# TEMPERATURE CASCADE LOHC DEHYDROGENATION AS A PROCESS INTENSIFICATION STRATEGY

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## ABSTRACT

Liquid organic hydrogen carriers (LOHCs) have taken a spotlight as a possible alternative for hydrogen  $(H_2)$ storage and transportation compared to more conventional methods such as pressurized  $H_2$  and liquified H<sub>2</sub>. In an increasingly alternative energy supply, efficiency of commercial scale H<sub>2</sub> release from LOHC systems is paramount for a viable H<sub>2</sub> economy. This work presents a process design for a novel process intensification strategy which combines two conventional LOHC chemicals (benzene and dibenzyl toluene) in a dehydrogenation process utilizing a shared heat source. Using rigorous Aspen Plus process simulation it has been demonstrated that this process design allows for an increased hydrogen release yield of 18.7%, when compared to systems which utilizes a single LOHC chemical. Strategy of temperature cascade dehydrogenation using different LOHC combinations, coupled with identification of process integration viability, specifically in utilization of waste heat can very likely prove to be an important pathway to a more efficient hydrogen economy.

**Keywords:** LOHC, hydrogen storage, process intensification, temperature cascade, process design, Aspen Plus

### NONMENCLATURE

Abbreviations	
LOHC	Liquid organic hydrogen carrier
DBT	Dibenzyltoluene

## TC Temperature cascade

## 1. INTRODUCTION

Utilization of hydrogen as an energy vector in a renewable energy economy presents significant advantages as it is abundant, has the largest gravimetric energy density[1] (120 MJ/kg), and the production can (and has been) integrated with peak renewable electricity. The price of H<sub>2</sub> produced from renewably powered water electrolysis has fallen from 3-3.6 EUR/kg in 2015 [2] to a projected 2.1 EUR/kg [3] in 2020 predominately due to the global increase in renewable electricity production scale. As the renewably generated hydrogen price trend continues downward the primary challenge of its utilization still lies in storage and transportation technologies.

Elemental hydrogen under normal conditions has a low density of 0.08375 kg/m<sup>3</sup> [4] and thus the lowest volumetric energy density of about 0.01 MJ/L compared to most of the commonly utilized fuels. Consequently to store economical content of hydrogen energy, most common, large-scale, hydrogen storage techniques such as compressed hydrogen (200-700 bar) [5], and liquefied hydrogen (-253°C) [6] require somewhat rigorous conditions of pressure and temperature which translates into significant energy expenditures, as well as safety considerations. As this inhibits the progress of hydrogen economy alternative hydrogen storage techniques in a form of a liquid organic carrier have been extensively researched and developed in the past decade[7–11].

Numerous advantages of LOHC as a storage concept due to its cyclical nature, relative safety, understood

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technology, and comparative lack of carbon emissions have been widely reported elsewhere, in particular by Reuß et al. [12,13], , Preuster et al. [14], Runge et al. [15] and many others and will not be discussed here in detail.

A notable advantage of LOHCs compared to conventional storage technologies relevant to the theme of this work is that the very concept allows for a wide selection of globally produced and well understood chemicals (in terms of their handling and chemistry) providing a suitable selection for integration in a current liquid-fuel based transportation infrastructure.

A suitable LOHC candidate can ideally be used to bridge the distance between locations of high renewable energy supply and high clean energy demand, which are on global average non-urban, and urban respectively. On the energy demand side hydrogen must be released from its LOHC in an endothermic chemical reaction at high temperatures. The source of the energy (fossil fuel or renewable) and the efficiency of its usage will directly affect the overall efficiency of the LOHC derived renewable electricity.

Dehydrogenation processes for various LOHC candidates have been designed and theoretically evaluated [16–18]. Eypasch et al. [19] has modeled and performed economical evaluation of an industrial scale LOHC system based on dibenzyltoluene (DBT) (an LOHC used in this work) and has concluded that an energy self-sufficient system (at this time) has a 47% higher cost per electricity produced than an average grid price.

This work in turn presents a strategy for LOHC dehydrogenation process intensification in fully utilizing available energy source by combining multiple LOHC chemicals in a "temperature cascade" fashion, for a more efficient and thus cheaper clean electricity.

## 2. MAIN

## 2.1 Materials and methods

The dehydrogenation process was designed and simulated in Aspen Plus software V10. The primary thermodynamic property method was based on Soave-Redlich-Kwon (SRK) cubic equation of state [20–22] as it is suitable for modeling non-polar and slightly polar mixtures such a hydrocarbons and light gasses and is consistent in a wide temperature and pressure ranges, making it suitable for catalytic LOHC dehydrogenation.

LOHC chemicals chosen were DBT and benzene as they are widely reported, and their hydrogenation chemistry well known. For both LOHCs a 100 % dehydrogenation was assumed at temperatures / reaction enthalpies of 300°C / 585 kJmol<sup>-1</sup>, and 180°C /



Fig 1. Single LOHC dehydrogenation process schematic

207 kJmol<sup>-1</sup> for DBT[23,24] and benzene[25,26] respectively. Both reactions occur at slightly elevated pressure of 1.1 bar.

## 2.2 Process design and description

A base dehydrogenation process was first conceived for a single LOHC chemical as it is depicted in Fig1. A heat source was the hot flue gas (HFG) from the combustion of 1kg/h of hydrogen with air in a molar ratio of 1:28, producing a total flue gas flow of 790 kg/h and at a temperature of 400°C. The hydrogenated or charged (+) LOHC (+) chemical is fed to the system by a feed pump at 1.1 bar. A series of 2 heat exchangers (HXs) bring it to reaction temperature using a hot reactor product stream and a HFG respectively. Reactor operates isothermally where the heat necessary for the dehydrogenation is supplied by HFG which exists the system at the reaction temperature of that particular LOHC. Reaction products are cooled down in the HX system and vapors are separated in a flash drum. As the vapors contain discharged (-) LOHC as well as hydrogen a multistage compressor with intercooling is utilized to pressurize the produced hydrogen and, in the process, bleed out the condensed LOHC (-). Pure hydrogen (0.999 mol fraction) is the product as well as liquid LOHC (-). The flow rate of the LOCH is tuned so that the maximum amount of energy from the heat source is utilized, which entails that the heat source exits at the same temperature as the dehydrogenation reaction temperature.

The novel process (**Fig2**.) uses the same concept as the base one with the difference that it combines 2 (and theoretically more) LOHCs. The same heat source as in the base case (type and amount) first provides energy for the dehydrogenation of heavier LOHC (+) (Perhydro-DBT) after which it still has high enough temperature to provide enough energy for the dehydrogenation of lighter LOHC (+) (cyclohexane), hence *"temperature*  *cascade*" (TC). The heavier LOHC (+) enters the process and is brought up to reaction temperature by a heat exchanger and by acting as a partial cooling medium for multistage compressors (which was assumed physically viable as DBT was reported to be used as a heat transfer fluid[27]). After reaction, the products are cooled in a HX system and separated in the same fashion as in the base case with an end pressure of 4 bar. Lighter LOHC (+) is brought up to reaction temperature by a series of HXs cooling down the reaction products of both LOHCs. Hydrogen is purified in a similar fashion, only here a higher end pressure of 40 bar is needed. As in the base case flows of LOHC chemicals are tuned to the maximum extraction of energy from the heat source which exits at the reaction temperature of the lighter LOHC.

### 2.3 Results and discussion

Single LOHC process was simulated in Aspen Plus to determine the energy requirement, the scale of both LOHC for maximum hydrogen yield from a fixed heat source. The results of the simulation (**Tab 1**) indicate that, in a single LOHC process, more hydrogen can be produced from the lighter LOHC but at a greater power and cooling expenditure which is thermodynamically realistic and unsurprising. TC LOHC however provides a numerical insight into energy benefits of utilizing multiple LOHCs in an integrated process. Scaled down to

#### Tab 1. Process simulation results comparing single and temperature cascade LOHC process

HEAT SOURCE: 710 KG/H HOT FLUE GAS A	AT 400°C (FROM 1 KG/H H₂)
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	LOHC flow; (kg/h)	Hydrogen (kg/h)	Power (kW/kg H <sub>2</sub> )	Cooling water (kg/kg H <sub>2</sub> )	
	Single LOHC process				
LIGHT LOHC (+)	64.3	4.63	1.91	81.35	
HEAVY LOHC (+)	42.3	2.64	0.77	79.72	
	Temperature cascade LOHC process				
LIGHT LOHC (+)	39.1	5.49	1.34	69.10	
HEAVY LOHC (+)	42.9				

the same hydrogen output as the TC process combined single processes have power consumption and watercooling requirements of 2.02 (kW/kg H<sub>2</sub>) and 121.6 (kg/kg H<sub>2</sub>) respectively which translates into 34 % and 43 % reductions. Benzene as a single LOHC has yielded a maximum of 4.63 kg/h of H<sub>2</sub> which has increased to 5.49 kg/h of H<sub>2</sub> when TC process was used on the same heat source which is an 18.7 % increase in yield. This clearly demonstrates that the TC LOHC dehydrogenation is a more energy efficient process compared to single LOHC process.



Fig 2. Temperature cascade LOHC dehydrogenation process schematic. H and L stand for heavy and light LOHC respectively, and (+) and (-) stand for charged and discharged LOHC respectively.

### 2.4 Conclusions

This work details the concept and design of a temperature cascade LOHC dehydrogenation process which utilizes multiple LOHC chemicals in an integrated fashion powered by the same heat source.

Compared to analog processes which use single LOHC chemical the TC proves to be more energy efficient resulting in an increased hydrogen yield of 18.7 % for the observed LOHC system.

Ultimately this work presents a pathway for more energy efficient LOHC supply chain and thus more viable hydrogen economy as a whole.

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