

Hydrogen Carriers : A Path Forward

by

Sayandeep Biswas

Submitted to the Department of Chemical Engineering
on November 19, 2025 in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

ABSTRACT

Hydrogen carriers offer a promising pathway to overcome the storage, transport, and infrastructure challenges that limit the large-scale deployment of molecular hydrogen. Yet, their broader adoption is hindered by conversion inefficiencies, system-integration barriers, and economic constraints. This thesis advances the practical utilization of hydrogen carriers by developing improved production pathways, demonstrating efficient hydrogen-release technologies, and evaluating their performance across multiple carrier systems.

First, ammonium formate is investigated as a safe, non-flammable, and energy-dense solid hydrogen carrier. An electrochemical dehydrogenation system is demonstrated at 105 °C, where ammonium formate forms an ionic liquid. The system achieves near-quantitative Faradaic efficiencies at both electrodes and exploits coupled thermal–electrochemical driving forces, enabling modular hydrogen release with the potential for net-zero carbon emissions. Second, a comprehensive costing and emissions analysis is conducted for blue, green, and integrated blue–green ammonia production pathways. The integrated pathway uses oxygen from electrolysis to feed the autothermal reformer, eliminating the need for an air-separation unit and significantly reducing energy use and capital cost, making it a strong candidate for transitional decarbonization.

Third, the thesis evaluates onboard dehydrogenation of Liquid Organic Hydrogen Carriers (LOHCs) as an alternative to centralized hydrogen release for heavy-duty trucking. This perspective identifies key reactor, catalyst, and engine-integration requirements for enabling an LOHC-fueled powertrain and shows that LOHCs charged with blue hydrogen can approach cost parity with diesel. Crucially, the final component of the thesis directly addresses these requirements. A pilot-scale benzyltoluene dehydrogenation reactor is designed, built, and experimentally validated to demonstrate the core enabling technology for the proposed powertrain. The reactor uses high-temperature exhaust gas directly to supply the endothermic heat demand and generates high-pressure hydrogen compatible with engine-based systems. The results align strongly with model predictions and confirm, at pilot scale, the technical feasibility of the onboard LOHC utilization pathway articulated in the third work.

Together, these contributions advance both the scientific foundations and engineering readiness of hydrogen carriers, providing new strategies to improve conversion efficiency, reduce system

costs, and enable scalable hydrogen distribution and utilization in future low-carbon energy systems.

Thesis supervisor: William H. Green

Title: Hoyt Hottel Professor in Chemical Engineering