A two-step methodology for the selection and process optimization of Liquid Organic Hydrogen Carriers (LOHCs)

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Abstract

The reduction of GHG emissions is clearly bounded to an increase in the use of renewable resources. Hence, the use of energy carriers such as hydrogen seems crucial to reduce the fluctuations in the power generation. However, the physico-chemical properties of hydrogen hinder its transportation and storage. Alternatives such as LOHCs are regarded as a promising option to improve them. The selection among the available LOHCs systems and the process optimization are some of the key points to enhance the deployment of this storage technology. In this work, a systematic two-step design methodology is proposed. First, a prescreening stage is developed to select the best LOHCs candidates considering the economy, safety and environmental of hydrogenation and dehydrogenation processes. In a second step, the optimization of the most promising LOHCs systems from the first stage is carried out. N-ethylcarbazole and indoles mixture systems resulted to be the most promising options from the first stage of the methodology to be used for hydrogen storage. Hence, both processes are optimized. Surrogate models are developed to represent the hydrogenation and dehydrogenation reactors. Although trickle bed and slurry reactor designs were considered for both tasks, the optimization results suggest the use of slurry reactors over trickle beds due to better catalyst use. However, the trickle bed technology presents numerous advantages and it cannot be discarded yet for LOHCs applications. The hydrogen storage costs ranged between 1.30-2.34 \$/kg H_2 for different plant capacities. The dehydrogenation stage, and specifically the dehydrogenation reactors and the heating agent used, resulted to have a major impact on it. Thus, this methodology allows to identify the most promising LOHCs options and to design its process, analyzing the challenges for its deployment.

Keywords: Energy Storage, Hydrogen, Liquid Organic Hydrogen Carriers, Process Optimization, Efficiency, Sustainability.

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1. Introduction

In the incoming years, an unprecedent increase in renewable energy sources, mainly through a higher share of wind and solar, is expected. This is regarded as mandatory to reduce the Greenhouse Gas Emissions (GHG) linked to electricity production (Bouckaert et al., 2021). However, the higher penetration of renewables introduces some new challenges to power generation systems. Renewable resources are highly fluctuating and represent a source of uncertainty. Therefore, the utilization of energy storage technologies is paramount to support the production of electricity based on these resources (Wang et al., 2022). Lately, hydrogen has gained attention as an alternative for this purpose. Its generation with renewable resources can be used to store energy and release it on demand. Other applications include its direct use in industry and transportation (Griffiths et al., 2021). However, the storage and transportation of hydrogen as such presents some issues (e.g., low volumetric density, material compatibility) (Moradi and Groth, 2019). There exist several alternatives for the feasible storage of hydrogen. Compression and liquefaction are options already used at industrial scale. Nevertheless, these require demanding conditions such as high pressures and/or low temperatures (Andersson and Grönkvist, 2019). Recently, other promising alternatives such as Liquid Organic Hydrogen Carriers (LOHCs) are attracting attention for this storage purpose. These consist of liquid organic compounds that are hydrogenated incorporating hydrogen on their chemical structure. Then, they release it via the inverse chemical reaction, namely dehydrogenation. They offer more favorable storage conditions compared to traditional technologies. Additionally, they enable to reuse the already constructed petroleum transportation and storage equipment (Reuß et al., 2017).

There exists a wide variety of LOHCs available for the storage of hydrogen. The selection of the most appropriate LOHCs is paramount to optimize the storage costs. However, in most cases, the selection of LOHCs is made considering the most extended options. Nevertheless, some authors have worked on the selection of LOHCs based on different criteria. Kwak et al. (2021) included some of the most relevant physicochemical properties for LOHCs. Moreover, they considered some metrics to evaluate several LOHCs during dehydrogenation (reaction heat requirements, coke formation in the catalyst, dehydrogenation degree and yield and simplified economics). Naseem et al. (2021) also analyzed the dehydrogenation stage, in this case, from a process perspective. Process simulations were performed to calculate the energy requirements and optimal dehydrogenation temperatures. However, both works, lack other relevant areas such as the material toxicity, safety or environmental impacts. The importance to account for them was highlighted in Markiewicz et al. (2015). The works from Tsogt et al. (2024) and Oner and Khalilpour (2022) included several technoeconomic and en-

ergy indicators. In this case, toxicity and safety indicators were also introduced for each LOHC. However, specifically, the safety indicator only took into account the LOHCs species, based on its properties, but omitted the interaction with the process. Hence, it was not possible to capture the hazards for the process itself (such as operating conditions, additional units, storage or utilities) and the interactions with each specific LOHC (e.g., flammability range, reactivity). The use of physicochemical properties (e.g. melting point, reaction enthalpy, flash and boiling temperatures, vapor pressure) to help in the LOHCs selection has been done in some works (Díaz et al., 2023). This kind of studies are useful to extract some preliminary conclusions. However, it is mandatory to analyze the performance of each LOHC system at process scale. Niermann et al. (2019a) included these LOHCs properties together with process conditions and then proposed a variety of indicators. Some of them were qualitative, but at the same time were useful to extract preliminary conclusions such as the potential application for each LOHC system depending on its characteristics. Although it can be regarded as a good starting point, still a more detailed evaluation from a process design perspective is required for each specific case.

Several efforts have been made to develop the LOHCs technology in the last years. For example, Distel et al. (2025) presented several projects developed by the company Hydrogenious for hydrogen transportation using LOHCs. The costs for the different stages of the whole supply chain (e.g., production, storage, transport, release) were estimated. Other results for LOHCs and other alternatives from other references were also included. The LOHCs option showed competitive costs. Furthermore, some heat integration opportunities were proposed. The use of residual heat from Solid Oxide Fuel Cells or from other industries can be promising to improve the system efficiency. Narayanan et al. (2022) showed the potential of using LOHCs and liquified hydrogen for seasonal energy storage compared to higher capital cost compression. They also remarked the benefits of having an external heat source for dehydrogenation. Abdin et al. (2021) introduced some key insights for the LOHCs technology and compared it against other options from a large-scale implementation perspective. These included other hydrogen storage alternatives and energy carriers. Energy consumption and capital and transportation costs were analyzed. The development of a cheap and abundant catalyst represents another area of concern. The improvements in catalysis are presented in several works. For example, Ramadhani et al. (2024) reviewed the hydrogenation catalysis for some typical LOHCs systems. They highlighted the differences between using high and low purity hydrogen. Finally, the possibility of using cheaper materials such as nickel showed a great potential for cost reduction. However, these present limitations against traditional precious materials. Kirichenko and Kustov (2024) presented

the use of several Pd catalysts for dehydrogenation. Moreover, the possibility of using bi-functional catalysts was explored. It was also emphasized that a catalyst cost reduction can be achieved if the palladium content can be reduced. Gemechu et al. (2023) also highlighted this fact. Several first principles-based models were reviewed for the optimization of dehydrogenation catalysts. For example, the use of Ni-Pt catalyst was proposed to reduce platinum.

The potential use of LOHCs has also driven thermodynamics and properties estimation research (Stark et al., 2015; Heublein et al., 2020; Müller et al., 2015; Berger Bioucas et al., 2020). These areas are essential for the modelling of the process and related LOHCs equipment. Other fields of interest for LOHCs are the kinetics of hydrogenation and dehydrogenation. For instance, hydrogenation over Ru/Al_2O_3 and dehydrogenation over Pd/Al_2O_3 were assessed for 1,2-dimethylindole (Dong et al., 2019) and 7-ethylindole (Chen et al., 2018). The reaction kinetics for other LOHCs such as N-ethylcarbazole (Wan et al., 2013) or dibenzyltoluene (Shi et al., 2020) were also studied. Some of the LOHCs kinetics were introduced in Prieto et al. (2023), where the design of the reactor was performed. Besides kinetics, the mass, heat and momentum transfer phenomena were incorporated in the model to design hydrogenation and dehydrogenation reactors (slurry and trickle bed). These phenomena are paramount to assess the reactor performance. Therefore, it indicates that a proper reactor scale-up from laboratory conditions to industrial units is mandatory.

Other works focus on the analysis of the hydrogenation and dehydrogenation stages from a process perspective. Byun et al. (2022) studied the hydrogenation of toluene, N-ethylcarbazole, dibenzyltoluene and CO_2 to produce methanol. This last alternative provided the lowest costs for hydrogen storage. A sensitivity analysis was conducted with some of the operating variables (e.g., recycle ratio, temperature) to evaluate their effect and then, techno-economic analysis and process scale-up studies were performed. However, that work only relied on kinetic expressions to model the reaction section without considering the mass transfer phenomena in the hydrogenation reactors. García et al. (2024) simulated the hydrogenation process for dibenzyltoluene, N-ethylcarbazole and 2-methylindole. The effect of several operating variables and process configurations was evaluated in this study. Dibenzyltoluene showed the best results. That work included mass and heat transfer in the reactor modelling. Despite that, only pre-fixed transfer coefficients based on correlations were used to model these reactors. Neither the momentum transfer nor other relevant parameters such as bubble characterization were considered in the reactor modelling. Dibenzyltoluene dehydrogenation process was modelled by Rao et al. (2022) with a detailed process flowsheet. They considered a fixed bed reactor for the reaction and included the external and internal

resistances in the reaction progress. The influence of several process parameters on the cost of the catalyst and other units such as heat exchangers were also assessed. Brigljević et al. (2020) conducted also the simulation for the dehydrogenation process with different LOHC systems. Two possibilities were evaluated: dehydrogenation of one single LOHC or dehydrogenation of several LOHCs at once. A process intensification approach using a LOHCs cascade-system was proposed. In spite of that, the design of the reaction systems was not assessed in depth. Other works as Spatolisano et al. (2024) simulated both hydrogenation and dehydrogenation processes. In that case, dibenzyltoluene and toluene were considered. The hydrogen transportation and storage were also accounted for in a techno-economic analysis. However, some conditions and variables from the process such as temperatures and reaction conversions were merely based on equilibrium conversions or taken from other studies in literature without any further analysis. Additionally, the cost of the catalyst was neglected. The hydrogenation and dehydrogenation processes for the toluene system were also simulated in Carvalho et al. (2021). Heat integration reduced significantly the use of utilities in both. Moreover, the importance of considering the reaction kinetics was highlighted. However, other relevant transfer phenomena were not accounted for. Niermann et al. (2019b) provided a simplified flowsheet for the hydrogenation and dehydrogenation stages. Several LOHCs systems were simulated. However, the work focused on hydrogen transportation using LOHCs but not analyzed the effect of relevant process and reaction conditions. Reuß et al. (2017) and Hurskainen and Ihonen (2020) also assessed the possibilities of using dibenzyltoluene for transportation purposes. However, they did not analyze LOHCs from a process perspective. Their works mainly focused on the techno-economic analysis for the transportation of hydrogen with LOHCs. The costs for different hydrogen demands and transportation distances were analyzed. Similar techno-economic studies were performed by other authors using toluene, N-ethylcarbazole and dibenzyltoluene for hydrogen transportation (Makepeace et al., 2024; Raab et al., 2021; Rong et al., 2024). Likewise, several techno-economic analysis were also conducted using LOHCs for stationary applications (Eypasch et al., 2017; Abdin et al., 2021, 2022). Finally, other studies such as Bontron et al. (2023) evaluated the environmental impacts of using different LOHCs systems. There, two LOHCs systems were studied: dibenzyltoluene and toluene.

However, the availability of LOHCs alternatives is broad and the methodologies used for its selection are not the most appropriate for the specific application, in this case, process scale hydrogenation and dehydrogenation. This is because other works may only be based on physicochemical properties, do not include relevant areas in the analysis (e.g. safety or environmental), are not as specific in the final application and/or

because some of the indicators used are not numerical or easily replicable. At the same time, in most cases, heat integration opportunities are not considered in LOHCs studies. Differently, in this work, this is taken into account in a detailed process optimization stage. Therefore, a replicable and rigorous selection procedure is developed once the current application is known. Another area of concern is the lack of attention to the scale up from laboratory to the industrial conditions. LOHCs studies may consider or not the reactor design. However, in those cases where it is accounted for, these often rely only on reaction kinetics, obtained on laboratory scale studies. Nevertheless, it has been proven that mass transfer resistance is negligible compared to the reaction kinetics at these conditions (Wan et al., 2013). As a result, mass, heat and momentum transfer are typically ignored in the reactor modelling within process design. Therefore, the transfer phenomena must be incorporated in the reactors modelling to accurately describe its behavior and limitations.

In this work a new two-step methodology is developed for LOHCs selection and hydrogen storage optimization from a process scale perspective. The first step consists of a prescreening stage to select promising LOHCs options among a set of LOHCs candidates. Here, some of the most promising alternatives found in the literature are considered. Hence, a holistic prescreening is proposed based on economics, environmental and safety within a process scale perspective. To the best of the authors knowledge, these three areas together have not been studied quantitatively yet for these LOHCs systems from a process scale perspective. Next, a detailed process scale formulation is developed with the best alternatives obtained from the prescreening. The reactors behavior is captured with surrogate models developed from previous work taking into account mass, heat and momentum transfer for these units (Prieto et al., 2023). The majority of process-scale LOHCs studies do not consider these phenomena in spite of its importance. Furthermore, the hydrogenation and dehydrogenation processes are modelled in the same formulation. This allows to consider the LOHCs product specifications from the hydrogenation into dehydrogenation and vice versa, instead of assuming complete conversions as in other studies and/or optimizing each process individually. The rest of this paper is structured as follows: section 2 presents the methodology, section 3 shows the application to process design and the results. Finally, section 4 draws some conclusions. The development of this work favors the selection and optimization of LOHCs technology for effective deployment.

2. Selection and optimization of LOHCs systems

A new two-step methodology is developed to select and optimize the hydrogen storage process for a series of LOHCs candidates. The first step, called prescreening, con-

siders three criteria: process economy, safety and environmental. An index is proposed for each of these areas. A set of simplified calculations are performed to compute each of the three indexes proposed in this work. This approach allows to discard/select the LOHCs candidates for the next step where a more detailed process design formulation is proposed. In the second stage of the methodology, the hydrogen storage cost for the most promising alternatives is optimized having a systematic process design procedure.

A wide range of LOHCs systems are available in the literature as reported in several works (Rao and Yoon, 2020; Chu et al., 2023; Zhu and Xu, 2015; Yang et al., 2023; Li et al., 2024; Modisha and Bessarabov, 2023). It seems mandatory to perform a preselection. For that purpose, we consider the preselection from Niermann et al. (2019a). There, most of the LOHCs systems proposed in the previous references were either considered or discarded based on simple criteria without any additional calculations. These criteria include: operating conditions, energy density, toxicity, selectivity or reaction yields among others. Therefore, this initial selection serves as a good starting point to be used as an example for this methodology. Notice however, that while a considerable number of options are already considered, not all LOHCs systems from the references presented above are covered. Nevertheless, the criteria used by Niermann et al. (2019a) can be extrapolated to other LOHCs found in the literature.

For example, benzyltoluene was discarded in Niermann et al. (2019a) because of its toxicity. Similarly, 2-(n-methylbenzyl-pyridine) or 2-methylpyridine, which have very similar structures, may have also been removed for comparable toxicity reasons (ChemicalBook, 2024a). Likewise, 4,7-phenantroline is very similar to phenazine. However, as it is more toxic, it is not included (PubChem, 2024). Other pyridines have been reported as potential LOHCs (benzylpyridine, 2,6-dimethylpyridine or 2,2-bipyridyl). These species are not introduced in this work either due to even higher toxicity and/or flammability compared to previous pyridines (ChemicalBook, 2024b,d,c). Other pyridines such as 4-amino-piperidine are removed because of the potential disproportionation reactions during hydrogenation, which is very likely to occur similarly in piperidine-4-carboxamide (Zhu and Xu, 2015). Similarly, the terphenyl systems are likely to suffer from side-reactions. These may include cracking, condensation, coking or hydrogenolysis (Zhou et al., 2024). Biphenyl system was discarded in Niermann et al. (2019a) for the low selectivity. Therefore, terphenyl systems are removed due to the same reason.

N-ethylcarbazole is already considered in Niermann et al. (2019a) due to its benefits. There are several carbazole compounds apart from it. For instance, some compounds, like carbazole, exhibit considerably lower kinetics (Zhu and Xu, 2015). Other potential derivatives are characterized by higher melting points and/or increased reaction en-

thalpy (Li et al., 2024). Therefore, only N-ethylcarbazole is considered from this group of compounds. Indole derivatives are regarded also as promising options for their use. They show a similar energy density compared to other LOHCs systems included in Niermann et al. (2019a). Among several indoles alternatives, 1,2-dimethylindole exhibits the fastest kinetics in hydrogenation but specially during the dehydrogenation (Li et al., 2024). This LOHC can be combined with 7-ethylindole to reduce the melting point as proposed in Dong et al. (2019). The use of quinoline has also been proposed. However, it is not considered for the next stage due to the demanding operating conditions during hydrogenation. Similarly, acridines have been removed from the selection because of the challenges faced during dehydrogenation (Li et al., 2024). Finally, although formic acid was initially considered in Niermann et al. (2019a), it is excluded. This is because of the low energy density (due to the high amount of water required as solvent) and the low energy efficiency (use of distillation columns) (Niermann et al., 2019b). The LOHCs systems selected are included in Table 1. In any case, this methodology offers a general procedure to evaluate any other candidate.

Table 1: LOHCs systems studied.

System	Source
Dibenzyltoluene /perhydro-Dibenzyltoluene (DBT-DBTH)	(Byun et al., 2022; Eypasch et al., 2017; Abdin et al., 2022; Hurskainen and Ihonen, 2020; García et al., 2024)
Toluene /Methylcyclohexane (TOL-MET)	(Byun et al., 2022; Niermann et al., 2019a; Li et al., 2024)
Naphtalene /Decalin (NAP-DEC)	(Abdin et al., 2021; Niermann et al., 2019a; Li et al., 2024)
N-ethylcarbazole /perhydro-N-ethylcarbazole (NEC-NECH)	(Byun et al., 2022; García et al., 2024; Zhu and Xu, 2015)
1,2-dimethylindol+7-ethylindole/perhidro-1,2-dimethylindol+perhidro-7-ethylindole (INDOLE-INDOLEH)	(Dong et al., 2019; Rao and Yoon, 2020; Li et al., 2024)
Phenazine /Tetradecahydrophenazine (PHEN-PHENH)	(Niermann et al., 2019a; Rao and Yoon, 2020; Li et al., 2024)
Carbon dioxide /Methanol (CO_2-MeOH)	(Byun et al., 2022; Niermann et al., 2019a,b)
1,2-dihydro-1,2-azaborine/1,2-BN-cylohexane (DAZ-DAZH)	(Niermann et al., 2019a; Zhu and Xu, 2015)

2.1. Prescreening stage

The aim of this step is to screen the best LOHCs candidates suitable for hydrogen storage from a process scale perspective. This stage, used to decide between the initial set of LOHCs, is based on the development of three indexes that consider economic, environmental and safety issues. Previously, a simplified flowsheet is used to compute

the basic yields and utility requirements. Based on this information, three indexes are calculated: economic, environmental and safety. The procedure for performing process analysis and calculating each index are described in the following and detailed in the Supplementary Material. The final results for each index are pair-represented graphically and the areas where all indexes are minimized, are considered the most beneficial for selecting LOHCs.

2.1.1. Process analysis

Before calculating each individual index, a simplified process analysis is required. The process is splitted into several sections. These include: intermediate temperature and pressure conditioning, reaction section, separation operations and storage. Each of these operations are included in a block flow diagram. For the analysis, a simplified flowsheet for the whole process, as depicted in Figure 1, is used. The process covers hydrogenation and dehydrogenation. The LOHC product from hydrogenation is the raw material for dehydrogenation and vice versa.

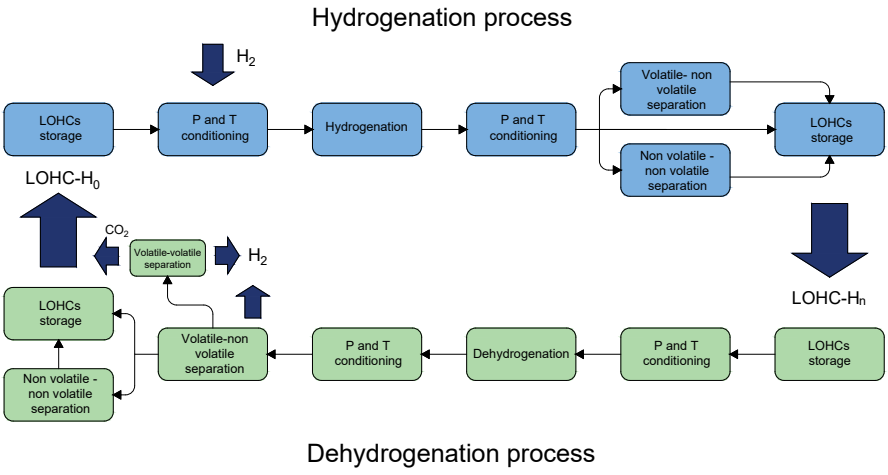

Figure 1: Simplified flowsheet for hydrogenation and dehydrogenation processes.

The inlet conditions for the raw materials are set. The hydrogen used in the hydrogenation comes from high pressure electrolysis operating at 80 bar and 333 K (Hancke

et al., 2022). The dehydrogenated and hydrogenated LOHCs are stored under ambient conditions (298 K, 1 bar), except for CO_2 (253 K, 20 bar). The reaction conditions, as well as the separation units used for each process system and any solvents required for hydrogenation (if required), are shown in Table 2. Likewise, the corresponding information for the dehydrogenation process is presented in Table 3. It is important to note that LOHCs must remain in liquid form under ambient conditions. Otherwise, hydrogen storage using LOHCs would not be feasible. Therefore, before estimating the utility consumption for each system, this condition must be assured. Different strategies are proposed to ensure LOHCs are liquid under ambient conditions:

1. If LOHCs are liquid under ambient conditions the use of solvents or any other compounds/strategies are not required. This is the case of DBT, TOL and MeOH.
2. If LOHCs are solid under ambient conditions a solvent may be used to maintain the mixture liquid. This is the case of NAP, PHEN and DAZ.
3. Finally, other strategies may be proposed for certain LOHCs which are solid under ambient conditions. For instance, the dehydrogenated form of NEC, is solid. However, the hydrogenated one is liquid. If the dehydrogenation conversion is below 90%, the LOHCs mixture can be maintained liquid (Brückner et al., 2014). 1,2-dimethylindole is also solid. However, according to Dong et al. (2019), it can form an eutectic mixture with 7-ethylindole to reduce the melting point.

Many authors consider the melting point and storage capacity to be relevant criteria for comparing LOHCs (Spatolisano et al., 2024; Brigljević et al., 2020). Regarding the melting point, its impact is already included in the calculations since feasible hydrogen storage is provided. The addition of solvents/compounds and/or reduction of conversions present several drawbacks. They reduce energy storage and energy efficiency or introduce species with higher toxicity and/or hazards. These actions impact on the calculations of the indexes proposed in the following. Similarly, the storage capacity of each LOHCs is considered. A lower storage capacity is penalized, as it leads to higher utility consumption. This is reflected in the economic and environmental indexes. Moreover, a larger amount of LOHCs combustible material stored, directly impacts the proposed safety index. Therefore, although indirectly, both the melting point and energy storage for each system have been taken into account for the LOHCs selection. However, please note that no threshold such as US DOE target, has been imposed as a hard constraint. This is within the objective aiming at the optimal trade-off (DOE, 2017).

The following step involves a simplified estimation of the utility and raw materials use. The assumptions for each process section are included in the subsequent points.

Table 2: LOHCs hydrogenation conditions in the prescreening stage.

System	Hydrogenation conditions	Process separations
(DBT-DBTH)	X= 1; 70 bar; 443 K; No solvent (Ali et al., 2022)	No separation, only storage.
(TOL-MET)	X= 1; 30 bar; 393 K; No solvent (Thomas et al., 2002)	No separation, only storage.
(NAP-DEC)	X= 1; 70 bar; 523 K (Park et al., 2002); 1.50 $mol_{Toluene}/mol_{NAP}$ (Niermann et al., 2019a)	No separation, only storage.
(NEC-NECH)	X= 1; 60 bar; 413 K ; No solvent (Wan et al., 2012)	No separation, only storage.
INDOLE-INDOLEH	X= 1; 70 bar; 443 K; (Dong et al., 2019; Chen et al., 2018) No solvent, 1,2-DMI:7-EI eutectic mixture 1:1	No separation, only storage.
(PHEN-PHENH)	X= 1; 50 bar; 388 K; 11.36 $mol_{dioxane}/mol_{PHEN}$ and 13.89 mol_{water}/mol_{PHEN} (Forberg et al., 2016)	Distillation stage to remove the hydrogenation solvent after the reaction since a different solvent is used in the dehydrogenation.
(CO_2-MeOH)	X= 0.33; 80 bar; 493 K; No solvent (Leonzio et al., 2019)	Flash unit (55 bar, 310 K) for MeOH and water separation from H_2 and CO_2. A recycle of the volatile compounds is done due to the low CO_2 conversions. Full fresh CO_2 conversion is achieved with the recycle.
(DAZ-DAZH)	X= 0.95; 10 bar; 353 K (Müller et al., 2012); 2.13 mol_{THF}/mol_{DAZ} (Niermann et al., 2019a)	No separation, only storage.

Intermediate temperature (t-cd) and pressure conditioning (p-cd). It refers to the utility demand required to adjust the pressure and temperature between sections. For the stream pressure conditioning, it is assumed that power requirements for gases are much higher compared to liquids. This is because liquids are considered to be incompressible. Hence, the energy required to increase the pressure of liquid streams is neglected. In the case of gases, it is recommended that the compression ratio at each stage does not exceed 4 (Couper et al., 2005). Hence, several stages with intermediate cooling operations are proposed. The temperature after cooling operations is adjusted to be the same in all cases. If gas or liquid stream demands from pressure reduction, a valve is installed. No operating cost is associated with it. The calculation of power and cooling demand for gas compressions along with other heating and/or cooling demands between other process units are detailed in the Supplementary Material.

Reaction section (rs). In this early stage, an isothermal reactor is assumed. Heat is provided/released in chemical reactions either they are endo- or exothermic. The calculations to estimate the utility demand on this operation are presented in the Supplemen-

Table 3: LOHCs dehydrogenation conditions in the prescreening stage.

System	Dehydrogenation conditions	Process separations
(DBT-DBTH)	X= 0.90; P_{atm}; 563 K; No solvent (Ali et al., 2022)	Flash unit (373 K) to separate H_2 and LOHCs.
(TOL-MET)	X= 0.95; P_{atm}; 593 K; No solvent (Okada et al., 2006)	Flash unit (273 K) to separate H_2 and LOHCs.
(NAP-DEC)	X= 0.95; P_{atm}; 553 K (Hodoshima et al., 2005); 1.50 $mol_{Toluene}/mol_{DEC}$ (Niermann et al., 2019a)	Flash unit (273 K) to separate H_2 and LOHCs.
(NEC-NECH)	X= 0.90; P_{atm}; 503 K; No solvent (Teichmann et al., 2011; Brückner et al., 2014)	Flash unit (373 K) to separate H_2 and LOHCs.
INDOLE-INDOLEH	X= 1; P_{atm}; 473 K; (Dong et al., 2019; Chen et al., 2018) No solvent, 1,2-DMI:7-EI eutectic mixture 1:1	Flash unit (373 K) to separate H_2 and LOHCs.
(PHEN-PHENH)	X= 1; P_{atm}; 463 K; 2.63 $mol_{diglyme}/mol_{PHENH}$ (Forberg et al., 2016)	Flash unit (298 K) to separate H_2 and LOHCs and distillation to remove the dehydrogenation solvent.
(CO_2-MeOH)	X= 0.84; P_{atm}; 373 K; 4 mol_{Water}/mol_{MeOH} (Fujita et al., 2015)	Flash unit (253 K) to separate H_2 from water and MeOH (recycled to reaction to achieve full conversion) and membrane to separate CO_2 and H_2 (6-8 bar (Martín, 2016)).
(DAZ-DAZH)	X= 1; P_{atm}; 353 K (Müller et al., 2012); 2.13 mol_{THF}/mol_{DAZH} (Niermann et al., 2019a)	Flash unit (263 K) to separate H_2 and LOHCs.

tary Material. These are based on the reaction conditions included in Tables 2 and 3. To simplify the calculations, it is assumed that LOHCs compounds do not evaporate. The evaporation is very likely especially during dehydrogenation reaction. However, this simplification helps avoid the complexity of liquid-vapor equilibrium calculations in the prescreening. Note, however, that LOHCs evaporation (and the heat requirements) are accounted for in the next stage of the methodology. Vapor pressures and Henry coefficients (for LOHCs and hydrogen respectively) are used to characterize the equilibria conditions as shown in the detailed model included in the Supplementary Material.

Separation operations (sep). After the reaction stage, some separation operations may be required. The utility demand for this stage is accounted for. There exist several options for these separations:

Volatile and non-volatile compound separations To separate compounds with high differences in volatility a flash stage is used. It operates at lower pressures and temperatures than the reaction. It is assumed that it can achieve complete separation.

The operating pressure is set with a valve and temperature adjusted with a cooling step. The heat demand is calculated using previous t-cd considerations. If the gas or liquid phases are recycled, further stream conditioning is required. The compression and heat exchange requirements are estimated from previous p-cd and t-cd assumptions. A flash stage is placed in dehydrogenation for all systems. The purpose is to purify hydrogen from the vapors of LOHCs and/or solvents. Moreover, a flash stage is included for the hydrogenation of CO_2 to condensate methanol and water and to recycle H_2 and CO_2 back to the reactor.

Non volatile and non volatile compound separations If two or more heavy compounds show similar volatility, an atmospheric distillation may be regarded a potential solution. However, the use of distillation is highly inefficient for the LOHCs technology (Niermann et al., 2019b). Therefore, distillation is never proposed as an option for LOHCs hydrogenated and dehydrogenated species separation. Incomplete conversions are allowed in all cases (except for CO_2-MeOH system as easy separation is possible in a flash stage). As a result, distillation is only indicated for those cases where it becomes the last option. The only situation where distillation is considered, is the PHEN system (as shown in Tables 2 and 3). This is because different solvents are used in hydrogenation and dehydrogenation. It is expected to be highly inefficient from the beginning, but in any case, it can be confirmed after the calculation of the different indexes. To estimate the consumption of utilities, sharp component separation is assumed. First, the inlet temperature to the column is adjusted to the saturation point of the mixture. It can be estimated based on an average saturation point. Previous t-cd equations are applied. Then, additional expressions are included in the Supplementary Material to account for the condenser and reboiler utility demand.

Volatile and volatile compound separations When there exists a mixture of gases (e.g., CO_2,H_2), membrane technology is proposed. If compression is required to reach the operating conditions, p-cd assumptions are applied. This technology is only considered for the removal of gases. In any case, it is used to remove vapors coming from volatile compounds evaporation (toluene, methanol, THF,...). Therefore, this separation technology is only applied in the dehydrogenation of the CO_2-MeOH system. It is used to purify the H_2 from the CO_2 once all methanol is condensed in a previous flash stage.

No separation required and/or product storage In those situations where no further separation is needed, only adjusting to storage conditions is required. This point also applies to situations in which separation has already taken place. Hence, to ad-

just the pressure, either a valve (when it is reduced) or compressors, considering p-cd assumptions, are used. The utility demand for the heating/cooling operations is calculated based on t-cd considerations.

Raw material demand. Theoretically, no reactant loss occurs inside the studied system. The LOHCs compounds and solvents may be recycled back between hydrogenation and dehydrogenation. In practice, some raw material losses may appear. There exist several reasons for that: LOHCs degradation between cycles, volatilization or other inefficiencies. Ideally, a specific loss factor should be assigned for each studied system. Nevertheless, there exists a lack of information for most of the LOHCs of study. Thus, a typical value of 0.1% wt., attributed to LOHCs losses in the NEC system, is considered to estimate the demand of fresh raw material for every eligible system. This approach has been used in other studies (Niermann et al., 2019b; Hurskainen and Ihonen, 2020). Some authors report higher LOHCs losses in heterocyclic systems (such as NEC) compared to homocyclic LOHCs (DBT) (Brückner et al., 2014). Since the material loss factor is based on the NEC system, the LOHCs replacement in homocyclic systems (DBT, TOL, NAFT) may be overestimated (conservative scenario for homocyclic compounds). However, in spite of that, the material losses (as regarded in the results) are not expected to have a major impact in the index calculations if the purchase prices are not considerably higher compared to other LOHCs candidates. In any case, to ponder the differences in the material losses, an optimistic scenario (no material losses) for the impaired systems (e.g. homocyclic compounds) can be used to see if there exists a great difference in the final selection. This approach has been used in the indexes calculation. Moreover, 0.1% wt. losses are also considered for hydrogen in the prescreening as done in Niermann et al. (2019b). This is due to the absorption of hydrogen in the liquid phase during hydrogenation at high pressures. The catalyst cost is not accounted for on this stage. This is because no reliable estimation is possible yet. Rigorous reactor modelling or industrial information would be required for this purpose. At this point, only kinetic expressions or reaction rates based on laboratory conditions are available for LOHCs systems. However, this is not enough, since for these conditions, transfer phenomena are negligible (Wan et al., 2013). Based on the experience from industrial units, these phenomena may represent the controlling step for the reaction (Roininen et al., 2009). Therefore, the results from the laboratory conditions are not enough since these do not include the effect of the transfer phenomena. Different, the catalyst cost is considered in the detailed process optimization. This is because, in this case, transfer phenomena and other relevant reactor design considerations (e.g., aspect ratios, pressure drop, gas sparger and heat exchange devices design) are taken into account. For that purpose, rigorous reactor assessment is considered to model the reactors (Prieto et al., 2023).

2.1.2. Economic index (EI)

This index assesses a simplified operating costs of the process for each eligible option. A simple estimation of the utility and raw material costs is performed. The unitary prices (p) for both are taken from the literature The demand for each utility k at each unit operation op and for each raw material j (F_{RM-j}) is calculated from the previous simplified process analysis section. The utilities are essentially the power requirements to compress gases (W) and the heating/cooling demands ($Q_{op}^{u_k}$). The total operating costs are normalized by the quantity of the final product (FP). It results in the calculation of EI as presented in Equation (1).

$$EI = \frac{\sum_{j=1}^{J}\left(F_{RM-j}\cdot p^{RM-j}\right)+\sum_{k=1}^{K}\sum_{op=1}^{OP}\left(Q_{op}^{u_k}\cdot p^{u_k}+W_{op}\cdot p^{power}\right)}{FP} \tag{1}$$

The prices for the process utilities together with other parameters are collected in Table 4. High pressure (HP) steam and hot oil are used for heating purposes. They are generated in a boiler and a fired heater respectively with natural gas (NG). The fuel cost and the combustion emissions are also accounted for. For cooling purposes, cooling water or boiling water are used for high-medium temperature (HMT) applications. The costs and emissions for this refrigeration include the pumping power, fresh water and the chemicals used to treat water. Ammonia is proposed for low temperature applications (LT). The costs and emissions linked to this utility are estimated based on the power and cooling requirements for a closed refrigeration loop. Finally, the prices for all LOHCs compounds and solvents are included in the Supplementary Material.

2.1.3. Environmental index (ENI)

This index provides a preliminary estimation of the environmental burden of each candidate system. Therefore, simple environmental indicators are considered. Two metrics are used. The first one is a simplified Global Warming Potential (GWP). It is based on the utilities calculation from the simplified process analysis through Equation (2). There, EF represents the emission factor for each utility. These are included in Table 4. Then, the GWP is normalized between 0-1 with Equation (3) considering the emissions from all eligible options. Since some LOHCs systems are at an early stage of development, no reliable information is found to estimate raw material emission factors. Then, this contributor is not included in this index.

$$GWP = \frac{\sum_{k=1}^{K}\sum_{op=1}^{OP}\left(Q_{op}^{u_k}\cdot EF^{u_k}+W_{op}\cdot EF^{power}\right)}{FP} \tag{2}$$

Table 4: Utilities parameters for LOHCs selection.

NG price (European Commission, 2023)	50 €/MWh
NG emissions (Gómez and Watterson, 2008)	0.202 ton CO_2/MWh
Boiler efficiency (Sinnott and Towler, 2020)	90%
Fired heater efficiency (Sinnott and Towler, 2020)	85%
HP steam price (calculated from (European Commission, 2023; Sinnott and Towler, 2020))	57.89 €/MWh
HP steam emissions (calculated from (Gómez and Watterson, 2008; Sinnott and Towler, 2020))	0.224 ton CO_2/MWh
Hot oil price (calculated from (European Commission, 2023; Sinnott and Towler, 2020))	58.82 €/MWh
Hot oil emissions (calculated from (Gómez and Watterson, 2008; Sinnott and Towler, 2020))	0.238 ton CO_2/MWh
Electricity price (European Commission, 2024)	150 €/MWh
Electricity emissions (Red Eléctrica, 2023)	0.15 ton CO_2/MWh
Cooling water power demand (Sinnott and Towler, 2020)	0.53 kWh/m^3_{cycle}
HMT cooling price (calculated from (Sinnott and Towler, 2020; European Commission, 2024))	7.25 €/MWh
HMT cooling emissions (calculated from (UK Government, 2023; Sinnott and Towler, 2020; Red Eléctrica, 2023)	0.009 ton CO_2/MWh
LT cooling energy demand (Luyben, 2017)	(0.714 MWh_{elec}+1.714MWh_{cool}) /MWh
LT cooling price (calculated from (Luyben, 2017; European Commission, 2024; Sinnott and Towler, 2020))	83.82€/MWh
LT cooling emissions (calculated from (Luyben, 2017; UK Government, 2023; Sinnott and Towler, 2020; Red Eléctrica, 2023))	0.107 ton CO_2/MWh
LOHCs and solvent losses (Niermann et al., 2019b; Hurskainen and Ihonen, 2020)	0.1% wt.
Hydrogen losses (prescreening) (Niermann et al., 2019b)	0.1% wt.

$$GWP_{norm} = \frac{GWP - GWP_{min}}{GWP_{max} - GWP_{min}} \tag{3}$$

Moreover, the NH factor from NFPA 704 rule is also considered (NFPA, 2022). This indicator measures the human health hazard from a compound. It ranges from 0 to 4. Hence, it is divided by a 4 factor and normalized from 0 to 1.

Finally, both metrics, GWP and NH factor are considered for the calculation of the ENI in Equation (4). Note this index favors the options showing lower toxicity and utilities use.

$$ENI = GWP_{norm} + \frac{NH}{4} \tag{4}$$

2.1.4. Safety index (SI)

To assess the safety of the process, the Dow's Fire and Explosion Index ($F\&EI$) (AIChE, 1994) is calculated for each process operation. This is usually applied to already built equipment. However, with some general assumptions, it is regarded as a useful tool to evaluate safety differences even at this early stage. The operations covered for each eligible option involve: the storage tanks for each hydrogenated and dehydrogenated compound (and if required for the solvents), the hydrogenation and dehydrogenation reactors, the heating and cooling operations before and after each reaction and all the separation operations detailed in Tables 2 and 3. The calculation procedure for the $F\&EI$ is briefly explained in this section. Note, however, that additional considerations are required for its calculation. These are further detailed in the Supplementary Material.

To obtain the $F\&EI$ for each operation, several factors must be previously calculated. These are the Material Factor (MF) and F_1, F_2 and F_3 factors. MF is linked to each substance and can be found either tabulated in Dow's $F\&EI$ Guide (AIChE, 1994), or be estimated according to NF and NR factors from NFPA 704 (NFPA, 2022). In both cases, it is usually referred to standard conditions. However, a correction may be needed depending on the process unit conditions. Further explanation can be found about it on the Dow's $F\&EI$ Guide (AIChE, 1994). As a general rule, for each unit, the highest MF from the compounds present, is considered.

Then, F_1 is to be calculated from a series of penalties ($P_{F_1,p}$) according to Equation (5). At this point, indoor process units, access and drainage and spill control penalties are discarded. It is assumed that all eligible options are on equal conditions and comply with the requirements to avoid these penalties. It allows to remove them from the estimations, due to the lack of information at this stage.

$$F_1 = 1 + \sum_{p=1}^{P} P_{F_1,p} \tag{5}$$

In the same way, F_2 is obtained from Equation (6), where $P_{F_2,p}$ represents the penalties for this factor. In this case, the process does not include operations with subatmospheric pressures, low temperatures or dust handling. Therefore, these penalties are not considered. Similarly, the hazards linked to fired equipment are not accounted for. It is assumed that the other process units are far enough to discard this penalty. Additionally, the penalties associated to the rotating equipment are neglected considering

that compressors and pumps will not surpass the threshold stablished in the guide.

$$F_2 = 1 + \sum_{p=1}^{P} P_{F_2,p} \tag{6}$$

Finally, F_3 is calculated in Equation (7) and the $F\&EI$ in Equation (8).

$$F_3 = F_1 \cdot F_2 \tag{7}$$

$$F\&EI = MF \cdot F_3 \tag{8}$$

The safety index (SI) is calculated using Equation 9. There, n_{OP} represents the total number of operations. It aims to represent the hazards linked to the entire process (storage, reaction, separation), and not only the risks linked to one specific section. Note also that different process configurations exist between the candidates. Therefore, in order to present a general index, the average $F\&EI$ of all the operations is considered.

$$SI = \frac{\sum_{op=1}^{OP} F\&EI_{op}}{n_{OP}} \tag{9}$$

2.2. Detailed analysis of LOHCs systems

In the first stage a reduced number of candidates is preselected. Then, a more detailed simulation and optimization is carried out with the most promising options. This problem is formulated as a Non Linear Programming (NLP) problem. This approach allows to propose a high-detail level process superstructure with two potential reaction technologies and several utilities available. The selection of these technologies is based on the flows determined by the optimization procedure. Moreover, more rigorous modelling is performed for each operation. Hence, it is possible to identify the best alternatives in the superstructure and assess how design and operation variables for each equipment impact on the storage costs. These costs are optimized for the hydrogenation and dehydrogenation processes together. They include the operating and the annualized investment costs. Finally, a techno-economic analysis is conducted for each of the LOHCs selected.

2.2.1. Detailed process description

The flowsheet from Figure 1 presents a general scheme for LOHCs hydrogenation and dehydrogenation. Although simple, it accounts for a variety of combinations of LOHCs features: different separations, liquid or gaseous reactants, solvent removal or

reaction in liquid or gas phase among others. However, a more detailed process design is required for a proper process analysis and to uncover potential heat integration opportunities. Therefore, a more specific process superstructure including detailed reactors technology is proposed for the two LOHCs systems selected in the prescreening. These are NEC and INDOL systems (see Results: LOHCs preselection section). For that purpose, the specific LOHCs characteristics are taken into account. Both NEC and INDOLE are liquid reactants, that do not require solvent nor specific separation operations (except from hydrogen and LOHCs separation) and react in the liquid phase in the hydrogenation and dehydrogenation. To propose a process superstructure for these systems, the hydrogenation and dehydrogenation processes for similar LOHCs can be used. Dibenzyltoluene has these same characteristics as NEC and INDOLE systems. The physical implementation for dibenzyltoluene is presented in Eypasch et al. (2017). Therefore, this setup can be considered as the starting point for NEC and INDOLE process design. Several areas can be distinguished there: hydrogenation and dehydrogenation reactions, reactant pumping and preheating (with the product outlet from reactor) and final cooling of hydrogen. Note that if any other LOHC with different characteristics is selected, this setup can be also considered as a basis. All candidates require the operations mentioned above (e.g., reaction, heating, hydrogen cooling). Then, only minor differences between flowsheets are expected even the LOHCs characteristics change.

The core units of the process are the reactors. Different from the process flowsheet, some differences can be found in the reaction technology (two or three-phase reactors). Both NEC and INDOLE systems use heterogeneous catalysts. Hence, the reactors for these systems will be three-phase reactors. Two reaction technologies are proposed to perform hydrogenation process. These are slurry and trickle bed reactors. They are placed in a series configuration based on similar systems in literature. A potential combination of slurry and fixed bed reactor is found in Zehner and Kraume (2000) for the hydrogenation of aromatic compounds. The reactions are in the liquid and gas phase in the slurry and fixed bed respectively. A plug-flow behavior can be assumed to fixed bed reactors and trickle bed reactors (Jakobsen et al., 2002; Iliuta and Larachi, 2016). Hence, in the LOHCs three-phase system, trickle may substitute fixed bed to complete the chemical reaction. Since no reported information exists about industrial reactors for NEC and INDOLE systems, a reactor design based on similar species is considered as valid. There exist other reactor configurations as shown in García et al. (2024). However, it is interesting to explore this configuration as well. According to previous work in Prieto et al. (2023), slurry systems present higher catalyst yields compared to trickle beds and their behavior can be close to perfect mixture and plug-flow respectively. Therefore,

it makes sense to place first the slurry reactor and then the trickle bed. Note that with the proposed NLP model, both reaction technologies can be placed in the hydrogenation superstructure. However, it is possible to discard one of them based on the optimization of the costs. Moreover, the potential combination of slurry and trickle is also extended to the dehydrogenation process. Likewise, this selection of reaction technologies is done in the dehydrogenation as well. In both processes, these reaction units are modelled developing surrogate models from a rigorous reactor assessment. These include not only kinetics but also mass, heat and momentum transfer (Prieto et al., 2023).

The process flowsheets for hydrogenation and dehydrogenation are included in Figures 2 and 3 respectively. Differently from the previous step process analysis, a detailed diagram is presented. Furthermore, other relevant differences are found with respect to the previous stage: more detailed modelling of the units, different process configurations (e.g., stream recycle), heat integration or liquid-vapor equilibria are introduced as modelling features among other differences. Further information about the modelling for each process unit is included in the Supplementary Material.

The same inlet conditions as for the screening stage are considered for the hydrogen and the LOHCs in the hydrogenation section, see Figure 2. The first reaction unit to perform the hydrogenation is the slurry reactor (R-01). The pressure for LOHCs is adjusted to the operating conditions of the reactor with pumps (PU-01). In the case of hydrogen, the pressure is set with valves as it comes from high-pressure electrolysis. Then, several heat exchange operations are included in the flowsheet for the LOHCs (HE-07 to HE-09) and hydrogen streams (HE-01 to HE-03) They adjust the temperature before the slurry reactor. After the reaction, the two output streams, liquid and gas, are separated in a flash (FL-01). Both can be recycled back or sent to the second reactor, the trickle bed (R-02). The slurry recycle adjusts its pressure in a compression stage (CP-01), while the streams directed to trickle bed modify the pressure with valves. The trickle bed can receive hydrogen either from a fresh stream, which is preheated (HE-05 and HE-06), or from the slurry reactor. Finally, both streams are mixed, and the temperature is adjusted to the inlet of the trickle bed (HE-10). Similarly, the LOHCs adjust their temperature in a heat exchanger (HE-12). After the trickle, the gas and liquid streams are separated in a flash (FL-02). These can be used eventually as recycle streams after compression stages (CP-02 or PU-03).

Finally, a LOHCs stream product, mostly hydrogenated, can be obtained from each of the reactors. It is sent to be stored, but previously, it is possible to recover energy from this stream. Therefore, it is used to preheat the raw material (HE-02, HE-06 and HE-08). Then, a final expansion and cooling step (HE-13) are carried out to release hydrogen that may be absorbed in the liquid phase in a flash unit (FL-03). It may be recycled back

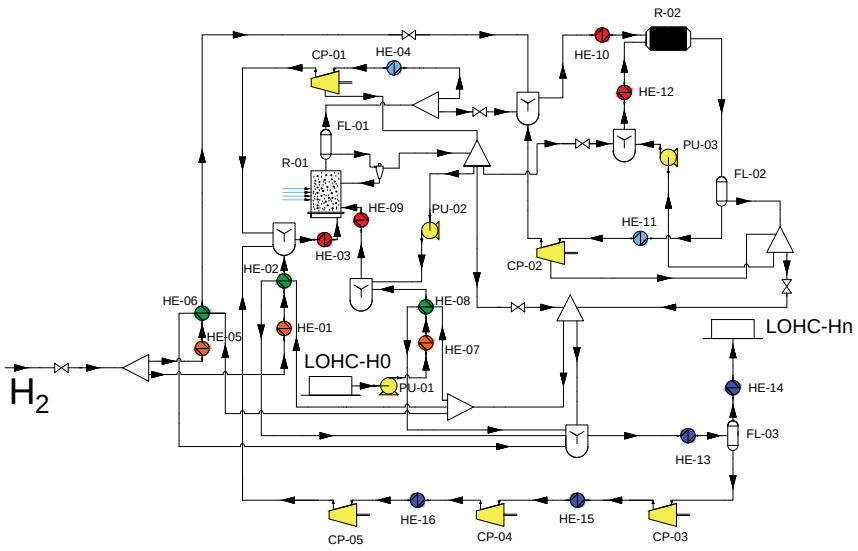

Figure 2: Detailed hydrogenation flowsheet. The external utilities used in this process are: power (yellow), high pressure steam (red) and cooling water (dark blue). Low pressure steam is also produced from boiling water as utility (light blue) before the compression stages and in the slurry reactor (3 bar). The low-pressure steam generated in the slurry is used in some heat exchangers (orange). Furthermore, some heat integrations (green) are proposed.

to the process before a compression in several stages with intercooling (CP-03 to CP-05).

The dehydrogenation process is very similar, see Figure 3. First, the pressure and temperature of the reactants are adjusted to the conditions of the slurry dehydrogenation reactor (R-03). The hydrogenated LOHCs are pumped (PU-04) to the slurry reactor operation pressure and the temperature is adjusted to the reaction conditions in a train of heat exchangers (HE-17 to HE-19). Hence, the LOHCs are fed to the slurry dehydrogenation reactor. Then, after gas-liquid separation in a flash vessel (FL-04), the partially dehydrogenated liquid is either recycled, sent to the trickle bed or stored. The benefits of using a gaseous stream in terms of heat and mass transfer enhancement on dehydrogenation reactors are shown in other works (Prieto et al., 2023). Therefore, a gaseous stream is introduced in both units. The slurry receives it from a recycle, whereas the hydrogen to be introduced in the trickle comes from a potential recycle and/or hydrogen released in the slurry. The pressure and temperature between reaction stages and recycles are adjusted to their respective operating conditions with compressors (CP-06 or

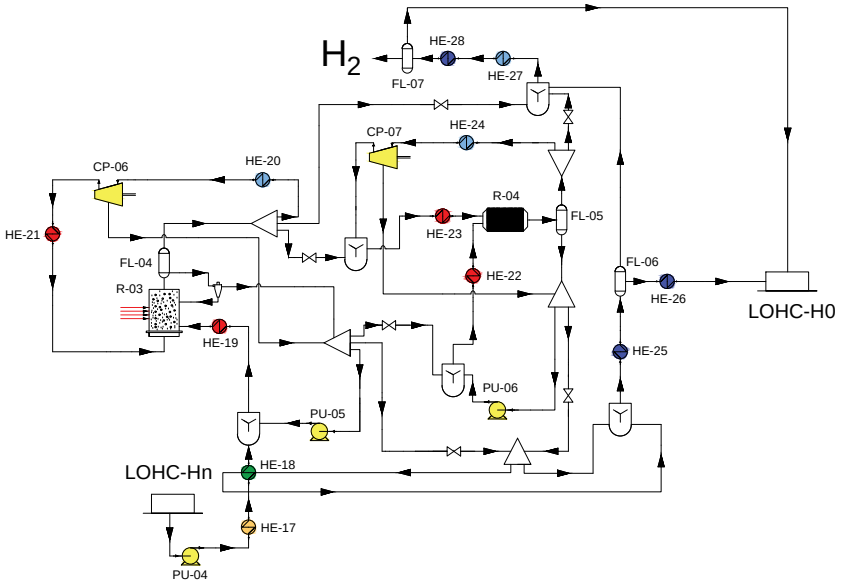

Figure 3: Detailed dehydrogenation flowsheet. The external utilities used in this process are: power (yellow), high pressure steam (red) and cooling water (dark blue). Low pressure steam is also produced from boiling water as utility (light blue) before the compression stages (1 bar) and is used in some heat exchangers (orange). Furthermore, some heat integrations (green) are proposed.

CP-07) or pumps (PU-05 or PU-06) and heat exchange devices (HE-21, HE-22 and HE-23) respectively. Finally, the dehydrogenated product is stored and used for raw material preheating (HE-18). Then, the remaining hydrogen is released on a flash separation step (FL-06) and together with the hydrogen coming from the reactors is purified in a final gas-liquid separation operation (FL-07). Thus, the LOHCs that remain in the gas phase as impurities are removed. This is done to provide high hydrogen purity, which is required for some of the most promising applications for hydrogen. These may involve: electricity generation in fuel cells, hydrogen as raw material (e.g., methanol, ammonia, refining), high temperature heat (e.g., steel, glass, cement) or residential heating (Griffiths et al., 2021).

Several utilities are used for both processes. Compressors and pumps require electricity. To provide cooling for the heat exchangers and reactors, several options are possible. To refrigerate streams in a lower temperature range, cooling water is used. For refrigeration at higher temperatures, boiling water is considered to remove the heat, and as a result, low pressure steam is generated. Therefore, this is considered for plant heat

integration and used in heating applications. In the hydrogenation process, this steam is generated in the slurry hydrogenation reactor and then used in the process. In the case of dehydrogenation, a lower pressure steam is produced from the refrigeration before high temperature compression stages. Although steam is also generated before high pressure compressors in the hydrogenation stage, it is not considered for heat integration. This is because the heat demand is already covered from the steam from the slurry, and it has lower temperature. High pressure steam is also available to provide heat at higher temperatures and it is either purchased or generated in the plant as utility. No heat integration is considered between hydrogenation and dehydrogenation processes. The difference in periods for the operation of each one and the possibility to separate both stages in case of different locations are selected, are the main reasons for that.

2.2.2. Process optimization

The detailed superstructure described above is formulated as an equation-based model for process optimization. The hydrogenation and dehydrogenation reactors are modelled using surrogate models. The procedure to develop these surrogates based on rigorous reactor assessment is presented in previous work (Prieto et al., 2023). The mass, heat and momentum transfer are taken into account. Moreover, the mass and energy balances are also performed for other units (e.g., heat exchangers, pumps, compressors, flash separators). The equations used to model each unit are detailed in the Supplementary Material. The utilities consumption (steam, cooling water, electricity) can be computed from them. Cost correlations are also included in the model for each individual equipment. Hence, an NLP is formulated in a General Algebraic Modelling System (GAMS). The parameters for the optimization include the operating conditions for each stream (e.g., temperature, pressure, enthalpy, flowrate), equipment parameters, investment cost for each unit and utilities consumption. The total storage cost, covering the operating and the annualized costs for both hydrogenation and dehydrogenation processes, represents the objective function of the optimization. However, it is possible to disaggregate the costs for hydrogenation and dehydrogenation processes, in the case of different locations are selected to install each one.

2.2.3. Techno-economic analysis

Finally, a techno-economic analysis is performed for both sections of the process (hydrogenation and dehydrogenation). This is done according to the factorial method proposed by Sinnott and Towler (2020). First, the fixed capital cost is calculated based on the purchase cost of the equipment as detailed in the Supplementary Material. For a process where only fluids are present, the inside battery limit (ISBL) investment can be roughly estimated as 330% of the equipment cost. Then, the offsites (OSBL) (30% ISBL),

engineering and construction costs (30% ISBL+OSBL), and the contingency charges (10% ISBL+OSBL) are obtained. Moreover, the working capital is also estimated as 15% of ISBL + OSBL. The sum of all these contributors represents the total capital cost of the process. It is annualized for a 20 years project with an interest rate of 15%.

With regards to the production costs, these are divided into variable and fixed. For the variable costs, utilities and fresh raw materials are the only contributors. Relevant parameters for the calculation of them are already summarized in the Table 4. The LOHCs used as fresh raw material are estimated as in the prescreening. This is because LOHCs degradation, for instance, cannot be accounted for using mass balances. However, the hydrogen losses are estimated from them. For the fixed operating costs, Green and Perry (2008) expression is used to estimate the labor. Other contributors (overhead, maintenance, ...) are calculated based on Sinnott and Towler (2020) assumptions.

3. Results

The proposed two stage methodology is used for the selection and optimization of LOHCs among the ones included in the Table 1. Note that this methodology may be extended to other LOHCs systems. First, the most promising candidates are selected based on the three indexes proposed. Then, these systems are considered for the optimization of the hydrogenation and dehydrogenation processes.

3.1. LOHCs preselection

The first step in the selection is based on the simplified process analysis by the preliminary calculation of the utilities demand and the process performance indexes. The utilities consumption results for each system are included in the Table 5. The highest operating temperatures and/or reaction enthalpy in dehydrogenation results in higher heat demand. Additionally, in some cases, hot oil is demanded to avoid thermal crossover. Similarly, the presence of compounds with a high volatility in certain LOHCs systems (TOL, NAP, DAZ and MeOH), require lower temperatures to separate the components from hydrogen. Therefore, these use ammonia as utility for this purpose (LT cooling). The results show a considerably higher energy demand for the PHEN system compared to the other candidates. This is mainly due to the distillation, which is highly inefficient for the process. Additionally, electricity use increases in those cases where gas compression is required (MeOH).

With the utility demand, the economic, environmental and safety indexes are calculated. These are included in Table 6, and they are pair-represented in Figures 4, 5 and 6. The aim of this work is to identify the LOHC systems which minimize the operating costs, the environmental impact and the process hazards. Then, the most favorable

Table 5: Utility demand for each LOHC system in kWh/kg_{H_2}.

System	HP Steam	Hot oil	MHT cooling	LT cooling	Electricity
(DBT-DBTH)	3.86	10.21	13.90	0.00	0.00
(TOL-MET)	4.62	10.96	15.99	0.30	0.00
(NAP-DEC)	10.16	10.66	21.65	0.50	0.00
(NEC-NECH)	10.66	0.00	10.50	0.00	0.00
(INDOLE-INDOLEH)	11.97	0.00	11.81	0.00	0.00
(PHEN-PHENH)	24.05	22.09	46.28	0.00	0.00
(CO_2-MeOH)	8.02	0.00	11.95	1.46	2.00
(DAZ-DAZH)	7.83	0.00	7.98	0.96	0.00

candidates are found in the lower-left section of the representations. In contrast, the upper-right area includes the worst options obtained with this methodology. Note that the results for the PHEN system (EI and ENI), are clearly higher compared to the other alternatives. Therefore, as it seems an uncompetitive option, it is not represented in the Figures 4, 5 or 6. This is done to show better the differences between the other eligible systems. It confirms the fact that using two different solvents between stages is highly limiting.

Table 6: Index calculations for each LOHC system.

System	EI ($/$kg_{H_2}$)	GWP (kg CO_2/kg_{H_2})	NH	ENI	SI
(DBT-DBTH)	1.00	3.41	1	0.41	51.56
(TOL-MET)	1.06	3.81	2	0.71	79.59
(NAFT-DEC)	1.42	5.05	2	0.84	82.57
(NEC-NECH)	0.74	2.48	1	0.31	43.95
(INDOLE-INDOLEH)	0.82	2.79	0	0.09	42.34
(PHEN-PHENH)	3.47	11.04	2	1.50	68.10
(CO_2-MeOH)	0.92	2.36	3	0.80	63.61
(DAZ-DAZH)	2.00	1.93	3	0.75	77.13

From the Figures (4-6), it is shown that only two LOHCs systems fall into the lower-left region in all cases. These are the NEC and INDOLE systems. Some facts have made these options to be the most favorable: mild reaction conditions, moderate toxicity, non-flammable compounds, no solvent required or low volatility of the compounds involved. These features are some of the most desirable characteristics for the LOHCs used in the hydrogen storage as reported in the literature (Abdin et al., 2021; Niermann et al., 2019a). Note however that these systems are not demonstrated yet at industrial scale and consequently the catalyst stability in the long term has not been tested. In spite of that, the hydrogenation and dehydrogenation catalyst stability for these or similar compounds has been evaluated in different works. These results are limited to the laboratory scale for several cycles (Fan et al., 2024; Xue et al., 2021; Lee et al., 2023; Huang et al., 2023). However, the results on this work suggest that it is interesting to

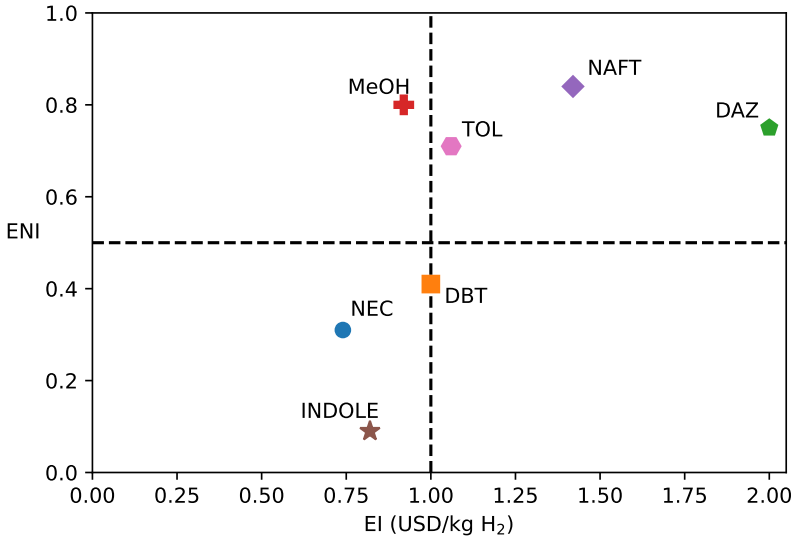

Figure 4: Representation of economic and environmental index results.

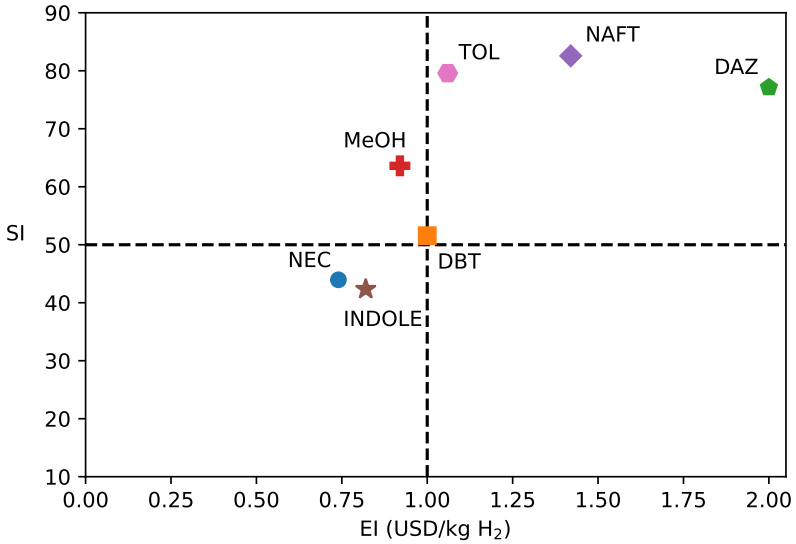

Figure 5: Representation of economic and safety index results.

evaluate these specific LOHCs systems in more detail. These favorable results combined with continuous research, may favor the development of better catalysts for these LOHCs systems.

At this point, it is possible to continue with the second stage of the methodology.

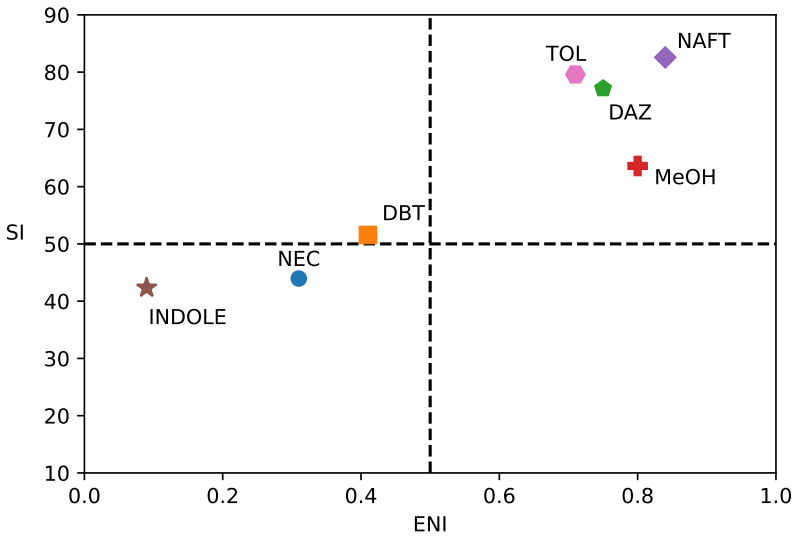

Figure 6: Representation of environmental and safety index results.

The mass and energy balances are performed using a more detailed formulation as presented in this work (LOHCs detailed process optimization). Then, if the results from this conceptual study are still promising, it may represent an interesting opportunity to gradually evaluate these systems more in depth (equipment scale-up, accurate thermodynamic information, laboratory or pilot plant testing deployment). If any limitation is found in any of these stages, these LOHCs can be then discarded. Note that the aim of this methodology is to limit the number of candidates that reach these subsequent stages (considerably more expensive and time-consuming). In any case, it is also reasonable to expect a considerable time delay between conceptual studies and potential implementation. For example, TOL system was proposed in the early 80's and after a few decades, proposed for demonstration projects (Rao and Yoon, 2020; Niermann et al., 2019a). Then, both NEC and INDOLE may follow a similar path for future implementation.

In contrast, other options such as TOL and NAP systems seem to be unattractive. This is due to the high energy demand, combined with high operating temperatures and the toxicity and flammability of the species involved. The DAZ system presents mild reaction conditions and low energy requirements compared to the other alternatives. However, the high raw material costs, together with the toxicity and hazards that introduce the solvent, penalize this option considerably. Some intermediate options also appear. For instance, MeOH shows competitive costs. However, it seems less convenient from a safe point of view and presents higher environmental impacts when

compared to the other LOHCs. Finally, DBT is regarded as a promising option as it is one of the safest LOHCs and the costs and the environmental impacts are moderate. Nevertheless, the higher thermal energy demand together with the use of less efficient utilities, make this option to be less favorable than NEC or INDOLE systems.

It is also interesting to compare the results from the EI for the homocyclic compounds if no material losses exist. The differences between the conservative scenario (similar LOHCs losses than heterocyclic compounds) and this assumption, represents a difference between 2-7% on the value of EI, which is within the error of estimation. However, it has no effect in the final decision of the LOHCs selection. The only LOHC system which is clearly affected in the EI calculation because of material losses is DAZ (heterocyclic compound). If this contribution is removed, the EI could be competitive with other alternatives. This occurs mainly because the price is two orders of magnitude higher compared to other systems. Then, for these situations, if necessary, the methodology could be adapted for different material losses scenarios. However, in this case, similar material losses as for NEC are expected because DAZ is a heterocyclic compound. This, together with the higher environmental and safety impacts, makes DAZ system to be discarded for the next stage of the methodology. Finally, the economic costs contribution from raw material losses in the PHEN system, although lower, are also relevant. However, in this case, the EI is still much higher than other candidates even if material losses are removed. This is due to the inefficiencies of the process and the higher utilities use.

3.2. LOHCs detailed process optimization

From the previous step, the selection methodology suggests that NEC and INDOLE systems may be potential LOHCs options for the storage of hydrogen. Hence, the entire hydrogenation and dehydrogenation coupled process is optimized for them. The most representative variables for this optimization are shown in Table 7 for an intermediate capacity of 25.92 ton H_2/d (0.15 kmol H_2/s). This plant size is within the typical range presented in the literature (20-60 ton H_2/d) (Reuß et al., 2017; Niermann et al., 2019b; Weichenhain, 2021).

The thermal energy use is the most relevant energy contributor for the process. The energy integration has reduced by 18-25% from the prescreening stage. The NEC continues to be less energy intensive if compared to INDOLE. This is mainly attributed to the inherent characteristics of each LOHC system (e.g., reaction enthalpy, specific heat, storage capacity). The energy use results obtained from this LOHCs technology are put in perspective with other LOHCs studies and hydrogen storage alternatives. The energy use and efficiency for each storage process are used for comparison purposes. Some results from other works are shown in Table 8.

Table 7: Optimization results from the entire process (hydrogenation and dehydrogenation).

System	EC	INDOLE
Hydrogen storage capacity (ton H_2/d)	25.9	25.9
Thermal energy use (kWh/ kg H_2)	8.95	$1.08 \cdot 10^{1}$
Cooling (kWh/ kg H_2)	1.68	3.13
Electricity use (kWh/ kg H_2)	$2.67 \cdot 10^{-1}$	$2.94 \cdot 10^{-1}$
Storage efficiency* (%)	72.3	66.6
Steam cost (M$/y)	2.16	2.62
Cooling cost (M$/y)	$5.77 \cdot 10^{-2}$	$1.07 \cdot 10^{-1}$
Electricity cost (M$/y)	$1.35 \cdot 10^{-1}$	$1.08 \cdot 10^{-1}$
Raw materials cost (M$/y)	$2.38 \cdot 10^{-1}$	$2.91 \cdot 10^{-1}$
Total operating cost (M$/y)	4.30	4.62
Equipment cost (M$)	5.17	3.95
Total investment (M$)	$3.26 \cdot 10^{1}$	$2.49 \cdot 10^{1}$
Annualized investment (M$/y)	5.22	3.98
Hydrogen storage cost ($/kg H_2)	2.01	1.82
Hydrogen storage emissions (kg CO_2/kg H_2)	1.85	2.24

*The storage efficiency is calculated based on the hydrogen LHV and accounts for the thermal and electrical energy use in the process.

In the case of LOHCs technology, the values reported for thermal energy in Reuß et al. (2017) or Eypasch et al. (2017) are similar to those obtained in this work. However, for electrical energy, some differences are found in the literature. In this work, the main power demand, very similar between both systems, is attributed to the hydrogen recycle streams. These contributors are not included in other studies. For instance, Eypasch et al. (2017) only accounted for LOHCs pumping. Finally, the cooling demand has dramatically decreased compared to the previous step. The energy integration is the main reason for that. Some energy use differences can be found with other storage technologies. Hydrogen compression is less energy intensive, whereas liquefaction offers a wide range for electricity use. Therefore, they may represent an attractive option for hydrogen storage. However, the storage and transportation for both present restrictive pressures and/or temperatures compared to LOHCs, which allow for ambient conditions. Another area of concern is the investment costs. The major contributors are the pressure storage tanks (0.70-0.85 MM$/t) and the equipment used during the liquefaction (2.10 MM$/(t/day)) respectively (Abdin et al., 2021; Reuß et al., 2017). From this work, the LOHCs require an investment of 0.96-1.26 MM$/(t/day) for the proposed capacity. Other technologies such as metal hydrides present also promising storage efficiencies. However, some drawbacks as slow kinetics or low conductivities are reported (Abdin et al., 2021).

With regards to the total production costs, the main contributor for utilities is the steam used in the dehydrogenation process (75-85%). As a result, the heating utility

Table 8: Energy use and hydrogen efficiencies for different hydrogen storage technologies.

Storage technology	Energy use/efficiency	Source
LOHCs	Hydrogenation and dehydrogenation: 8.95-10.84 kWh/kg H_2 (thermal). 0.27-0.29 kWh/kg H_2 (electrical).	This work
LOHCs	Dehydrogenation: 9 kWh/kg H_2 (thermal)	(Reuß et al., 2017)
LOHCs	71% hydrogen efficiency	(Abdin et al., 2022)
LOHCs	Dehydrogenation: 12.54 kWh/kg H_2 (thermal). Hydrogenation and dehydrogenation: 0.0163 kWh/kg H_2 (electrical)	(Eypasch et al., 2017)
Liquified hydrogen	6.78-15 kWh/kg H_2 (electrical)-55-80% efficiency	(Reuß et al., 2017)
Compression	4 kWh/kg H_2 (electrical)	(Reuß et al., 2017)
Compression	92% hydrogen efficiency	(Abdin et al., 2022)
Metal hydrides	78% hydrogen efficiency	(Abdin et al., 2022)

cost is a matter of importance to evaluate the competitiveness of the LOHCs technology. However, the major contributor to the storage costs in this work is the global annualized investment cost from hydrogenation and dehydrogenation processes. In the dehydrogenation process, the equipment costs are mainly attributed to the reactors (55-70%). These represent approximately a 30-45% for both processes together as shown in the Figure 7. In contrast, the hydrogenation reactors play a lower role for the equipment cost in the hydrogenation, compared to dehydrogenation ones. Other equipment such as flash separators are also relevant and eventually the heat exchangers and compressors. Finally, the remaining costs are linked to fixed operating costs and raw materials while other utilities have a residual contribution (cooling and electricity).

The modelling of the reactors through a detailed analysis using surrogate models (including the most relevant design and operating parameters for them) is important in this assessment. The reactors design has a large contribution in the costs, because they are the main technology of the LOHCs hydrogenation/dehydrogenation process. The optimization results from the proposed superstructure showed that the combination of slurry-trickle reactors is favorable in the NEC system during hydrogenation. However, for the same carrier, only a slurry reactor is set during the dehydrogenation reaction. For the INDOLE system, only a slurry reactor is used during hydrogenation and another in the dehydrogenation process. The results for each slurry reactor are shown in Table 9, whereas the results for the hydrogenation trickle bed in the NEC system are included in Table 10.

The catalyst used in the chemical reactions has a large impact on the total hydro-

gen storage cost. It represents the highest contributor for the dehydrogenation reactors investment (80-90%). In the case of hydrogenation reactors, this contribution is lower (15-30%). Slurry reactors use catalyst more efficiently. Therefore, a higher investment per unit of product is expected in trickle bed reactors compared to slurry ones. Moreover, trickle bed reactors do not allow for high LOHCs reactant concentrations. Otherwise, long temperature variations would occur along the bed as a result of the adiabatic operation of these units (Prieto et al., 2023). For both reasons, the reactors technology selection in the superstructure is mostly based on the slurry reactor design. In spite of that, NEC system results include a hydrogenation trickle bed. However, it represents a minor contribution to the plant hydrogenation load (~1%). The purpose of this reactor is only to adjust the final LOHCs product composition for the ongoing dehydrogenation process. It avoids the oversizing of other process units and/or higher energy requirements. However, in spite of the selection made by the optimization, the trickle bed reactor technology cannot be fully discarded for LOHCs applications. It presents other benefits compared to the slurry: low energy dissipation, lower reactor volumes and catalyst losses or easier operation. Similarly, the slurry reactors are also interesting for the excellent heat and mass transfer, low pressure drop and other reasons such as being suitable for viscous liquids (Buwa et al., 2016; Mederos et al., 2009; Forret et al., 2006; Al-Dahhan et al., 1997). As a result, the LOHCs reaction technology becomes a matter of study to enhance its development.

In spite of the importance of these units, different results are found if compared to previous work where reactors are optimized as isolate units (Prieto et al., 2023). These differences have been shown previously in other production processes where first the reactors and then the whole process are optimized (Martín and Grossmann, 2012). In this case, the differences between the process scale and the reactor optimizations for the LOHCs are mainly attributed to energy use minimization. Other reasons include a reduction in the capital costs of other equipment such as heat exchangers, compressors or flash separation units. For instance, it was found that the hydrogen flow after the slurry reactors was critical for the ongoing flash units and compressors. Increasing the superficial gas velocity has a positive effect on conversion. Notwithstanding, it represents higher power requirements and larger diameters in the vessels (at high pressures), directly linked to higher capital costs. Lower operating temperatures are obtained in some cases for the process units. The reduction in steam use is attributed to be the main reason for that. Other parameters such as the liquid and gas flow relationship in the trickle bed reactor also varied from the reactor unit optimization. Higher values are obtained with the aim of reducing the pressure drop along the catalyst bed.

To compensate for the reduction in the reaction temperature, higher catalyst loading

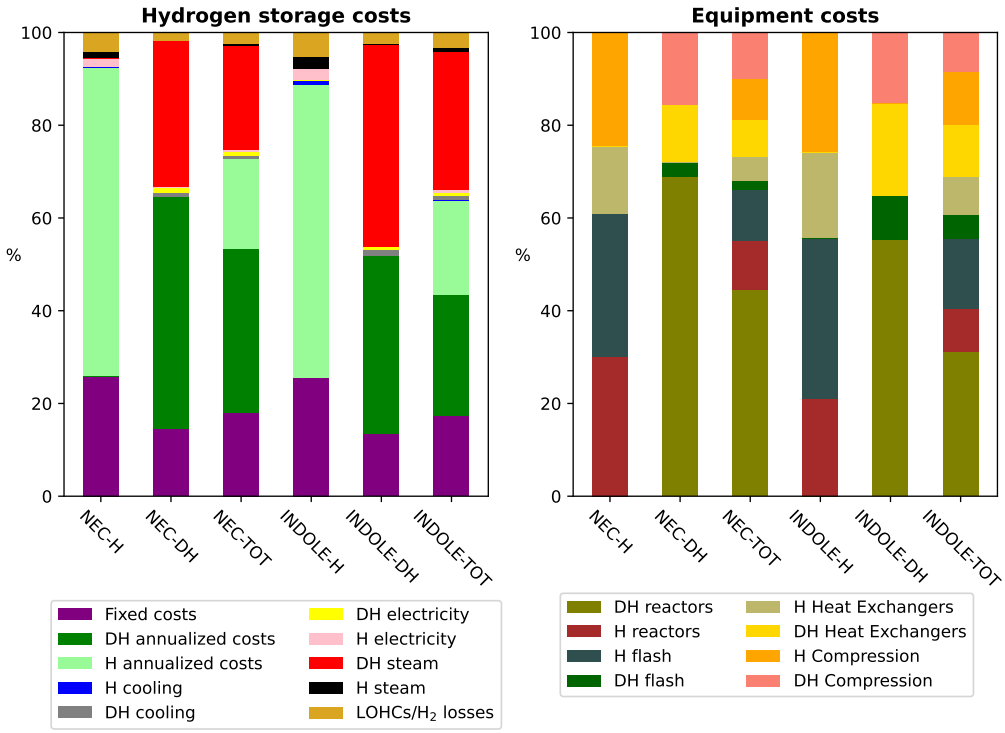

Figure 7: Hydrogen storage and equipment costs distribution in the hydrogenation (H), dehydrogenation (DH) and both processes (TOT).

and/or slurry volumes are expected. Hence, the use of catalyst is less efficient compared to the isolate unit optimization. However, this fact turned out to be less expensive for the entire process. Furthermore, some relevant differences are found in the conversion results. The most significant case is the INDOLE system dehydrogenation. The per-pass conversion is considerably lower when compared against similar reactor units. However, as long as a liquid recycle stream is sent back to this reactor, in the end, higher global conversion is obtained for this system. Differently, no liquid recycle stream is introduced in any of the NEC dehydrogenation and hydrogenation reactors, whereas a gaseous stream, mainly composed by hydrogen, is directed to all reactors in the dehydrogenation and hydrogenation processes (either trickle or slurry).

A scale-up study is also performed. For that purpose, different hydrogen demands are imposed as restrictions. The model is able to compute the demand of utilities for each case and modify the scale of each equipment individually. For example, the areas for the heat exchangers or the reactor dimensions increase for higher process loads as expected. Hence, the investment costs for each unit are scaled individually since the

Table 9: Slurry reactors results.

	Hydrogenation			Dehydrogenation		
System	NEC	INDOLE	INDOLE	NEC	INDOLE	INDOLE
Source	This work	This work	(Prieto et al., 2023)	This work	This work	(Prieto et al., 2023)
V_{sl} (m^3)	2.67	2.12	1.96	40.38	20.21	15.49
C_{sl} (kg/m^3)	50.00	94.52	50.00	100.00	100.00	100.00
T (K)	423.00	431.07	443.00	493.00	467.08	473.00
P (bar)	50.32	50.25	50.00	3.80	5.00	2.00
$u_{g,0}$ (m/s)	0.26	0.23	0.56	0.20	0.20	1.46
D (m)	1.00	1.00	1.00	2.43	2.00	2.00
L (m)	5.77	4.00	4.00	10.35	8.00	8.00
X*	0.94	0.87	0.77	0.81	0.47	0.63
cost (M$)	0.41	0.36	0.29	2.30	1.23	0.92
ton H_2/d	25.67	25.92	25.92	25.92	25.92	25.92

*Conversion is referred to the maximum hydrogenation or dehydrogenation degree.

Table 10: Trickle bed reactors results.

	Hydrogenation	
System	NEC	INDOLE
Source	This work	(Prieto et al., 2023)
W_{cat} (kg)	190.85	190.85
T_{in} (K)	423.00	413.00
P_{in} (bar)	50.00	50.00
L_{in}/G_{in}	21.68	12.06
D (m)	0.50	0.50
L (m)	1.00	1.00
X*	1.00	0.88
cost (M$)	0.14	0.14
ton H_2/d	0.25	0.25

*Conversion is referred to the maximum hydrogenation or dehydrogenation degree.

correlations for each one are introduced. The storage costs of hydrogen (operating and annualized costs) are plotted against different capacities in Figure 8. The hydrogenation and dehydrogenation contributions are splitted for clarity. The economies of scale are able to reduce the total cost per kg unit of hydrogen. It shows the convenience of having larger LOHCs capacities to reduce the total costs in both processes. Dehydrogenation costs are larger if compared to hydrogenation ones. This is attributed to the higher thermal energy used during the dehydrogenation of LOHCs and the higher investment costs of dehydrogenation reactors compared to hydrogenation ones.

The storage costs of hydrogen from this work are compared with the literature. Several types of studies are found for LOHCs utilization. Similar or other considerations are taken to assess the total costs of hydrogen storage. These are summarized in Ta-

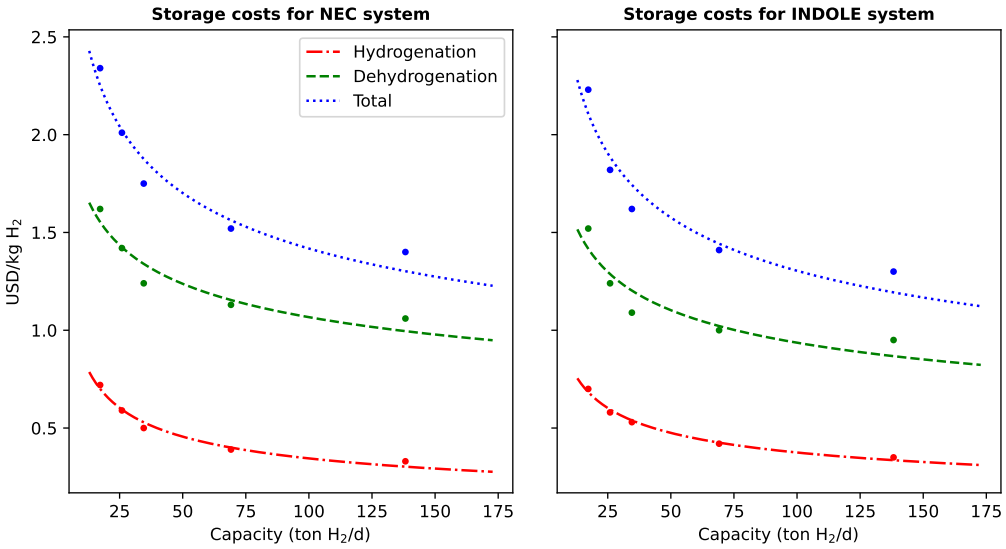

Figure 8: Hydrogen storage costs for NEC and INDOLE systems against plant capacity

ble 11. The wide range of capacities together with the assumptions for each work (e.g., price variability, LOHCs reusability, yields, storage tanks included) and the uncertainty of main equipment cost estimation, make it hard to extract clear conclusions. For instance, in this work, the costs of hydrogenation reactors, modelled from rigorous reactor assessment, range from 10-12 \$/kW for an intermediate capacity of 25.92 ton/d (36 MW). Higher reactor costs were reported in other studies (Hurskainen and Ihonen, 2020; Byun et al., 2022; Reuß et al., 2017; Abdin et al., 2022). They rely on Eypasch et al. (2017) correlations (adjusted up to 1.8 MW) to estimate the reactor costs, which results in approximately 56 \$/kW for the proposed capacity in this work. The difference in the cost estimation may be attributed to several reasons. The LOHCs used are different. Hence, their behavior during hydro and dehydrogenation may change (Prieto et al., 2023). Moreover, the performance of the reactors in this work is introduced in the model from surrogate models obtained from rigorous reactor assessment for each LOHC of study. They are based on relevant operating and design variables (gas velocities, temperature, pressure, catalyst,...). Then, it is optimized to reduce the storage costs. In other works, the influence of some of these variables in the reaction progress is not assessed, since they are pre-fixed (García et al., 2024) or are not accounted for and only cost estimation is done. Another reason can be the differences of scale between the original work from Eypasch et al. (2017) and this one. Other studies, however, reported similar values (13-15\$/kW) compared to the present study (García et al., 2024). Similarly, the costs of dehydrogenation reactors from this work (34-64\$/kW), also modelled

from rigorous models, present certain differences with Eypasch et al. (2017) correlations (80$/kW). In this situation, the cost estimation is closer. In spite of that, similar reasons as for hydrogenation can be key to explain these differences.

Table 11: Hydrogen storage costs with LOHCs in different studies.

Storage cost	Description	Source
1.30-2.34 $/kg H_2	Hydrogenation and dehydrogenation costs.	This work
1.41-6.40 $/kg H_2	Hydrogenation costs (raw material contribution subtracted) (up to 300 m^3/h capacity).	(Byun et al., 2022)
1.20 $/kg H_2	Hydrogenation and dehydrogenation costs (4000 ton H_2/d).	(Abdin et al., 2022)
1.50 $/kg H_2	Hydrogenation costs (full LOHCs recovery) (1578 ton H_2/y).	(García et al., 2024)
~3.68 $/kg H_2	The study covers: production, hydro and dehydrogenation, storage and transportation. Only hydro and dehydrogenation contribution is considered for comparison purposes (50 ton H_2/d). However, additional hydrogen compression stages, not considered in this work, can not be disaggregated.	(Reuß et al., 2017).

The economic results from this work are reasonable regarding the values found in the literature. For instance, Byun et al. (2022) plant capacities are considerably lower. At the same time, the reactor costs are estimated with more restrictive correlations. Similarly, García et al. (2024) hydrogenation capacity is lower. With regards to Abdin et al. (2022), the economies of scale resulted in a clear reduction of its storage costs compared to other works. However, the Eypasch et al. (2017) expression is still used. This may explain the similarity of costs compared to some capacities from this work, in spite of being lower. Finally, Reuß et al. (2017) reported higher costs maybe due to additional contributors not included in this work (storage tanks, additional compressions, additional investment in fuel stations,...).

4. Conclusions

This work presents a new methodology to address the process and product design problem related to hydrogen storage in the form of LOHCs. It consists of a two-stage approach: a prescreening and a process design optimization. The screening stage is based on economic, environmental and safety indicators allowing the decision making at an early stage. It is applied to select some of the most promising LOHCs candidates for hydrogen storage. NEC and INDOLE systems were chosen providing favorable options from the economic, environmental and safety point of view. They presented some

of the most desirable characteristics for LOHCs: mild reaction, no solvents or purification, low toxicity and flammability. The second stage involves a detailed process design. Surrogate models from a rigorous reactor evaluation were used to model the reactors performance. The operating and annualized costs (storage costs) were optimized for the hydrogenation and dehydrogenation processes. The results showed that the cost of storing hydrogen with this technology can cover 1.30-2.34 \$/kg H_2 for some of the proposed capacities. These results were compared against other hydrogen storage studies using LOHCs.

The energy efficiency for NEC and INDOLE systems is expected to be between 65-75%. It indicates better results when compared to other traditional storage options (liquefaction in some cases). Thermal energy represents the highest energy requirements in both systems where, the steam used in the dehydrogenation reactors was the largest contributor. The dehydrogenation unit itself was also the main, or one of the main, sources of investment in the total equipment costs. Therefore, the dehydrogenation section is a clear target to optimize the LOHCs technology. Specifically, energy efficiency and the reactor performance are paramount. However, these units must be assessed together with the process, and not only considering the reactor unit alone. This is reflected in the general differences shown between hydrogenation and dehydrogenation reactor designs from this work and others where reactors are only studied. The combination of slurry and trickle bed reactors technology was explored in this work. However, the optimization results show that during dehydrogenation only slurry reactors are used. Similarly, it represents clearly the main technology for hydrogenation. This was attributed to the least efficient catalyst use in the trickle bed reactors, although this reaction technology cannot be fully discarded for LOHCs technology because it may bring other benefits. The results from this conceptual work are still useful for the LOHCs development. At this stage, the scale-up of the reactors is one of the key points for this purpose. Therefore, it is interesting to study more in depth and test the LOHCs reactor technology. The methodology developed in this work can be applied for the process design and optimization of promising LOHCs candidates for the future implementation of LOHCs technology.

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5. Nomenclature

C_{sl}	Catalyst concentration in the slurry phase (kg/m^3)
CP	Compressor
D	Reactor diameter (m)
DH	Dehydrogenation
EF	Emission Factor (ton CO_2/MWh)
EI	Economic Index (\$/kg H_2)
ENI	Environmental Index
F_1	F&EI F_1 factor
F_2	F&EI F_2 factor
F_3	F&EI F_3 factor
F&EI	Fire & Explosion Index
F_{RM-j}	Raw material j (kg)
FL	Flash vessel
FP	Final Product (kg H_2)
G_{in}	Gas flowrate (kg/m$^2 \cdot s$)
GAMS	General Algebraic Modelling System
GHG	Greenhouse Gases
GWP	Global Warming Potential (ton CO_2/kg H_2)
H	Hydrogenation
HE	Heat Exchanger
HMT	High-medium temperature
HP	High pressure steam
ISBL	Inside Battery Limit Investment (MM\$)
L	Reactor length (m)
L_{in}	Liquid flowrate (kg/m$^2 \cdot s$)
LOHCs	Liquid Organic Hydrogen Carriers
LT	Low temperature
MF	Material Factor
n_{op}	Number of operations
NG	Natural gas
NLP	Non Linear Programming
OSBL	Outside Battery Limit Investment (MM\$)
p	Unitary price (\$/unit)
P	Pressure (bar)
$P_{F_{1,p}}$	Penalty p from F&EI F_1 factor

$P_{F_{2,p}}$	Penalty p from F&EI F_2 factor
PU	Pump
$Q_{op}^{u_k}$	Heating/cooling demand for utility k in operation op (kW)
R	Reactor
SI	Safety index
T	Temperature (K)
TOT	Total
$u_{g,0}$	Superficial gas velocity (m/s)
V_{sl}	Slurry phase volume (m^3)
W	Compression power (kW)
W_{cat}	Catalyst weight (kg)
X	Reaction Conversion

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