Hydrogenation of liquid organic hydrogen carriers: Process scale-up, economic analysis and optimization

Adrián García, Pablo Marín, Salvador Ordóñez*

Catalysis, Reactors and Control Research Group (CRC), Dept. of Chemical and Environmental Engineering, University of Oviedo, Julián Clavería 8, Oviedo 33006, Spain

HIGHLIGHTS

- Process evaluated for 3,5-dibenzyl toluene, 2-methyl indole, N-ethylcarbazole LOHCs.
- Process scale-up and optimization for LOHC hydrogenation: 190 °C and 6 MPa.
- Economic evaluation suggests that 3,5-dibenzyl toluene is the best LOHC.
- Cost of LOHC make-up is the most important for the H_2 storage cost.

ARTICLE INFO

ABSTRACT

Hydrogen has been proposed as energy vector because it can be produced from renewable energy sources and its use produces no carbon dioxide. Moreover, many industrial processes (e.g., steel industry, ammonia, and fertilizer industry, etc.) are also adopting renewable-produced hydrogen as raw material, replacing traditional fossil sources. In this context, the storage and transportation of hydrogen using liquid organic hydrogen carriers (LOHC) is interesting to deal with the discontinuous production of renewable energies.

The work addressed the study of the hydrogenation process for three compounds, 3,5-dibenzyl toluene, 2-methyl indole and N-ethylcarbazole, on Ni and Ru-based catalysts. The reactor consisted of a three-phase slurry stirred tank reactor, which has been scale-up together with the rest of the process equipment units using Aspen Hysys simulation software. The hydrogen storage cost has been determined applying an economic evaluation to the overall process. The most important costs of the process are the reactor cost and the cost of raw materials (the liquid organic hydrogen carrier). The main design variables, plant capacity, reactor temperature and pressure, were optimized to reduce the storage cost. The liquid organic hydrogen carrier with the minimum storage cost at the optimum operating conditions is 3,5-dibenzyl toluene with a reactor configuration of two parallel tanks.

Introduction

After decades of increasing CO_2 emissions to the atmosphere, world climate is being affected at large scale. From the Artic to the Equatorial regions, temperature and climate instability is increasing. The use of fossil fuels for energy production and industrial purposes is the main source of anthropogenic CO_2 emissions. Furthermore, the availability of fossil resources (e.g., petroleum and natural gas) is concentrated in few countries. For this reason, the actual energetic model creates strong dependencies and strains in the global geopolitics, supports dictatorships that deny human rights, and use the fuel supply as a weapon. In this context, the European Union is determined to decarbonize the economy and abandon the use of fossil fuels, as soon as possible [1].

Several measurements have been proposed and implemented to reduce CO_2 emissions, such as, the increase of efficiency and save of energy, the promotion of renewable energies and biofuels, etc. [2,3]. One important problem of most of the renewable energies in expansion, like wind and solar, is the high variability in their production. For this reason, different methodologies are being developed to store energy, when there is an excess of generation, and to use this excess when there is a deficit of generation. The electrical energy must be transformed into other type of energy for the storage, for instance, mechanical energy in damps and pressurized vessels or chemical energy in electrical batteries. In these systems, during the discharge stage the energy is recovered as electrical energy, which can be introduced in the network. However, these forms of energy storage might not be suitable for the industry, which typically consumes considerable amounts of energy. In many cases, like in chemical, food and process industries, the energy is consumed as thermal energy, so the use of hydrogen as energy carrier is a better choice [4–7].

Hydrogen can be produced by electrolysis during periods of generation surplus from renewable sources. Hydrogen is a viable candidate as energy carrier: it is a concentrated energy source, it does not produce pollutants during utilization and it can be used as raw material, replacing other fossil sources. In the chemical industry, hydrogen is used as reducing agent for the manufacture of many chemicals, such as, ammonia (used to produce fertilizers), methanol (used as solvent, production of special chemicals, polymers, and resins), hydrogenation of organic compounds, etc. In the iron and steel industry, the use of hydrogen in the direct reduction of iron process is called to replace the traditional blast furnace process based on the use of coke [8,9].

The storage of hydrogen is particularly important to couple a discontinuous renewable production with a continuous industrial use. There have been proposed different alternatives of storage, as summarized below [10–12]. The physical methods consists on the storage of hydrogen in tanks, as a compressed gas (50–70 MPa) or liquefied (−253 °C) [13]. The main drawbacks of these methods are safety and the low energy density of the storage.

The adsorption methods are based on the use of solids, typically porous materials with high surface area, capable of adsorbing hydrogen of their surface. Materials, like active carbon, carbon nanotubes or zeolites, have been investigated; however, the conditions required to storage (−200 °C and 5.5 MPa) limit their practical applications [14–16].

The reaction methods use hydrogen as reactant to generate chemical compounds suitable for the storage. The reactions involved must be reversible to recover the hydrogen molecule from the compound when needed. The use of metal hydrides (like $LiBH_4$) [10,17], ammonia, methanol, formic acid and unsaturated liquid organic compounds has been investigated [11,18,19]. Ammonia is very interesting due to its high hydrogen density and the direct applications in industry [7,18,20]. Methanol and formic acid have moderate storage capacity and they can be generated directly by electrolysis [21]; however, at the point of use, where hydrogen is released, CO_2 is emitted [22,23].
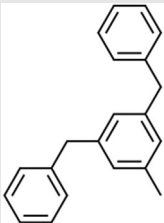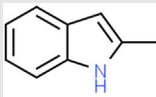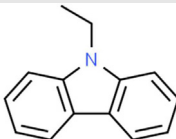
The unsaturated liquid organic hydrogen carriers (LOHC) are organic compounds capable of reacting with hydrogen to generate a saturated form. The hydrogenation reaction is an exothermic reaction, requiring high pressure, moderate temperature, and the use of a catalyst. The reverse dehydrogenation is an endothermic catalysed reaction, favoured at low pressure (typically atmospheric) and high temperature [24,25]. The main advantages of unsaturated LOHC are their handling easiness, safety, and the possibility of using the actual infrastructure for petroleum oil and derived fuels. This is very interesting to reduce the investment and help to redeem the systems and installations in use with fossil fuels [26,27].

The compounds considered as LOHC must fulfil some requirements, such as, high capacity (minimum 5 wt %), availability (easy to produce and inexpensive compounds), low toxicity, ease of handling (high boiling and low freezing points, stability), and low dehydrogenation temperature (too high temperature would increase considerably the operational costs) [28]. Most commonly proposed LOHC are aromatic compounds (benzene, toluene, benzyl toluene, dibenzyl toluene, naphthalene or biphenyl) [24,29–32] and heterocyclic compounds (quinoline, 2-(N-methylbenzyl)pyridine, N-ethylcarbazole or 2-methyl indole) [33–37]. The aromatic compounds have a higher hydrogen storage capacity (>6 wt %), but require a higher temperature for dehydrogenation (more than 270 °C, against 150-190 °C of the heterocycle compounds) [26,38,39].

Although there are many published papers about the screening of chemicals and catalysts for being used for this purpose, there is a general lack of information about the designing of these units. It should be considered that, although the involved reactions are known from other applications, reaction conditions are quite different in the LOHC application. Aspect as the absence of solvents in the hydrogenation steps completely modify the design of these reactors. Thus, the scope of this work is to perform a detailed design and optimization of the hydrogenation step (LOHC loading) using three different commonly used LOHCs (3,5-dibenzyl toluene, 2-methyl indole and N-ethylcarbazole). These products are commonly proposed in the literature as LOHCs because of their physics-chemical properties, summarized in Table 1.

The first compound, 3,5-dibenzyl toluene, is an aromatic hydrocarbon with industrial applications as thermal fluid. This compound can be hydrogenated into perhydro-dibenzyl toluene at 140 °C and up to 70 MPa using supported precious metal catalysts (e.g., Ru/Al_2O_3 or Pt/Al_2O_3) without formation of secondary or degradation products [32,40–42].

Table 1 – Properties of the LOHC studied in the present work.			
Name	3,5-dibenzyl toluene	2-methyl indole	N-ethylcarbazole
Formula			
Freezing	−39 °C	58 °C	70 °C
Boiling	390 °C	273 °C	295 °C
Stoichiometry coef.	9 mol H_2/mol LOHC	4 mol H_2/mol LOHC	6 mol H_2/mol LOHC
Reaction enthalpy	−530 kJ/mol	−206 kJ/mol	−342 kJ/mol
Weight capacity	6.2 wt%	5.8 wt %	5.6 wt%
Volumetric capacity	762 L H_2/L	705 L H_2/L	736 L H_2/L
H_2 solubility at 1 MPa, 150 °C	17.6 mol/m^3	16.3 mol/m^3	17 mol/m^3

The other two compounds, 2-methyl indole and N-ethylcarbazole, are both heterocycle compound with equivalent properties. Like for 3,5-dibenzyl toluene, the hydrogenation takes place using supported precious metal catalysts at similar conditions [36,37,43–45]. These compounds are also stable and non-toxic, but the hydrogenated forms have high freezing points, which can complicate the storage. The main advantage of these compounds is their lower dehydrogenation temperature [34].

The proposed reactor consisted of a continuous three-phase stirred tank slurry reactor. Hydrogen is fed in excess, so unreacted hydrogen is separated and recycled to the reactor. This reactor type is more advantageous for heat and mass transfer. The hydrogenation reactions are very exothermic (see reaction enthalpies reported in Table 1) and, given that no solvents are used, temperature must be carefully controlled. Stirred tanks equipped with a jacked for refrigeration are simple and efficient. In stirred tank reactors, the catalyst is in the form of a slurry. To facilitate the suspension, the catalyst particles must be of small size, which means that mass transfer to the particles and in the inside is fast. The use of a stirred also helps to transfer and dissolve hydrogen in the liquid phase. For these reasons, the use of stirred tank reactors is a good option to carry out the hydrogenation process at the industrial scale.

The reactor scale-up has been based on a kinetic model of the respective hydrogenation catalytic reactions; the influence of mass transfer on reaction rate has been estimated and discussed. In the economic evaluation section, the capital investment and operating costs of the process are estimated and used to determine the unitary cost of hydrogen storage. Finally, the main operating and design variables of the process are optimized by means of a sensitivity analysis with the aim of decreasing the unitary cost of hydrogen storage.

Material and methods

Kinetic model

The catalytic hydrogenation of the LOHC is a three-phase reaction involving gaseous hydrogen, liquid LOHC and the solid catalyst. This reaction is accomplished according to three steps in series: (1) hydrogen transfer and dissolution in the liquid phase, (2) hydrogen transfer to the catalyst surface and (3) reaction on the catalyst surface. Using the film theory to describe the mass transfer steps and assuming a reaction kinetics of first order with respect to each reactant (LOHC and H_2), the following equations can be formulated:

$$-r_{H_2} = ak_L\left(p_{H2}/H_{H_2} - C_{H_2 liq}\right) \quad (1)$$

$$-r_{H_2} = f_s a_P k_C\left(C_{H_2 liq} - C_{H_2\ sup}\right) \quad (2)$$

$$-r_{LOHC} = \frac{-r_{H_2}}{v_{H_2}} = f_s k_v C_{LOHC} C_{H_2\ sup} \quad (3)$$

Where $-r_{H_2}$ and $-r_{LOHC}$ are, respectively, the hydrogen and LOHC, reaction rates per unit volume of reactor, v_{H_2} is the stoichiometric coefficient of H_2 in the hydrogenation reaction (see Table 1), ak_L is the gas-to-liquid mass transfer coefficient, $a_P k_C$ is the liquid-to-solid mass transfer coefficient, k_v is the kinetic constant per unit volume of catalyst (i.e., $k_v = k_w \rho_{cat}$), p_{H_2} is the partial pressure of hydrogen in the gas phase, H_{H_2} is the Henry's law constant for hydrogen, $C_{H_2 liq}$ and $C_{H_2\ sup}$ are, respectively, the molar hydrogen concentrations in the bulk liquid and the surface of the catalyst, C_{LOHC} is the molar concentration of LOHC, and f_s is the volumetric fraction of catalyst in the reactor.

Equations (1)–(3) have been solved for $C_{H_2 liq}$ and $C_{H_2\ sup}$, to obtain an expression of the reaction rate as a function of hydrogen partial pressure, the transport coefficients and the kinetic constant. The reaction rate of the LOHC is given by the following expression, where each term of the denominator corresponds to a resistance (respectively, mass transfer to the liquid phase, mass transfer to the catalyst surface and reaction):

$$-r_{LOHC} = \frac{-r_{H_2}}{v_{H_2}} = \frac{\left(p_{H_2}/H_{H_2}\right)}{\frac{v_{H_2}}{ak_L} + \frac{v_{H_2}}{f_s a_P k_C} + \frac{1}{f_s k_v C_{LOHC}}} \quad (4)$$

For the case of fast mass transfer steps with respect to the reaction, eq. (4) can be simplified eliminating the first two terms of the denominator:

$$-r_{LOHC} = f_s \, k_v \, C_{LOHC} \, p_{H_2} \Big/ H_{H_2} \qquad (5)$$

The reactions considered in the present work are the hydrogenation of 3,5-dibenzyl toluene on Ni Raney, and 2-methyl indole and N-ethylcarbazole on Ru/Al$_2$O$_3$. The kinetic constants have been calculated using reaction experiments from the bibliography, which were carried out in the absence of mass transfer resistances [41,44,45]. Arrhenius-type dependence with temperature of the kinetic constant is assumed, $k_v = k_{v0} e^{-E_a/RT}$, where k_{v0} is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant and T is temperature. Table 2 shows the fitted parameters of the kinetic model, eq. (5).

Process simulation

The study of the hydrogenation process has been carried out by simulating with the software Aspen Hysys. Peng-Robinson thermodynamic model was selected, and the properties of the hydrogenated compounds were introduced in the model.

Fig. 1 shows the flowsheet of the hydrogenation process. The hydrogenation reactor is a three-phase slurry reactor, equipped with a mechanical stirrer to maintain the solid catalyst in suspension and a diffuser to disperse hydrogen gas in the liquid LOHC. This reactor has been modelled using the continuous stirred tank reactor model, which assumes perfect mixture inside the reactor. The kinetic model of section 2.1 has been used to predict reaction rates. Two cases have been considered, a reactor made of one tank and two tanks in series; the latter one corresponds to the flowsheet shown in Fig. 1.

Hydrogen fed to the process is produced in an electrolytic cell using renewable electricity and water. Typical electrolytic cells operate at 6 MPa and 80 °C [46], so these are the conditions chosen for the hydrogen feed stream. The reactor operates using hydrogen in excess to shift the reaction towards products. However, given its low solubility, not all the hydrogen is dissolved in the liquid. As shown in Fig. 1, the hydrogen streams leaving the reactors without dissolving and reacting are recycled and mixed with the fresh feed. This loop of hydrogen is important to maintain the required excess of hydrogen and a good dispersion of the gas inside the liquid phase.

The LOHC is introduced in the tanks using pumps. At the end of the process, the hydrogenated form of the LOHC is cooled in a heat exchanger and expanded to atmospheric pressure. This causes that a bit of dissolved unreacted hydrogen desorbs from the liquid phase. This gas can be vented or, otherwise, collected, recompressed, and recycled to the reactor.

Table 2 – Hydrogenation kinetic model of the LOHC used in the present work [41,44,45].

	3,5-dibenzyl toluene	2-methyl indole	N-ethylcarbazole
Catalyst	Ni-Raney	Ru/Al$_2$O$_3$	Ru/Al$_2$O$_3$
ln k_{v0} (m^3/mol s)	12.1	18.2	22.5
E_a (kJ/mol)	48.4	73.8	93.9
Temperature (ºC)	150–200	120–170	120–170
Source data	[41]	[44]	[45]

Results and discussion

Assessment of mass transfer limitations

The reactor selected to carry out the three-phase hydrogenation reaction consists of a slurry stirred tank. This reactor is equipped with a mechanical stirrer to maintain the solid catalyst in suspension and a diffuser to disperse hydrogen gas in the liquid LOHC. In order to help the suspension of the catalyst, a particle size of 0.1 mm and a fraction catalyst of 0.5 vol % have been selected [47]. As shown in eqs. (4) and (5), higher catalyst fractions (f_w) result in higher reaction rates but hindering the catalyst-liquid mixing. In these multi-phase systems, good mixing inside the reactor is ensured using, at least, a stirring speed of 90 rpm and a specific power of 1.6 kW/m^3 [47].

The mass transfer coefficients of eq. (4) have been determined using correlations for stirred tanks [48,49]. These correlations have been evaluated using the above parameters and the physical properties, estimated at a temperature of 190 °C. The results of the calculations are summarized in Table 3. As shown, the estimated mass transfer resistances are much lower than the reaction one. This means that the reaction step is the slowest one and controls the overall reaction rate. The main operating and design variables affecting the mass transfer resistances are stirring speed (90 rpm) and power (1.6 kW/m^3), catalyst particle size (0.1 mm) and catalyst fraction (0.5 vol %). The values considered for these variables were chosen to maintain good catalyst suspension and mixing, and, at the same time, they were enough to make mass transfer resistances negligible.

Process scale-up and simulation

The hydrogenation process has been simulated and scaled up considering the kinetic model presented in section 2.2. The nominal capacity supposed for the process is 6 MW of hydrogen power, which corresponds to a H$_2$ consumption of 1578 t/year. According to the reaction kinetics, a reactor temperature of 170 °C and pressure of 6 MPa are appropriate to operate the reactor, so these values were fixed as a first estimation. These variables will be optimized in the sensitivity analysis of section 3.4.

Considering these specifications, the reactor volume required to achieve 99% conversion of the LOHC was calculated. A height of liquid inside the tank equals to the diameter is assumed to size the tank. For the case of 3,5-dibenzyl toluene and 2-methyl indole, it is considered the possibility of using either a reactor made of one tank or, otherwise, two tanks in series. The latter option is interesting to reduce the total reactor volume for the same final conversion, because a higher LOHC concentration in the first tank increases the reaction rate. For N-ethylcarbazole, the reaction rate is lower and the option of using only one tank is discharged, because of the large volume required.

The hydrogenation reactions are exothermic (the enthalpies of the reaction are displayed in Table 1), so the reactors require refrigeration to maintain the desired reaction temperature. The refrigeration of the reactors is done using
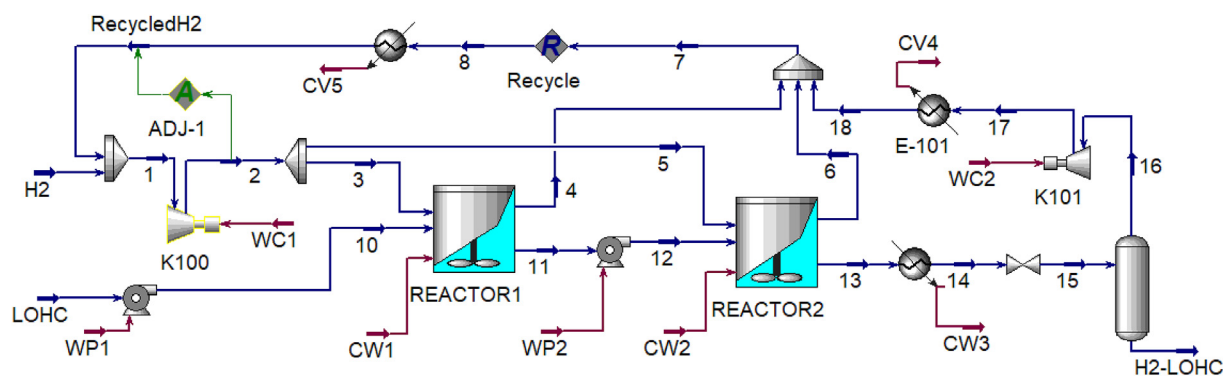
Fig. 1 – Flowsheet of the hydrogenation process.

Table 3 – Assessment of mass transfer limitations in the slurry reactors at 190 °C.			
	3,5-dibenzyl toluene	2-methyl indole	N-ethylcarbazole
Kinetic constant, k_v (m³/mol s)	0.6	0.2	0.01
Gas-to-liquid mass transfer coefficient, ak_L (s⁻¹) [48]	0.096	0.12	0.10
Liquid-to-solid catalyst mass transfer coefficient, $a_P k_C$ (s⁻¹) [49]	215	255	232
Resistances (s)			
Gas-to-liquid, $1/ak_L$	10.4	8.3	10
Liquid-to-solid, $1/f_s a_P k_C$	0.93	0.78	0.86
Reaction, $1/f_s k_v C_{LOHC}$	$7.1 \cdot 10^4$	$21.3 \cdot 10^4$	$426 \cdot 10^4$

cooling water that flows through the reactor jacket, given that the use of coils is not recommended for slurry reactors. The area needed for the reactor jacket is calculated using an overall heat transfer coefficient of 0.5 kW/m² K. In case this area is larger than the available in the tank, its geometry is adjusted to fulfil with the cooling requirements. Table 4 shows the results of the scale-up for the main units of equipment.

The power consumed by the impeller of the reactor, the compressor and pumps has also been calculated. This is needed to estimate the consumption of electricity and the operating costs.

Table 4 – Scale-up of the main units of equipment.					
	3,5-dibenzyl toluene		2-methyl indole		N-ethyl carbazole
	1 tank	2 tanks	1 tank	2 tanks	2 tanks
H₂ feed (kg/h)	185	186	180	190	182
LOHC flow rate (m³/h)	3.35	3.35	3.28	3.42	3.35
Reactor size (m³, each tank)	8	8	8	6	6
Compressor (kW)	21.6	23.7	23	20	115
Pump (kW)	7.5	7.5	7.4	7.7	7.6
Heat exchanger area (m²)	12	13	13	13	12
Separator (m³)	0.31	0.31	2.6	0.43	1.52

Economic evaluation

The aim of this section is to carry out an estimation of the costs of the process, in order to calculate the cost of H₂ storage. The cost of the process is divided into capital investment and operating costs.

The capital investment has been estimated as a function of the cost of the main pieces of equipment (reactors, separator, compressor, etc.). The purchase cost of the equipment units has been calculated using correlations from the bibliography [50], which depends of the corresponding design variables displayed in Table 4. The purchase costs have been updated to 2021 using the Chemical Engineering Process Cost Index (CEPCI). The delivery cost of the equipment units is estimated as 10% of the purchase cost. The capital investment includes the fixed capital (cost of equipment, installation, piping, instrumentation, electrical, building, services, engineering, contingencies, etc.) and working capital (estimated as 15% of the total investment). The total capital investment is calculated as 6.05 times the total cost of the delivered equipment units. Further details can be found in the bibliography [51]. The results of these estimations are summarized in Table 5.

The LOHC process requiring the lowest capital investment is the one based on 3,5-dibenzyl toluene and a reactor of one tank. The options based on a two-tank reactor require, in general, a higher capital investment. The piece of equipment with the higher contribution to the total cost is the reactor (40–50%), so the cost of an additional tank has an important influence. The process based on N-ethyl carbazole requires the higher capital investment.

The total investment has been annualized considering a 10-year period and an interest rate of 15%; the corresponding annual capital charge ratio (ACCR) is 0.199 [50].

The operating costs are divided into fixed cost (insurances and taxes) and variable costs (raw materials, labour, utilities, etc.). The estimates of these costs according to the methodology proposed in the bibliography [51] is summarized in Table 6. The main costs correspond to raw materials, utilities (cooling water, 2.17 €/1000 kg) and electricity (0.0645 €/kWh).

Regarding the raw materials, it is considered that most of the LOHC can be re-used after H₂ is released in the dehydrogenation process. For estimating purposes, 90% of the LOHC feed flow rate would correspond to re-used compound and the remaining 10% to make-up. The make-up would compensate

Table 5 – Summary of the capital investment calculations (currency in Euro).

INVESTMENT	3,5-dibenzyl toluene		2-methyl indole		N-ethyl carbazole
	1 tank	2 tanks	1 tank	2 tanks	2 tanks
Reactors	112 500	225 000	113 000	191 000	191 000
Agitation	18 000	53 600	53 600	45 100	90 100
Compressors	39 000	56 000	54 700	51 000	126 000
Pumps	4900	9900	4800	9700	9600
Heat exchangers	29 700	51 200	29 800	51 300	30 300
Separator	36 700	36 700	37 600	36 700	37 000
Total equipment cost	240 800	432 400	293 500	384 800	484 000
TOTAL CAPITAL INVESTMENT	1 623 300	2910 000	1 970 000	2590 000	3 260 000
ANNUALIZED INVESTMENT	**323 000**	**579 000**	**392 000**	**516 000**	**648 000**

Table 6 – Summary of the operating costs calculations (currency in Euro).

OPERATING COSTS	3,5-dibenzyl toluene		2-methyl indole		N-ethyl carbazole
	1 tank	2 tanks	1 tank	2 tanks	2 tanks
Fixed costs					
Insurances	27 600	49 500	33 500	44 000	55 400
Taxes	13 800	24 700	16 800	22 000	27 700
Variable costs					
Raw materials	2 217 000	2220 000	2 250 000	2350 000	4 290 000
Labour	771 000	771 000	771 000	771 000	1 030 000
Supervision	116 000	115 000	115 000	116 000	154 000
Utilities	1378 000	1 390 000	1030 000	1 080 000	1390 000
Electricity	40 100	64 500	43 700	47 800	160 000
Maintenance	96 600	173 000	117 000	154 000	194 000
Supplies	14 500	26 000	17 600	23 000	29 000
Laboratory	116 000	116 000	116 000	116 000	154 000
Cannon	88 700	88 700	89 900	94 000	171 000
Catalyst	2600	2600	400 000	200 000	300 000
TOTAL OPERATING COST	**4 881 900**	**5041 000**	**5 000 500**	**5017 800**	**7 955 100**

losses of LOHC in the transportation, storage, or hydrogenation/dehydrogenation processes. Therefore, only the cost of that 10% of LOHC is accounted for in the operating costs of Table 6. The prices of the LOHC are 0.90 €/kg for 3,5-dibenzyl toluene, 0.86 €/kg for 2-methyl indole, and 1.64 €/kg for N-ethyl carbazole. It should be noted that as the storage technology is spread and optimized, the LOHC recovery may increase and the amount of make-up considerably reduced, improving the economy of the process.

The operating costs are quite similar for 3,5-dibenzyl toluene and 2-methyl indole for the different process configurations with one and two tanks. However, they are considerably higher for N-ethyl carbazole, which is due to the higher price of this LOHC.

Table 7 shows a summary of the total annual costs, including the annualized investment and the operating costs, for the different alternative LOHC. The lowest total annual cost corresponds to 3,5-dibenzyl toluene and the case of using a reactor of one tank. The cost of H_2 storage has also been calculated using the actual plant capacity and H_2 consumption. The nominal design H_2 plant capacity was fixed to 6 MW. However, after the scale-up, the actual plant capacity can be slightly higher (deviations are within 5%). This is mainly due to reactor over-sizing to ensure an adequate heat removal to the tank jacket.

For 3,5-dibenzyl toluene, the cost of H_2 storage is 3.22 €/kg for the one-tank configuration. Nevertheless, the costs for 3,5-dibenzyl toluene and 2-methyl indole are remarkably close, in the range 3.22–3.45 €/kg. The cost of N-ethyl carbazole is clearly higher 5.38 €/kg.
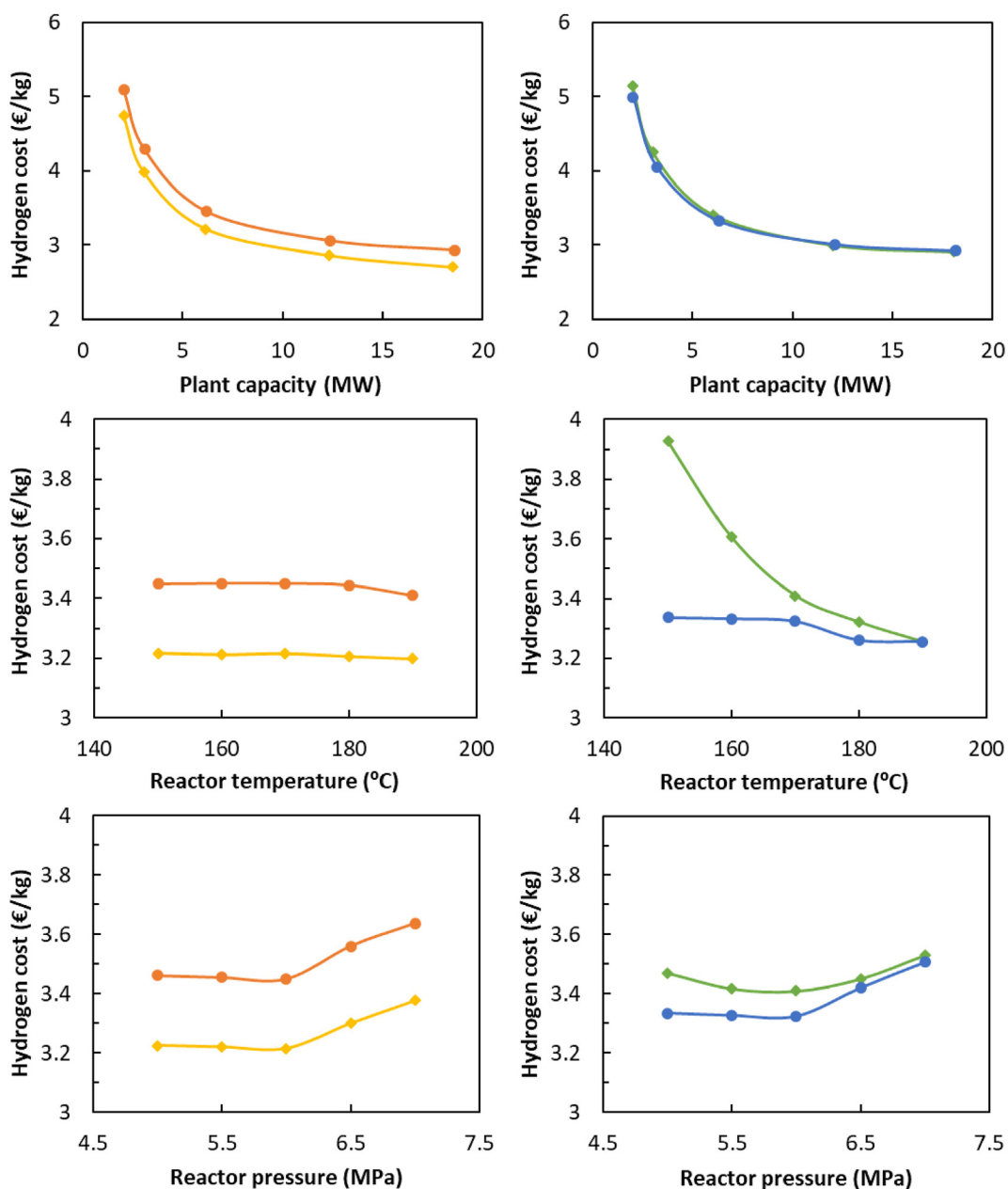
Sensitivity analysis

The aim of the sensitivity analysis is the study of the main operation and design variables on the production cost of hydrogen. The considered variables are plant capacity (measured in terms of hydrogen power), reactor temperature and pressure. These variables have been varied one at a time with respect to the base case of sections 3.2 and 3.3 (respectively, 6 MW of hydrogen power, 170 °C and 6 MPa). For each combination of variables, the main pieces of equipment of the plant (i.e., reactor, vessels, heat exchangers and pumping) have been sized, the capital and operational costs determined, and the production cost of hydrogen calculated, as explained in sections 3.2 and 3.3.

Fig. 2 (left) shows the results for the process based on 3,5-dibenzyl toluene as LOHC. The configuration of a reactor made of one and two tanks has been compared in terms of the production cost of hydrogen. The plant capacity has the highest influence on the production cost of hydrogen, which decreases sharply in the range 2–10 MW; above 10 MW, with H_2 costs around 3 €/kg, the influence is less marked. The curves for one and two tanks are close, being the configuration made of one tank more favourable. This curve is

Table 7 – Summary of process costs and calculation of H$_2$ storage cost (currency in Euro).

	3,5-dibenzyl toluene		2-methyl indole		N-ethyl carbazole
	1 tank	2 tanks	1 tank	2 tanks	2 tanks
ANNUALIZED INVESTMENT	323 000	579 000	392 000	516 000	648 000
OPERATING COST	4 881 900	5041 000	5 000 500	5017 800	7 955 100
TOTAL ANNUAL COST	5 204 900	5620 000	5 392 500	5533 800	8 603 100
H$_2$ plant (MW)	6.2	6.2	6.0	6.3	6.1
H$_2$ consumption (t H$_2$/year)	1630	1630	1580	1660	1600
Storage cost (€/kg H$_2$)	**3.22**	**3.45**	**3.41**	**3.32**	**5.38**

Fig. 2 – Sensitivity analysis of the main design variables on hydrogen cost. Left graphs: 3,5-dibenzyl toluene with a reactor of one (—) and two (—) tanks in series. Right graphs: 2-methyl indole with a reactor of one (—) and two (—) tanks in series.

particularly useful to select the plant capacity for a given application.

The reactor temperature has almost no influence on the production cost of hydrogen, being the configuration with one tank the best option. On increasing reaction temperature, the reaction rate increases (according to Arrhenius equation and the kinetic parameters of Table 2), which may lead to a lower reactor size and cost. However, the LOHC 3,5-dibenzyl toluene has a remarkably high reaction enthalpy (−530 kJ/mol, Table 1) and the reactor must be designed to extract all this heat and maintain the required temperature. For this reason, the reactor volume cannot be reduced and there is no benefit when increasing temperature.

Finally, the reactor pressure has no influence on H_2 cost up to 6 MPa and, above this value, the cost increases linearly. This behaviour is explained because hydrogen is supplied from an electrolytic cell at 6 MPa. Thus, above 6 MPa, a compressor is required to raise pressure and, hence, the costs increase.

The sensitivity analysis for 2-methyl indole is shown in Fig. 2 (right). The influence of plant capacity on hydrogen cost has a similar curve to that of 3,5-dibenzyl toluene. At low plant capacity values, the cost decreases sharply and, for high values, it decreases asymptotically to a value around 3 €/kg. For this LOHC, there is no difference between one and two tanks since their curves overlap.

In this case, the reactor temperature has a positive influence on the cost of H_2, particularly for the configuration with one tank. This LOHC has a lower reaction enthalpy, and the reactor design is ruled by the reaction kinetic, rather than the heat exchange to the tank jacket. Thus, on increasing the reaction temperature, reaction rate increases and, hence, the reactor volume and cost decreases, leading to a lower H_2 cost. For a reactor configuration of two tanks, this behaviour is not observed, because the reduction in the total reactor volume obtained with two tanks cannot be implemented due to the requirements of the reaction heat removal. Regarding the reactor pressure, the behaviour is quite similar to 3,5-dibenzyl toluene with an increase of H_2 cost above 6 MPa.

The sensitivity analysis of the last LOHC, N-ethylcarbazole, for the case of a reactor configuration of two tanks is shown in Fig. 3. The curves of the other LOHCs for the same reactor configuration have also been included. It can be observed that the overall behaviour of N-ethylcarbazole can be extrapolated from that of the other LOHC. However, the H_2 cost scale range is much higher for this LOHC. The reactor temperature has a small influence on the cost, which decrease on increasing temperature. This can be explained by the lower reaction rate of this LOHC, which means that the reactor sizing is ruled by the reaction kinetics. The trends of plant capacity and reactor pressure are similar to the other LOHC.

Overall, it can be said that 2-methyl indole is the LOHC providing the lowest H_2 storage cost; however, 3,5-dibenzyl toluene performs similar with a slightly higher cost.

The optimum design variables are plant capacity of 18 MW, reactor temperature of 190 °C and pressure of 6 MPa. As shown in Fig. 3, the plant capacity has an asymptotic behaviour, which means that an increase above 18 MW produces little
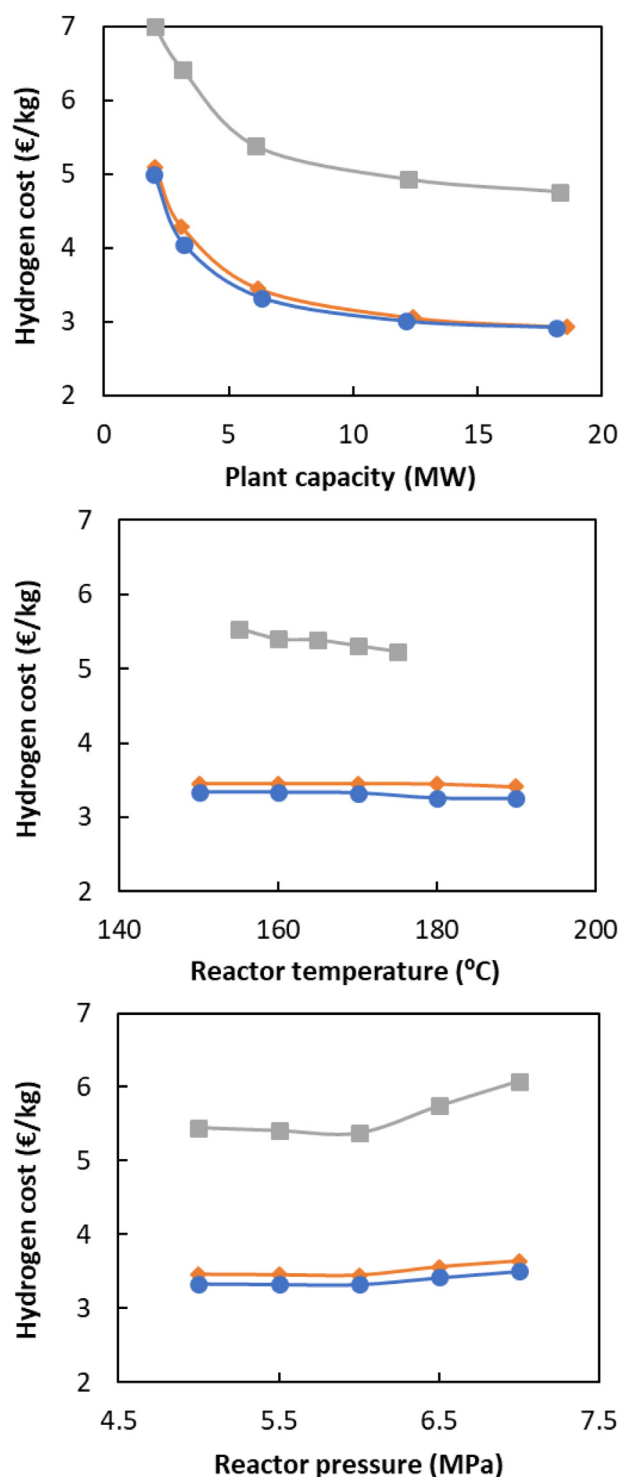

Fig. 3 – Sensitivity analysis of the main design variables on hydrogen cost for a reactor made of two tanks in series. Comparison of LOHC: (—) 3,5-dibenzyl toluene, (—) 2-methyl indole and (—) N-ethylcarbazole.

reduction on the cost. However, larger plants required higher capital investment and have a reduced operability, e.g., to adapt to market variations. For this reason, 18 MW is selected as an adequate optimum value.

Table 8 – Summary of the economic analysis for the optimum conditions: 18 MW of plant capacity, 190 °C of reactor temperature and 6 MPa of pressure (currency in Euro).

	3,5-dibenzyl toluene		2-methyl indole	
	2 tanks parallel	2 tanks series	1 tank	2 tanks series
Reactor size (m^3, each tank)	14	40	25	25
TOTAL CAPITAL INVESTMENT	3 700 000	6550 000	3 400 000	5070 000
ANNUALIZED INVESTMENT	740 000	1300 000	670 000	1 010 000
OPERATING COSTS	12 540 000	12 950 000	12 710 000	12 550 000
TOTAL ANNUAL COST	13 280 000	14 250 000	13 380 000	13560 000
H$_2$ plant power (MW)	18.5	18.6	17.8	18.1
H$_2$ consumption (t H$_2$/year)	4860	4890	4680	4760
H$_2$ storage cost (€/kg H$_2$)	2.73	2.92	2.86	2.86

Process scale-up and economic analysis at optimum conditions

The plant has been scale-up at the optimum conditions determined in the sensitivity analysis of the previous section: plant capacity of 18 MW, reactor temperature of 190 °C and pressure of 6 MPa. Table 8 summarizes the main economic indicators and the H$_2$ storage cost for the two LOHC that performed better: 3,5-dibenzyl toluene and 2-methyl indole. The reactor configurations with one and two tanks were considered. However, for 3,5-dibenzyl toluene, the use of just one single tank would require large tank size, exceeding the maximum recommended. Therefore, the use of two tanks in parallel of equal size was considered for this case.

The economic analysis for the optimum conditions indicates that the process with the lowest capital investment is the one based on 2-methyl indole with a reactor of one tank. The operating costs are quite similar for all the processes, the lowest one being that based on 3,5-dibenzyl toluene with a reactor of two tanks in parallel. This process is also the one with the lowest total annual cost and hydrogen storage cost, 2.73 €/kg. Consequently, this is the recommended process and operating conditions of all the processes studied in this work. The use of a reactor made of two tanks in parallel reduce considerably the capital investment and makes it easier the control of the reactor temperature.

The generation of hydrogen using renewable energy (e.g., solar and wind power) may suffer from intermittent production with periods of surplus (for example, in spring-summer) and periods of depletion, when the plant must be stopped. The economic analysis has been carry out considering a 10-year period (with interest rate of 15%) to annualise the capital investment and that the plant operates for 300 days every year. In case the plant operated for fewer days a year, the consumption of H$_2$ and generation of LOHC would decrease and, hence, the cost of H$_2$ storage would increase. To evaluate the impact of this, one should examine the contribution of the different costs to the total annual costs. Thus, 94% of the total annual costs correspond to operating costs (Table 8), of which 74% are due to raw materials (mainly LOHC make-up) and utilities (Table 6). When the plant stops, raw materials and utilities are not consumed. Since they are the greater contributors to the total annual costs (70% of them) and the H$_2$ storage cost, the impact of fewer operating days a year would be limited.

To verify this, the influence on the H$_2$ storage cost of the annual usage of the plant capacity has been evaluated for the case of the 3,5-dibenzyl toluene process with a reactor of two tanks in parallel (the process with the lowest H$_2$ storage cost). The nominal plant capacity is 18 MW, (Table 8). As shown in Fig. 4a, if the annual use of plant capacity decreases to a 50% of the nominal, the storage cost will increase ca. 20%.

In the calculations, it was assumed a LOHC recovery of 90% considering all the stages, i.e., hydrogenation, storage, and dehydrogenation. The LOHC recovery is negatively affected by undesired reactions, taking place during the hydrogenation
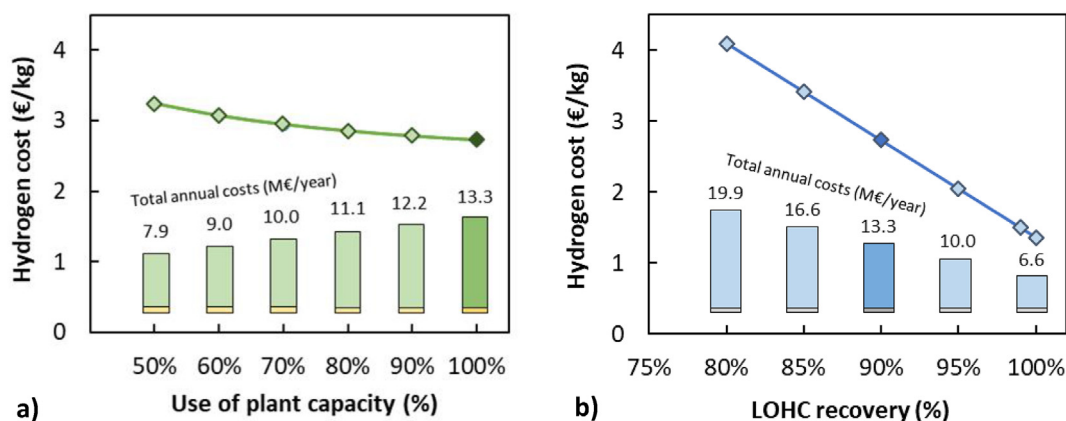
Fig. 4 – Analysis of the influence of the annual use of plant capacity (a) and LOHC recovery yield (b) on the hydrogen storage cost. Nominal plant capacity: 18 MW. LOHC: 3,5-dibenzyl toluene with a reactor of two tanks in parallel. Bar diagrams: annualized investment and operating costs.

and dehydrogenation, and transforming the LOHC into other compounds not suitable for hydrogen storage. One of the most important criteria when selecting a LOHC candidate is their high selectivity, to reduce the formation of these undesired compounds.

As shown in the sensitivity analysis of Fig. 4b, the LOHC recovery has an important impact on the final cost of hydrogen storage. The operating costs, of which the most important is the cost of the LOHC make-up, have a great impact in the storage costs. Thus, for 3,5-dibenzyl toluene, an increase of LOHC recovery from 90% to 99% would decrease the storage cost from 2.73 to 1.50 €/kg (these figures correspond to the optimized process). This increase in recovery is plausible as the technology is completely developed and stablished to industrial scale.

Conclusions

The adequacy of 3,5-dibenzyl toluene, 2-methyl indole and N-ethylcarbazole as liquid organic hydrogen carriers (LOHC) has been evaluated. The hydrogenation of these compounds in three-phase stirred tank reactors, loaded with a slurry of Ni and Ru-based catalysts, has been scaled-up. The proposed process is formed by the following stages: compression, reaction, separation, and hydrogen recycle. An economic evaluation performed on the process suggested that the most important costs are the operating costs associated to raw materials (the LOHC) and the investment cost corresponding to the reactor.

The influence of the main operating variables on the cost of hydrogen storage has been evaluated by means of a sensitivity analysis. The optimum variables are plant capacity, 18 MW, reactor pressure, 6 MPa, and reactor temperature, 190 °C. The LOHC with the minimum hydrogen storage cost at optimum operating conditions is 3,5-dibenzyl toluene with 2.73 €/kg. Specifically, a reactor configuration made of two stirred tanks in parallel was found to be optimum. It can be concluded that the storage cost can be reduced considerably (even down to 1.5 €/kg) by increasing the LOHC recovery of the overall storage process (made of hydrogenation, storage, and dehydrogenation stages). Given the high selectivity of the involved reactions, this is plausible in the short term as the technology is established at industrial scale.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

REFERENCES

[1] https://www.europarl.europa.eu/factsheets/en/sheet/72/combating-climate-change.

[2] Álvarez M, Marín P, Ordóñez S. Production of dimethyl carbonate by gas-phase oxidative carbonylation of methanol over Cu/Y zeolite: mechanism and kinetics. Fuel Process Technol 2023;247:107805.

[3] Peláez R, Marín P, Ordóñez S. Direct synthesis of dimethyl ether from syngas over mechanical mixtures of CuO/ZnO/Al2O3 and γ-Al2O3: process optimization and kinetic modelling. Fuel Process Technol 2017;168:40—9.

[4] Stöckl F, Schill W-P, Zerrahn A. Optimal supply chains and power sector benefits of green hydrogen. Sci Rep 2021;11:14191.

[5] Yee Mah AX, Ho WS, Hassim MH, Hashim H, Liew PY, Muis ZA. Targeting and scheduling of standalone renewable energy system with liquid organic hydrogen carrier as energy storage. Energy 2021;218:119475.

[6] Liu W, Zuo H, Wang J, Xue Q, Ren B, Yang F. The production and application of hydrogen in steel industry. Int J Hydrogen Energy 2021;46:10548—69.

[7] Kojima Y, Yamaguchi M. Ammonia as a hydrogen energy carrier. Int J Hydrogen Energy 2022;47:22832—9.

[8] Marín P, Patiño Y, Díez FV, Ordóñez S. Modelling of hydrogen perm-selective membrane reactors for catalytic methane steam reforming. Int J Hydrogen Energy 2012;37:18433—45.

[9] Ma K, Deng J, Wang G, Zhou Q, Xu J. Utilization and impacts of hydrogen in the ironmaking processes: a review from lab-scale basics to industrial practices. Int J Hydrogen Energy 2021;46:26646—64.

[10] Ren J, Musyoka NM, Langmi HW, Mathe M, Liao S. Current research trends and perspectives on materials-based hydrogen storage solutions: a critical review. Int J Hydrogen Energy 2017;42:289—311.

[11] Schlapbach L, Züttel A. Hydrogen-storage materials for mobile applications. Nature 2001;414:353—8.

[12] Preuster P, Alekseev A, Wasserscheid P. Hydrogen storage technologies for future energy systems. Annu Rev Chem Biomol Eng 2017;8:445—71.

[13] Barthelemy H, Weber M, Barbier F. Hydrogen storage: recent improvements and industrial perspectives. Int J Hydrogen Energy 2017;42:7254—62.

[14] Ramirez-Vidal P, Canevesi RLS, Sdanghi G, Schaefer S, Maranzana G, Celzard A, et al. A step forward in understanding the hydrogen adsorption and compression on activated carbons. ACS Appl Mater Interfaces 2021;13:12562—74.

[15] Fomkin A, Pribylov A, Men'shchikov I, Shkolin A, Aksyutin O, Ishkov A, et al. Adsorption-based hydrogen storage in activated carbons and model carbon structures. Reactions 2021;2:209—26.

[16] Thomas KM. Hydrogen adsorption and storage on porous materials. Catal Today 2007;120:389—98.

[17] He T, Wu H, Wu G, Wang J, Zhou W, Xiong Z, et al. Borohydride hydrazinates: high hydrogen content materials for hydrogen storage. Energy Environ Sci 2012;5:5686—9.

[18] Juangsa FB, Irhamna AR, Aziz M. Production of ammonia as potential hydrogen carrier: review on thermochemical and electrochemical processes. Int J Hydrogen Energy 2021;46:14455—77.

[19] Heris M-N, Mirzaei MA, Asadi S, Mohammadi-Ivatloo B, Zare K, Jebelli H, et al. Evaluation of hydrogen storage technology in risk-constrained stochastic scheduling of multi-carrier energy systems considering power, gas and heating network constraints. Int J Hydrogen Energy 2020;45:30129—41.

[20] Makepeace JW, He T, Weidenthaler C, Jensen TR, Chang F, Vegge T, et al. Reversible ammonia-based and liquid organic hydrogen carriers for high-density hydrogen storage: recent progress. Int J Hydrogen Energy 2019;44:7746–67.

[21] Ferreira APRA, Oliveira RCP, Mateus MM, Santos DMF. A review of the use of electrolytic cells for energy and environmental applications. Energies 2023;16:1593.

[22] Bollmann J, Schmidt N, Beck D, Preuster P, Zigan L, Wasserscheid P, et al. A path to a dynamic hydrogen storage system using a liquid organic hydrogen carrier (LOHC): burner-based direct heating of the dehydrogenation unit. Int J Hydrogen Energy 2023;48:1011–23.

[23] Kim C, Lee Y, Kim K, Lee U. Implementation of formic acid as a liquid organic hydrogen carrier (LOHC): techno-economic analysis and life cycle assessment of formic acid produced via CO2 utilization. Catalysts 2022;12:1113.

[24] Hamayun MH, Hussain M, Maafa IM, Aslam R. Integration of hydrogenation and dehydrogenation system for hydrogen storage and electricity generation – simulation study. Int J Hydrogen Energy 2019;44:20213–22.

[25] Preuster P, Papp C, Wasserscheid P. Liquid organic hydrogen carriers (LOHCs): toward a hydrogen-free hydrogen economy. Acc Chem Res 2017;50:74–85.

[26] Niermann M, Beckendorff A, Kaltschmitt M, Bonhoff K. Liquid organic hydrogen carrier (LOHC) – assessment based on chemical and economic properties. Int J Hydrogen Energy 2019;44:6631–54.

[27] Lee S, Kim T, Han G, Kang S, Yoo Y-S, Jeon S-Y, et al. Comparative energetic studies on liquid organic hydrogen carrier: a net energy analysis. Renew Sustain Energy Rev 2021;150:111447.

[28] Markiewicz M, Zhang Y-Q, Empl MT, Lykaki M, Thöming J, Steinberg P, et al. Hazard assessment of quinaldine-, alkylcarbazole-, benzene- and toluene-based liquid organic hydrogen carrier (LOHCs) systems. Energy Environ Sci 2019;12:366–83.

[29] Díaz E, Rapado-Gallego P, Ordóñez S. Systematic evaluation of physicochemical properties for the selection of alternative liquid organic hydrogen carriers. J Energy Storage 2023;59:106511.

[30] Hiyoshi N, Rode CV, Sato O, Shirai M. Biphenyl hydrogenation over supported transition metal catalysts under supercritical carbon dioxide solvent. Appl Catal, A 2005;288:43–7.

[31] Leinweber A, Müller K. Hydrogenation of the liquid organic hydrogen carrier compound monobenzyl toluene: reaction pathway and kinetic effects. Energy Technol 2018;6:513–20.

[32] Huynh N-D, Hur SH, Kang SG. Tuning the dehydrogenation performance of dibenzyl toluene as liquid organic hydrogen carriers. Int J Hydrogen Energy 2021;46:34788–96.

[33] Hu P, Fogler E, Diskin-Posner Y, Iron MA, Milstein D. A novel liquid organic hydrogen carrier system based on catalytic peptide formation and hydrogenation. Nat Commun 2015;6:6859.

[34] Brigljević B, Byun M, Lim H. Design, economic evaluation, and market uncertainty analysis of LOHC-based, CO2 free, hydrogen delivery systems. Appl Energy 2020;274:115314.

[35] Oh J, Jeong K, Kim TW, Kwon H, Han JW, Park JH, et al. 2-(N-Methylbenzyl)pyridine: a potential liquid organic hydrogen carrier with fast H2 release and stable activity in consecutive cycles. ChemSusChem 2018;11:661–5.

[36] Yang X, Wu Y, Yu H, Sun M, Zheng J, Li X, et al. A YH3 promoted palladium catalyst for reversible hydrogen storage of N-ethylcarbazole. Int J Hydrogen Energy 2020;45:33657–62.

[37] Fei S, Han B, Li L, Mei P, Zhu T, Yang M, et al. A study on the catalytic hydrogenation of N-ethylcarbazole on the mesoporous Pd/MoO3 catalyst. Int J Hydrogen Energy 2017;42:25942–50.

[38] Yang M, Dong Y, Fei S, Ke H, Cheng H. A comparative study of catalytic dehydrogenation of perhydro-N-ethylcarbazole over noble metal catalysts. Int J Hydrogen Energy 2014;39:18976–83.

[39] Gianotti E, Taillades-Jacquin M, Rozière J, Jones DJ. High-purity hydrogen generation via dehydrogenation of organic carriers: a review on the catalytic process. ACS Catal 2018;8:4660–80.

[40] Brückner N, Obesser K, Bösmann A, Teichmann D, Arlt W, Dungs J, et al. Evaluation of industrially applied heat-transfer fluids as liquid organic hydrogen carrier systems. ChemSusChem 2014;7:229–35.

[41] Ali A, Kumar GU, Lee HJ. Investigation of hydrogenation of Dibenzyltoluene as liquid organic hydrogen carrier. Mater Today Proc 2021;45:1123–7.

[42] Shi L, Qi S, Qu J, Che T, Yi C, Yang B. Integration of hydrogenation and dehydrogenation based on dibenzyltoluene as liquid organic hydrogen energy carrier. Int J Hydrogen Energy 2019;44:5345–54.

[43] Wan C, An Y, Xu G, Kong W. Study of catalytic hydrogenation of N-ethylcarbazole over ruthenium catalyst. Int J Hydrogen Energy 2012;37:13092–6.

[44] Li L, Yang M, Dong Y, Mei P, Cheng H. Hydrogen storage and release from a new promising liquid organic hydrogen storage carrier (LOHC): 2-methylindole. Int J Hydrogen Energy 2016;41:16129–34.

[45] Sotoodeh F, Zhao L, Smith KJ. Kinetics of H2 recovery from dodecahydro-N-ethylcarbazole over a supported Pd catalyst. Appl Catal, A 2009;362:155–62.

[46] Runge P, Sölch C, Albert J, Wasserscheid P, Zöttl G, Grimm V. Economic comparison of different electric fuels for energy scenarios in 2035. Appl Energy 2019;233–234: 1078–93.

[47] Woods DR. Rules of thumb in engineering practice. Wiley-VCH; 2007.

[48] Azzopardi BJ, Mudde RF, Lo S, Morvan H, Yan Y, Zhao D. Sparged stirred vessels. Hydrodynamics of gas-liquid reactors. 2011. p. 61–89.

[49] Biardi G, Baldi G. Three-phase catalytic reactors. Catal Today 1999;52:223–34.

[50] Towler G, Sinnott R. Chemical engineering design. Principles, practice and economics of plant and process design. 2nd ed. Elsevier; 2008.

[51] Peters MS, Timmerhaus KD, West RE. Plant design and economics for chemical engineers. 5º ed. McGraw-Hill; 2003.