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# Sustainable Green Hydrogen Transport: A Systematic Framework for the Design of the whole Supply Chain

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## ABSTRACT

In view of achieving the decarbonization target, green hydrogen is commonly regarded as the alternative capable of reducing the share of fossil fuels. Despite its wide application as a chemical on industrial scale, hydrogen utilization as an energy vector still suffers from unfavorable economics, mainly due to its high cost of production, storage and transportation. To overcome the last two of these issues, different hydrogen carriers have been proposed. Hydrogen storage and transportation through these carriers involve: 1. the carrier hydrogenation, exploiting green hydrogen produced at the loading terminal, where renewable sources are easily accessible, 2. the storage and transportation of the hydrogenated species and 3. its subsequent dehydrogenation at the unloading terminal, to favour $H_2$ release. Although there is a number of studies in literature on the economic feasibility of hydrogen transport through different $H_2$ vectors, very few of them delve into the technical evaluation of the hydrogen value chain. From the process design point of view, the hydrogenation and dehydrogenation stages are of paramount importance, considering that they are the cost drivers of the whole system. This work aims to address this gap by presenting a systematic methodology to technically analyse different hydrogen vectors. For the sake of example, ammonia and dibenzyltoluene are considered. Weaknesses of the overall value chain are pointed out, to understand where to focus research efforts for future process intensification.

**Keywords**: H2 transport, H2 carriers, sustainable energy, techno-economic assessment, computer-aided process design.

## INTRODUCTION

In the transition towards sustainable energy, green hydrogen has emerged as a promising low-emission alternative. Nonetheless, its transportation is hampered by its low volumetric density. To address this problem, different $H_2$ carriers have been proposed as a reliable solution. The typical $H_2$ value chain is depicted in Figure 1, considering ammonia ($NH_3$) and liquid organic hydrogen carriers (LOHCs) as hydrogen vectors. $NH_3$ and LOHCs are commonly perceived as the most encouraging choices, due to the easiness adaptability to the existing infrastructures. These hydrogen-bearing molecules can be hydrogenated at the loading terminal, exploiting green hydrogen produced through renewable sources, more easily stored, transported and, upon arrival, dehydrogenated for $H_2$ release. The released hydrogen can serve either the mobility or the industrial sectors [1].

$NH_3$ is a global commodity, already produced in large scale facilities and distributed worldwide. On the other hand, a variety of LOHCs have been considered in literature [2-3]. While some chemical structures are more susceptible to hydrogenation/dehydrogenation than others, certain rules have been identified for selecting favourable compounds. The optimal LOHC has to show low melting point and high boiling point, to avoid solidification and volatilization issues; high $H_2$ storage capacity; low

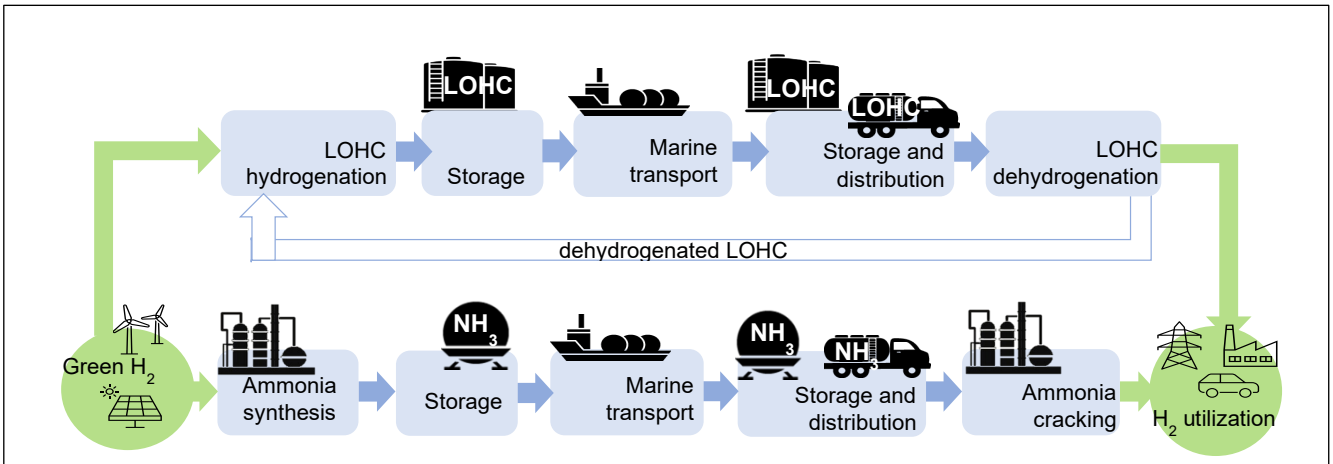



**Figure 1**: Hydrogen value chain exploiting LOHCs and $NH_3$ as $H_2$ carriers.

dehydrogenation enthalpy; low toxicity and low cost [2]. Selected the best candidate as hydrogen carrier, the essential starting point for the feasibility study of the hydrogen value chain is the identification of the basis of the design, including:

1. production rate of green $H_2$, to be fed to the system. Specifically, tuning the plant size according to the land footprint of renewables is crucial for the assessment of realistic scenarios. Renewable sources are characterized by a power density several orders of magnitude lower than fossil fuels. The transition pathways towards sustainability must consider both the limitations of available land and the specific geophysical conditions [4]. Understanding the extent of land needs can put the feasible scale of green hydrogen production into perspective [5]. In this analysis, flat $H_2$ production of 20000 $Nm^3/h$ is supposed via 100 MW alkaline electrolysers, available at 20 bar and 25°C.

2. Loading and unloading terminal location and, consequently, distance to be covered for $H_2$ transport. Different scenarios can be inferred, as the long-distance harbour-to-harbour hydrogen transport, which involves the $H_2$ seaborne transport or the short distance hydrogen transport, that implies the road or pipeline hydrogen transport. In the hydrogen value chain of Figure 1, the seaborne $H_2$ transport is considered.

3. $H_2$ utilization and its centralized or decentralized application. According to the centralized scenario, the $H_2$ produced is conveyed into a power plant for green electricity production. In this case, less stringent specifications on $H_2$ purity are needed, likely. On the other hand, for the decentralized $H_2$ utilization, $H_2$ has to be distributed to several hydrogen refuelling stations, to serve the mobility sector. Thus, high $H_2$ purity is necessary. The selection of the centralized/decentralized scenario also affects the process design of the whole value chain and, consequently, the operating conditions of the delivered hydrogen (*i.e.*, temperature and pressure of discharge at the end user, together with required purity). In the present study, $H_2$ centralized application at a $H_2$ valley is considered, such that the hydrogen product is released at 30 bar and with a purity of 99.9 mol%.

Defined the basis of design, both technical and economic assessments can be carried out. However, it is worth noticing that the economic evaluations are, generally, strongly dependent on the hypotheses introduced and on the methodology adopted. Variable results can be obtained, such that it is difficult to draw general conclusions. For this reason, from the process engineering point of view, it is more relevant to focus on the design of the whole value chain and its technical assessment, with a particular attention to the cost-driving stages, rather than demonstrating the economic viability of hydrogen transport. In this respect, this work aims at presenting a systematic methodology to analyse different hydrogen value chains. Ammonia and dibenzyltoluene (H0-DBT) are selected as the representative carriers, due to their promising features. Hydrogenation and dehydrogenation stages have been designed in Aspen Plus V11®. Based on the simulations presented, a detailed technical analysis is discussed, to pave the way for future process intensification.

## SIMULATION OF THE COST-DRIVING PROCESSES

### Ammonia ($NH_3$)

Ammonia is a global commodity, already distributed worldwide and used in the chemical industry. Recently, it

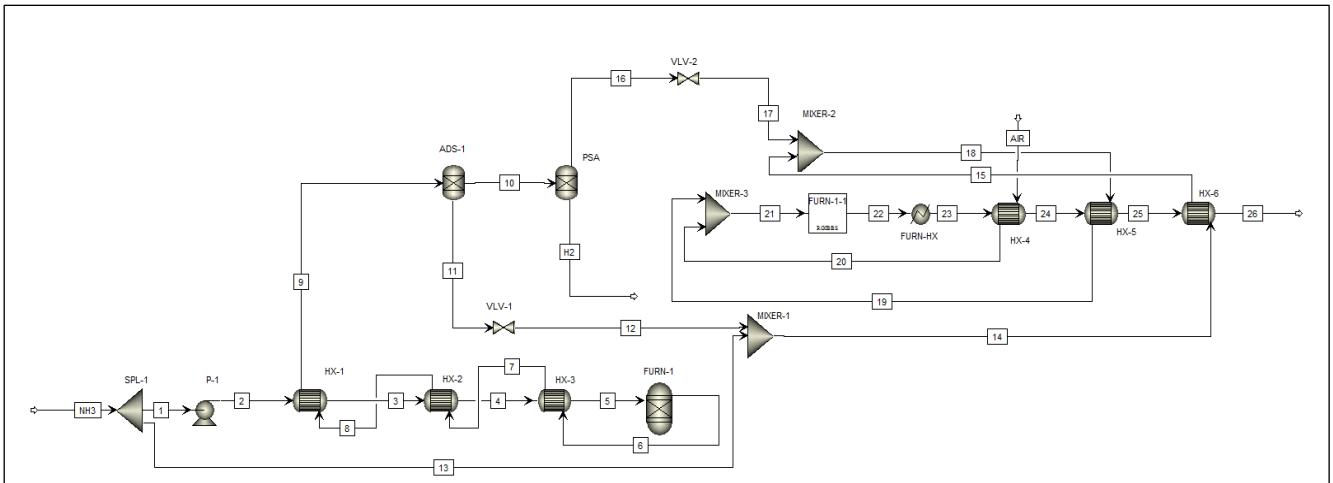



**Figure 2**: $NH_3$ dehydrogenation section. Simulation in Aspen Plus V11®.

has been regarded as a promising hydrogen vector due to its high hydrogen content (about 17.8 wt.%) and well-established global infrastructure for transportation and storage. Moreover, the hydrogenation stage for $NH_3$ as $H_2$ carrier, *i.e.*, ammonia synthesis from hydrogen, is already a well-established process, extensively optimized over the last years. For this reason, the hydrogenation section of $NH_3$ as $H_2$ carrier will be not discussed in this work. For the technical analysis of $NH_3$ synthesis within the $H_2$ value chain framework, reference can be made to Restelli et al. [6]. On the other hand, the $NH_3$ decomposition through cracking (reaction (1)) is not as mature as the ammonia synthesis. While different strategies are available to accommodate ammonia decomposition [7,8], the thermochemical ammonia decomposition shows the highest technology readiness level (TRL) for industrial application.

$$2NH_3 \rightarrow 3H_2 + N_2 \quad (1)$$

The typical process scheme is shown in Figure 2.

Liquid $NH_3$ is pumped, heated in a train of process-process heat exchangers (*HX-1*, *HX-2*, *HX-3* in Figure 2) and fed to the cracking unit (*FURN-1* in Figure 1). This unit is modelled through the *RGibbs* module of Aspen Plus, where thermodynamic equilibrium conditions are reached at the specified temperature and pressure of 900°C and 30 bar, respectively [6]. Downstream the reaction section, the uncracked $NH_3$ is adsorbed in an activated carbon bed (*ADS-1* in Figure 2), while hydrogen is separated from the coproduced $N_2$ through pressure swing adsorption onto a zeolite bed (*PSA* in Figure 2).

The heat necessary for the cracking is provided burning a $NH_3$ and $H_2$ mixture in the furnace combustion section. The hydrogen fed to this section is the PSA blowdown stream, while $NH_3$ fresh flowrate fed to the combustion section is regulated in such a way that the heat necessary for the cracking to occur is equal to the one generated by the combustion reaction. Inlet air to the combustion section is slightly above the stoichiometry, to minimise the concentration of unburned fuel.

## Liquid Organic Hydrogen Carriers (LOHCs)

As opposite to $NH_3$, LOHCs are not as well-established. Among the most promising candidates as organic carriers, nitrogen and oxygen substituted heterocycles are getting attention because of their reduced dehydrogenation enthalpy. Moreover, oxygen-based organic molecules which can be produced from biomasses show the advantage of increasing the sustainability of the overall hydrogen value chain. When these complex molecules are selected as the potential $H_2$ carriers, the process design of the overall system becomes challenging because these species are usually not available in commercial engineering simulators. For this reason, a significant effort is required to include them in the software databank. To do so, accurate thermophysical and thermochemical properties of the pseudo-components are needed for a detailed simulation.

In the following, a systematic methodology for the simulation software set-up is discussed, considering dibenzyltoluene (H0-DBT)/perhydro-dibenzyltoluene (H18-DBT) pair as the hydrogen vector.

### H0/H18 DBT properties

The H0-DBT/H18-DBT pair has seen a surge of interest from researchers since 2014, when it was proposed as a potential LOHC by Hydrogenious LOHC Technologies GmbH [9]. With a relatively high hydrogen storage capacity of 6.2 wt.%, H0-DBT/H18-DBT offers several advantages over other LOHC systems, as good thermal stability, high boiling point (390°C at atmospheric pressure), low toxicity and low melting point, ranging between -39°C to -34°C.

Müller et al. [10] performed a comprehensive experimental characterization of dibenzyltoluene and perhydro-dibenzyltoluene, including boiling point, enthalpy of formation, density, specific heat capacity, and vapour pressure. This data, reported in Table 1, was useful for

including the new pseudo-components in Aspen Plus simulation software. Once these properties are introduced, the compounds physical-chemical characterization occurs in Aspen Plus® with the aid of NIST TDE (ThermoData Engine) tool and the Aspen property estimation system.

**Table 1**: Dibenzyltoluene (DBT) and perhydrodibenzyltoluene (H18-DBT) properties [10].

| Property | Value | |
|---|---|---|
| | DBT | H18-DBT |
| TB [°C] | 390 | 371 |
| MW [kg/kmol] | 272.4 | 290.4 |
| SG* @ 60°F [-] | 1.047 | 0.916 |
| $\Delta H_{form}$ [kJ/kmol] | 225700 | -387400 |

*SG: Specific Gravity.

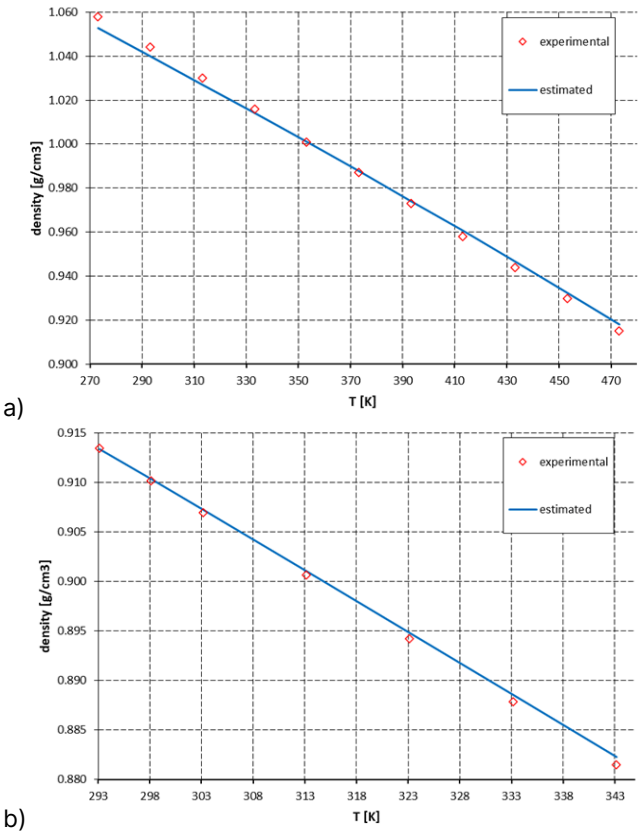


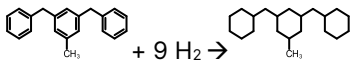

**Figure 3**: Comparison between experimental and predicted density values for: a) H0-DBT and b) H18-DBT.

In addition to what provided in Table 1, supplying experimental molar volume and ideal gas heat capacity can enable the development of a more robust model. Implemented all the available experimental datasets, in view of assessing the reliability of the models, the predicted physical properties can be compared with the experimental ones. Results are reported in Figure 3 considering the density of the hydrogenated and dehydrogenated species for the sake of example. A satisfactory agreement is obtained between the experimental and calculated values.

## H0/H18 DBT hydrogenation and dehydrogenation

Once the process simulator has been set up, both hydrogenation and dehydrogenation stages have been designed in Aspen Plus V11®.

The hydrogenation section is represented in Figure 4. The process receives at its battery limits the hydrogen produced via the alkaline electrolysers, at 50°C and 20 bar. This stream undergoes compression up to 35 bar and is fed to the reactor (*B2* in Figure 4), together with a nitrogen stream that acts as a thermal diluent. Also dibenzyltoluene coming both from the make up stream and the dehydrogenation process is fed to the hydrogenation reactor, after preheating in a process-process heat exchanger (*PREHEAT* in Figure 4). The reactor operates at a pressure of 35 bara and a temperature of 210°C for the catalytic hydrogenation reaction (2) to occur. While the exothermic nature of the hydrogenation reaction would suggest lower temperatures for enhanced reaction equilibrium, the operating temperature also considers the catalytic activity requirements [11]. Based on what available in literature [12], the reactor is simulated through the *RStoic* module of Aspen Plus at quantitative conversion and selectivity.



(2)

Downstream the reaction section, the outlet stream, which contains the perhydro-dibenzyltoluene along with unreacted hydrogen and nitrogen, is cooled and expanded to favour the separation of light gases from the heavier H18-DBT, which can be sent for storage and then transported to the spot of hydrogen delivery.

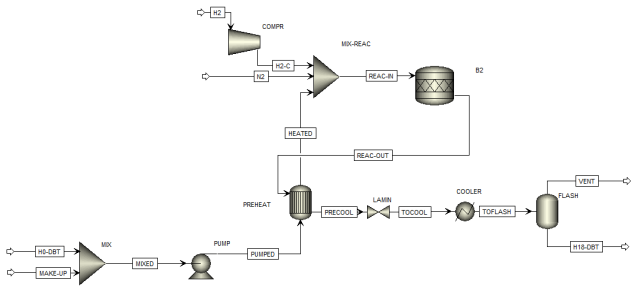



**Figure 4:** H0-DBT hydrogenation section. Simulation in Aspen Plus V11®.

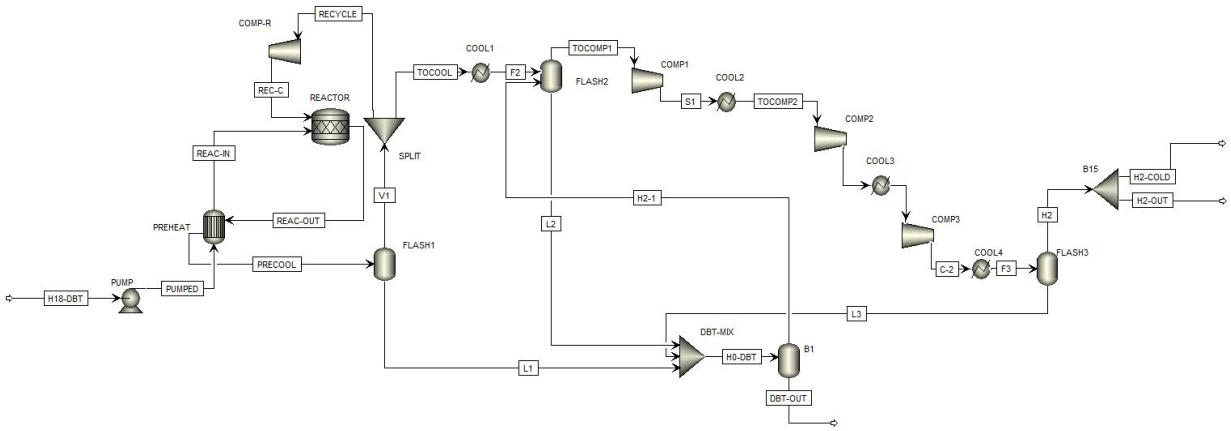



**Figure 5**: H18-DBT dehydrogenation section. Simulation in Aspen Plus V11®.

The hydrogenated species thus produced is fed to the dehydrogenation section, reported in Figure 5.

The H18-DBT is pumped, preheated in a process-process heat exchanger and fed to the reactor (*REACTOR* in Figure 5), operating at 320 °C and 1.1 bara. Also in this case, the unit is modeled through the *RStoic* module of Aspen Plus according to the experimental data collected by Modisha et al. [13]. The findings demonstrated that a 96% conversion rate could be achieved at 320°C using a 0.5 wt.% $Pt/Al_2O_3$ catalyst. Downstream the reactor, the outlet stream is directed to a gas-liquid separator (*FLASH1* in Figure 5). The top vapour phase, a hydrogen-rich stream, is recycled back to the reactor via the compressor *COMP-R*. This recycled hydrogen plays a crucial role in averting undesired coking phenomena, thus ensuring the activity of the catalyst.

The remainder of the hydrogen stream undergoes cooling in *COOL1* before being sent to a second gas-liquid separator. The separator facilitates the extraction of another liquid stream, rich in H0-DBT, while a vapor phase stream, enriched with hydrogen, exits from the top of the unit. The produced $H_2$ is compressed up to 30 bar by means of a three inter-refrigerated compression stages (*COMP-1*, *COMP-2*, and *COMP-3* in Figure 5). In this way, high pressure and high purity hydrogen is obtained, whose specifications meet the requirements at the value chain battery limits.

The liquid stream coming from the series of gas-liquid separators is H0-DBT, to be recycled back to the hydrogenation section.

In order to cope with the endothermic nature of the reaction, a portion of the transported hydrogen is burnt, thus lowering the $H_2$ flow rate exiting the battery limits. The combustion section has been simulated in Aspen Plus with a similar rationale of the $NH_3$ one, already disclosed in the previous section. Here, the fuel flow rate is selected in such a way that the heat produced in the combustion section equals to the one necessary for the dehydrogenation reaction to occur, while the air flow rate is slightly above the stoichiometric value.

## TECHNICAL ASSESSMENT

The process simulations discussed allow to point out weaknesses of the two carriers and to understand where to focus research efforts for process intensification.

As regards $NH_3$, it has the intrinsic advantage of being a well-known chemical, already used worldwide. Despite $NH_3$ synthesis has been extensively optimized, when dealing with green ammonia produced by renewable hydrogen, the plant must be likely downscaled [14]. To favour the operability of this reduced $NH_3$ plant, lower pressures than the traditional Haber-Bosch could be needed. Different strategies are under consideration by researchers in this respect, namely: the identification of more active and selective catalysts at milder operating conditions [15] or the $NH_3$ removal downstream the reaction stage, either with solid-state species (*i.e.*, metal halides or borohydrides [16]) or liquid solvents (water, aqueous acids or $NH_4H_2PO_4$ [5]).

Concerning ammonia cracking, the process simulation performed pointed out that the only external utility needed is electricity, used to drive the pump *P-1* in Figure 2, with an associated consumption of 23.72 kW. Despite the low utility consumption, the designed process scheme has the drawback of a reduced $H_2$ flowrate exiting the battery limits. For 592.33 kmol/h of $NH_3$ entering the process, 698.07 kmol/h of $H_2$ are produced. This evidence is due to the consumption of part of the inlet $NH_3$ in the combustion section, on the one hand, and to the low $H_2$ recovery rate from the PSA unit on the other hand, set at 85% to be consistent with literature values [17]. Process intensification for ammonia cracking should focus on the identification of catalysts capable of operating at milder operating conditions, together with on the optimization of the $N_2$-$H_2$ separation section downstream the reactor, to maximize $H_2$ recovery.

As for the pair H0-DBT/H18-DBT, the process simulation suffers from the not detailed reactor modeling, such that fundamental research is needed to identify a well-established kinetic expression to be included in the Aspen Plus scheme. Despite the drawback of low maturity, the dibenzyltoluene shows the intrinsic advantage of a reduced volatility, which allows the production of high purity hydrogen after dehydrogenation, facilitating the $H_2$ separation from unconverted gases downstream the reaction section.

The hydrogenation section electricity consumption amounts to 615.96 kW, for the compression and pumping of reactants at the battery limits, while only cooling water is needed as external utility, to provide a cooling duty of 482.3 kW. The high endothermicity of the hydrogenation reaction (16462.3 kW) could represent a plus point in the overall energy balance. When designing the whole value chain, strategies for heat integration have to be figured out to understand how to maximise revenues.

Concerning the dehydrogenation section, 3758.97 kW of electricity consumption are registered for the H18-DBT dehydrogenation process. Despite this number could seem high at a first glance, most of the electric energy required by the process is due to the hydrogen compression up to the delivery pressure, which cannot be reduced. Thermal energy consumption of the process is related to the cooling duty by means of cooling water, which accounts for a total of 4822 kW, together with the heat necessary for the hydrogenation reaction to occur. Despite no external utility is required, the high reaction endothermicity (19887.3 kW) is responsible for a dramatic reduction of the hydrogen flow rate exiting the battery limits. For 103.83 kmol/h of H18-DBT entering the process, 575.65 kmol/h of hydrogen are produced. The choice of coping the reaction endothermicity by burning part of the hydrogen produced is for sustainability purposes. It is true that $H_2$ is a high value-added product, probably too valuable to be burnt in a combustion chamber, but, on the other hand, the utilization of any fossil-based fuels does not make sense environmentally, if $CO_2$ is emitted upon combustion. Research efforts for process intensification should focus, primarily, on the identification of a suitable organic molecule to be used as $H_2$ vector, to reduce the heat requirements of the dehydrogenation section as much as possible. Selected the best candidate as LOHC, heat integration in the whole hydrogen value chain, together with the selection of a suitable clean burning fuel, compliant with plant location and needs, could be strategies for energy savings and, ultimately, operating cost reduction.

## CONCLUSIONS

Green hydrogen transport through different $H_2$ carriers still suffers from unfavourable economics. With the aim of understanding where to focus research efforts for process intensification, this work offers a systematic methodology for the analysis of the value chain cost drivers, *i.e.*, hydrogenation and dehydrogenation stages. Ammonia and the pair dibenzyltoluene/perhydrodibenzyltoluene are selected as representative carriers.

For ammonia value chain, focal points of research to be investigated for cost reductions are:

- the $NH_3$ synthesis process intensification on small scale, to enable green ammonia production at milder operating conditions;
- the $NH_3$ thermocatalytic cracking process intensification, to enable the reaction to occur at milder operating conditions and to optimize the $N_2$-$H_2$ separation downstream the reactor as much as possible.

For LOHC value chain, active and fundamental research is still needed to identify the most promising candidate to be used as the hydrogen carrier, to assess its physical-chemical properties and to investigate the hydrogenation and dehydrogenation reaction kinetics at the laboratory scale. Furthermore, points to be investigated are:

- for the hydrogenation section, the maximisation of the heat integration, taking into account the reaction exothermicity;
- for the dehydrogenation section, the identification of alternative methods for heat supply to cope the reaction endothermicity.

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