenated and dehydrogenated using catalysts at elevated temperatures. Commercial LOHC concepts are already available. Another flexible route to store energy is through “circular” hydrogen carriers, such as methanol and methane produced from atmospheric carbon dioxide (CO₂). These fuels have a long history as fossil fuels. In this review, the chemistry and state-of-the-art of LOHCs are explored and discussed against defined criteria with comparison made to existing energy storage systems. The LOHCs and “circular” hydrogen carriers were found to be particularly promising hydrogen storage systems.

1. Introduction

Fossil energy reserves are sufficient for hundreds of years at the current rate of energy consumption. However, the threat of climate change may end the era of fossil energy before the reserves are depleted. In 2013, world total primary energy supply (TPES) was 13 555 Mtoe (570 EJ), 13.5% of this was produced by renewable energy sources; mainly by traditional biomass used for heating and cooking in developing countries (73.4%) and hydroelectric power (17.8%) [1]. The “New Policies Scenario” of the International Energy Agency (IEA) [2] projected that the share of renewables in the primary energy will be 18% by 2035 as the hydropower, bioenergy, wind and solar photovoltaic (PV) increases. Renewable energy is estimated to cover from 100 EJ to 400 EJ of world energy production by 2050 [3]. In 2013, for

the first time more capacity was added for renewable power than for coal, natural gas, and oil combined [4].

The need for novel energy storage media arises from the imbalances between regions for production and consumption of renewable energy and the fluxionality of its generation. For example, the regions best suited for the production of renewable energy are often far away from the greatest demand. Consequently, long-distance and overseas transport of energy is needed. In the northern latitudes, the potential for solar energy production is at the highest over the summer season, when the energy consumption is at the lowest. Wind conditions may change rapidly. Overall, the irregular production of renewable energy is challenging. Even hydropower capacity is not fully utilized over the low consumption periods.

Feasible energy storages are needed to remove the bottlenecks of

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the deployment of the renewable energy in large scale in order to improve energy security and balance the energy prices. Oil, gas and coal are excellent energy storages, while the other energy storage technologies have their pros and cons; there are differences in the size classes, on the duration of the storage periods and on the energy transport capabilities. For example, duration of discharge is short for compressed air and pumped hydro energy storages. Batteries are available from kW to over 100 MW, but their gravimetric energy density is low and electricity cannot be stored in batteries for extensive time periods. One type of energy storage does not fit in all purposes. For example, aviation and long-distance ground transport are dependent on the high-quality liquid fuels, while the power and heat sector, as well as shipping, can cope with more challenging fuels.

Hydrogen creates possibilities for transportation and long-term storage of renewable energy. Recently, the IEA [5] defined hydrogen as a flexible energy carrier, which can be produced from any energy source, and which can be converted into various energy forms. The main challenges with hydrogen implementation are related to its production and storage. In energy equivalents, global annual hydrogen demand (172 Mtoe, 60 Mt) is below 2% of the world energy production. Approximately 48% of hydrogen is produced from natural gas (NG) using steam methane reforming (SMR), 30% is a by-product from the petroleum refining, 18% is produced from coal, and 4% from water electrolysis [5]. In the US, 59% of hydrogen is produced on-purpose in oil refineries and ammonia plants, and almost 36% as a by-product from catalytic reforming at oil refineries and at chlor-alkali plants [6]. In future, biomass or organic wastes could be hydrogen sources via the gasification, and carbon-neutral hydrogen could be produced by water electrolysis using electricity based on renewables or nuclear power. Ball and Wietschel et al. [3] found direct use of solar and wind to be the most efficient forms to produce hydrogen when the yield per hectare was evaluated; more efficient than producing electricity from biomass. Prices of hydrogen produced from NG vary regionally (\$0.9 per kg in the US, \$2.2 per kg in Europe and \$3.2 per kg in Japan) [5]. Price of hydrogen produced by distributed wind is \$7–11 per kg, by solar \$10–30 per kg and by electrolysis \$6–7 per kg when delivered with grid power in the US. Hydrogen produced by gasification from biomass was estimated as from \$1.50 to \$3.50 per kg at large-scale [6]. Lipman [6] estimated that the future cost of hydrogen produced by wind and solar have the potential price of \$3–4 per kg.

Use of hydrogen as an energy carrier demands effective, safe, user-friendly and economical storage. In general, hydrogen can be compressed (CH₂), liquefied (LH₂) or binded into solid or liquid storage materials for later use in turbines, in internal combustion engines (ICEs), in high-efficiency fuel cells (FCs) or for chemicals (Fig. 1). Hydrogen can be stored in an underground cavern or in a pressurised tank until it is re-electrified. Hydrogen can also be physically adsorbed in metals and high surface area adsorbents. By forming a chemical bond, hydrogen can be stored in hydrides, boranes and liquid organic hydrogen carriers (LOHCs). Low temperatures or high pressures are essential to store hydrogen by physisorption, while elevated temperatures

are needed to release hydrogen stored by chemisorption. Solid systems require a new infrastructure, while liquids can use the existing fuel infrastructure. Reversible hydrogen carriers can be hydrogenated and dehydrogenated without need to produce a new batch of material for every cycle (Fig. 2). Hydrogen can also be converted irreversibly into synthetic liquid fuels, such as methanol, methane, liquid hydrocarbons, formic acid, ammonia and its derivatives. These “circular” hydrogen carriers cannot be regenerated meaning that new batch of material is needed for each cycle (Fig. 3) as is the case with traditional fossil fuels. However, when circular hydrogen carriers are produced from renewable hydrogen and atmospheric CO₂ or nitrogen, the total cycle is carbon-neutral in contrary to fossil fuels [7–9].

LOHCs are regarded as newcomers in the energy storage field, though the concept was initially suggested already in the 1970's. Hydrogenation of aromatics and dehydrogenation of cyclic hydrocarbons are mature industrial processes, for example in oil refineries. Using the LOHC concept on a smaller scale requires new processes and catalysts with priority placed on the selectivity, safety, robustness and fast kinetics of the system, even at the cost of increased expenses. Organic species other than cyclic hydrocarbons warrant investigation as LOHCs if the thermodynamics of both hydrogenation and hydrogen release are favourable. In this work, chemical status of the LOHC concept is reviewed. Hydrogen storage in LOHC is discussed against the defined criteria and compared with compressed and liquid hydrogen as well as with solid and circular hydrogen carriers.

2. Liquid organic hydrogen carriers

2.1. Principle

LOHCs are liquids or low-melting solids that can be reversibly hydrogenated and dehydrogenated at elevated temperatures in the presence of catalyst. The initial structure of the LOHC compounds remain the same after the rechargeable hydrogen is released, while traditional fossil fuels and circular CO₂-based fuels are combusted as a whole. As the core structure of the LOHC remains untouched, production of new carrier in every cycle is avoided [9]. Clear benefits of LOHCs are their compatibility with the existing fuel infrastructure, and their capability to store hydrogen without losses even in the long-term or when transported overseas under standard conditions. The purity of the hydrogen released from LOHCs is high. Catalyst design aims at high selectivity at sufficiently mild reaction conditions to avoid breaking of the covalent carbon-carbon bond (or bonds with heteroatoms), and consequent cracking and coking [7,10]. Some chemical structures are more susceptible for hydrogenation or dehydrogenation than the others. Some common rules for the design of the compounds with favourable thermodynamics have been identified:

- Heterocyclic compounds, particularly bicyclic heteroarenes, are favourable due to decreased aromaticity of the molecule [7,9,11,12].
- A 5-membered heterocyclic ring is favourable [7].
- NH or NR in the 1-position of a hydrocarbon ring is favourable. The N–H bond is weaker than the C–H bond, and the C–H bonds adjacent to an N atom are weaker than the C–H bonds adjacent to C atom [7]. Steric hindrance around N-atom increases the dehydrogenation rate [13].
- N atoms or substituents in an 1,3-arrangement are favourable, but certain azoles, e.g., imidazole, are resistant towards hydrogenation [7].
- Favourable hydrogen binding enthalpies of LOHCs are sufficient to secure stability of the hydrogenated molecule and to achieve acceptable dehydrogenation temperature. Wild et al. [14] defined the desired enthalpy range from 40 to 70 kJ mol⁻¹ H₂ and Cooper et al. [15] from 42 to 54 kJ mol⁻¹ H₂.
- Increasing the number of fused aromatic rings decreases the hydrogenation enthalpies, however, the large polyaromatic

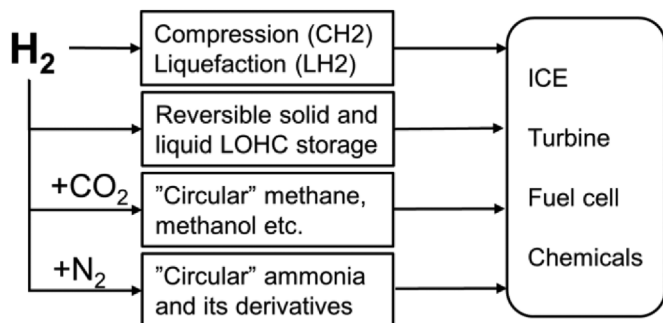


Fig. 1. Utilisation of the renewable energy through hydrogen storage pathways.

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