Research Papers

Systematic evaluation of physicochemical properties for the selection of alternative liquid organic hydrogen carriers

Eva Díaz, Pablo Rapado-Gallego, Salvador Ordóñez *

Catalysis, Reactors and Control Research Group (CRC), Department of Chemical and Environmental Engineering, University of Oviedo, Julián Clavería s/n, 33006 Oviedo, Spain

A B S T R A C T

Chemical hydrogen storage is a key step for establishing hydrogen as a main energy vector. For this purpose, liquid organic hydrogen carriers (LOHCs) present the outstanding advantage of allowing a safe, efficient, and high-density hydrogen storage, being also highly compatible with existing transport infrastructures. Typical LOHCs are organic compounds able to be hydrogenated and dehydrogenated at mild conditions, enabling the hydrogen storage and release, respectively. In addition, the physical properties of these chemicals are also critical for practical implementation.

In this work, key properties of potential LOHCs of three different chemical families (homoaromatics, and N- and O-heteroaromatics) are estimated using molecular simulations. Thus, density, viscosity, vapour pressure, octanol-water coefficient, melting point, flash point dehydrogenation enthalpy and hydrogen content are estimated using the programs COSMO-RS and HYSYS. In addition, we have also evaluated the performance of several binary mixtures as LOHCs using these methodologies.

Considering the hydrogen content, characteristic temperatures, and previous experimental results of the cyclic process; our simulation results suggest that 1-methylnaphthalene/1-methyldecahydronaftalene and methyl-benzylpyridine/perhydromethylbenzylpyridine pairs are appropriate candidates for chemical hydrogen storage. Binary mixtures of LOHCs are also relevant alternatives since substances with a great potential can be used as LOHCS when dissolved. That is the case of naphthalene and 1-methyl-naphthalene mixtures or indoles dissolved in benzene or benzylbenzene. Concerning O-compounds, although several pairs could be used as LOHCs, thermodynamic and kinetic feasibility of the hydrogenation/dehydrogenation cycles must be better studied.

1. Introduction

Hydrogen promotion initiatives (as "Hydrogen Roadmap Europe") [1] are not only useful for reducing carbon emissions, but also for limiting resource and energy dependence. Hydrogen will also play a systemic role in the transition to renewables, providing mechanisms to seasonally storage, as well as transporting and distributing energy throughout different industrial and residential utilities. However, its low energy density and its complicate handling largely hinders the development of hydrogen-based processes.

For overcoming these challenges, chemical hydrogen storage in organic molecules, which are liquids at ambient conditions, is nowadays considered as a key strategy [2–4]; these organics being called liquid organic hydrogen carriers (*LOHCs*). These compounds allow hydrogen molecules storage by catalytic hydrogenation (exothermic), being the

hydrogen released by catalytic dehydrogenation (endothermic) reactions. A great advantage of this system is that it allows safe and efficient high-density hydrogen storage in an easy-to-handle oil, without requiring pressurized tanks for storage and transport. Furthermore, these compounds are compatible with existing transport infrastructures and refuelling facilities since they are liquid at ambient conditions, although the need of a bidirectional transport (loaded and unloaded LOHC), as well as storage in separate tanks, is required. Due to the interest of these compounds, several recent reviews [3,5–7] deal with the optimal features of these substances: low melting points (<-25 °C) and high boiling points (> 300 °C), high storage capacity (gravimetric, preferable >4 or 5 %), low dehydrogenation enthalpies (preferable, <60 kJ mol H_2^{-1}), safety and environmental aspects must be also considered.

The high hydrogen loading capacity of formic acid (4.4 %) and,

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* Corresponding author.
   E-mail address: sordonez@uniovi.es (S. Ordóñez).

especially, methanol (12.1 %), has justified the studies on the use of both compounds as fuels [6,8,9], with some drawbacks related to degradation [3] which limit these commercial applications. Both compounds have in common that carbon dioxide is the starting material for hydrogen storage. This fact presents several concerns: first, from the point of view of the intrinsic meaning of *LOHC*, both the hydrogenated and dehydrogenated compound should be liquid under ambient conditions; and more relevantly, hydrogenation reactions yielding these compounds are equilibrium-limited and not fully selective.

With these premises, *LOHCs* are organic compounds whose unsaturations (multiple bonds) are easily either hydrogenated or dehydrogenated in presence or absence of molecular hydrogen, respectively. Among these compounds, aromatic rings are the first candidates. Thus, toluene/methylcyclohexane and benzene/cyclohexane [10,11] were the first compounds proposed for this purpose. Other pairs also considered in the literature were naphthalene/tetralin/decalin, biphenyl/bicyclohexane and dibenzyltoluene/perhydrodibenzyltoluene (commercialized by Hydrogenious) [2,12,13]. All these compounds, which belong to homocyclic compounds group, are compatible with existing infrastructures, but present high dehydrogenation enthalpies. At this point, the incorporation of heteroatoms into homocyclic *LOHCs* structure is proved to reduce the dehydrogenation enthalpy, promoting H_2 release at milder conditions [14].

A common feature of the above proposed hydrogen carriers is that most of them are mainly obtained from petrochemical feedstocks, but only some of them from renewable sources. Ideally, and from the point of view increasing the sustainability of the entire process, obtaining *LOHCs* from renewable feedstocks, such as biomass, is a great challenge for this purpose. In addition, in the case of biomass, there is the concomitant advantage that hydrogenation and dehydrogenation reactions are widely implemented in the sector with the aim of obtaining deoxygenated fuels [15–19].

The challenge is to identify compounds obtained from renewable sources that meet the requirements to be considered *LOHC*: liquid state under ambient conditions, high hydrogen storage capacity, appropriate reactivity (especially in dehydrogenation reactions), stability to cycles of hydrogenation/dehydrogenation and safe handling (Table 1).

Considering all these challenges, the scope of this article has been to systematically identify chemical compounds suitable for being used as *LOHCs* in terms of their main physical properties. Three different kinds of molecules have been considered: aromatic compounds (without heteroatoms), nitrogenated compounds and oxygenated compounds. The potential *LOHCs* have been evaluated on terms of their main physicochemical properties. In addition, the use of binary mixtures (especially useful for those compounds that are solid at room temperature) has been explored, evaluating the solubility of the considered compound in liquid solvents. These systematics studies are of interest for designing chemical hydrogen storage units, being not systematically studied up to now.

2. Methodology

The investigated properties are summarized in Table 1. The hydrogen storage capacity has been obtained from stoichiometric considerations, whereas reaction enthalpy has been calculated from the bond enthalpies, considering the stability of the molecules in their aromatic form from the energy resonance [20]. For those cases in which these values have not been published or is not possible its calculation, simulation tools had been used.

ADF COSMO-RS (Conductor like Screening Model for Realistic Solvents), 2021.104 version, developed by *SCM* (Software for Chemistry & Materials) is used in this work. Homocyclic hydrocarbons such us toluene, benzene or naphthalene, and common heterocyclic molecules, such as quinoline or phenazine were already in the *ADFCRS-2018* database. However, most of the heterocyclic molecules, as N-ethylcarbazole, and not common homocyclic molecules like dibenzyltoluene (*DBT*) were created using the *ADF* parametrization method, and the

Table 1
Key properties considered in the selection of appropriate *LOHCs*.

Property	Justification
Density	Handling: LOHC should be pumped as a Newtonian liquid
Viscosity	
Vapour pressure	Handling: avoiding evaporative losses during storage and safety issues.
Octanol-water partition coefficient, log K_{ow}	Environmental protection: it is a measure of lipophilicity and bioaccumulation potential.
Melting temperature	Handling: ensuring liquid state at the operation conditions.
Boiling temperature	
Flash temperature	Safety issues
Dehydrogenation enthalpy	Feasibility of dehydrogenation reaction
Hydrogen loading capacity	Storage capacity

Hartree-Fock method for obtaining an optimal configuration [21]. For most of the created molecules, the geometry optimization was performed with a basis set of *TP2Z* for big molecules, a scalar relativity level which gives an small cost of calculations, an *XC* functional of *GGA:BP86*. Once created the molecule, this program allows using *COSMO-RS*, *COSMO-SAC* or *UNIFAC* implementations. *COSMO-RS* and *COSMO-SAC* perform theoretical calculations though intermediate results from quantum mechanical calculations, thus allowing to obtain properties both individually and in mixtures. On the other hand, *UNIFAC*, a derivation of *UNIQUAC*, performs estimations without a previous estimation of the *3D* structure. Due to the complexity of some molecules and, in agreement with McBride et al. [22] and Linke et al. [23], the implementation of COSMO-RS in ADF, which is based on the COSMO-RS method developed by Klamt et al. [24], is used.

The Property Prediction program in *ADF* estimates physical properties of pure compounds [25]. The way it is done is mapping *QSPR* descriptors from quantum mechanical calculations of an input molecule to return some of the property values needed such as density, melting point, boiling point, flash point and vapour pressure. These quantum mechanical calculations include the sigma-profile values the *COSMO-RS* method needs to calculate the main properties of the method, the solubility and the partition coefficients [26].

Viscosity, as involves the molecule in liquid state, was estimated by *ASPEN HYSYS* [5]. Molecules not found in the database area created as hypothetical by addition of the different functional groups. *UNIQUAC* was selected as Fluid Package since it allows working with nitrogenised molecules [27].

In order to check the validity of the proposed estimation codes, the correlation between the estimated values and those values reported in the literature are shown in Fig. 1 for the key properties and different kinds of organic chemicals. As observed in this Figure, the prediction codes provide accurate prediction trends for most of the considered molecules for all the estimated parameters, except melting points. Melting point is quite difficult to predict since it depends on the pairwise interactions of the molecules at the phase transition temperature (as boiling point), and on the unpredictable ability of the molecules to be packed maximizing attractive interaction in the crystal lattice [28]. This fact means that the molecular geometry presents a key role on the melting point values. All these facts hinder the accurate prediction of this parameter.

3. Results and discussion

As mentioned in the Introduction section, most of the chemicals nowadays proposed as *LOHCs* are either polyaromatic structures without heteroatoms or nitrogen-containing aromatic compounds. Although, largely less proposed, oxygenated polyaromatics are attractive alternative since many of them can be obtained from renewable resources. Different organics have been identified as potential *LOHCs*, their properties being estimated and discussed in the following sections grouped in aromatic, nitrogen-containing molecules and oxygen-
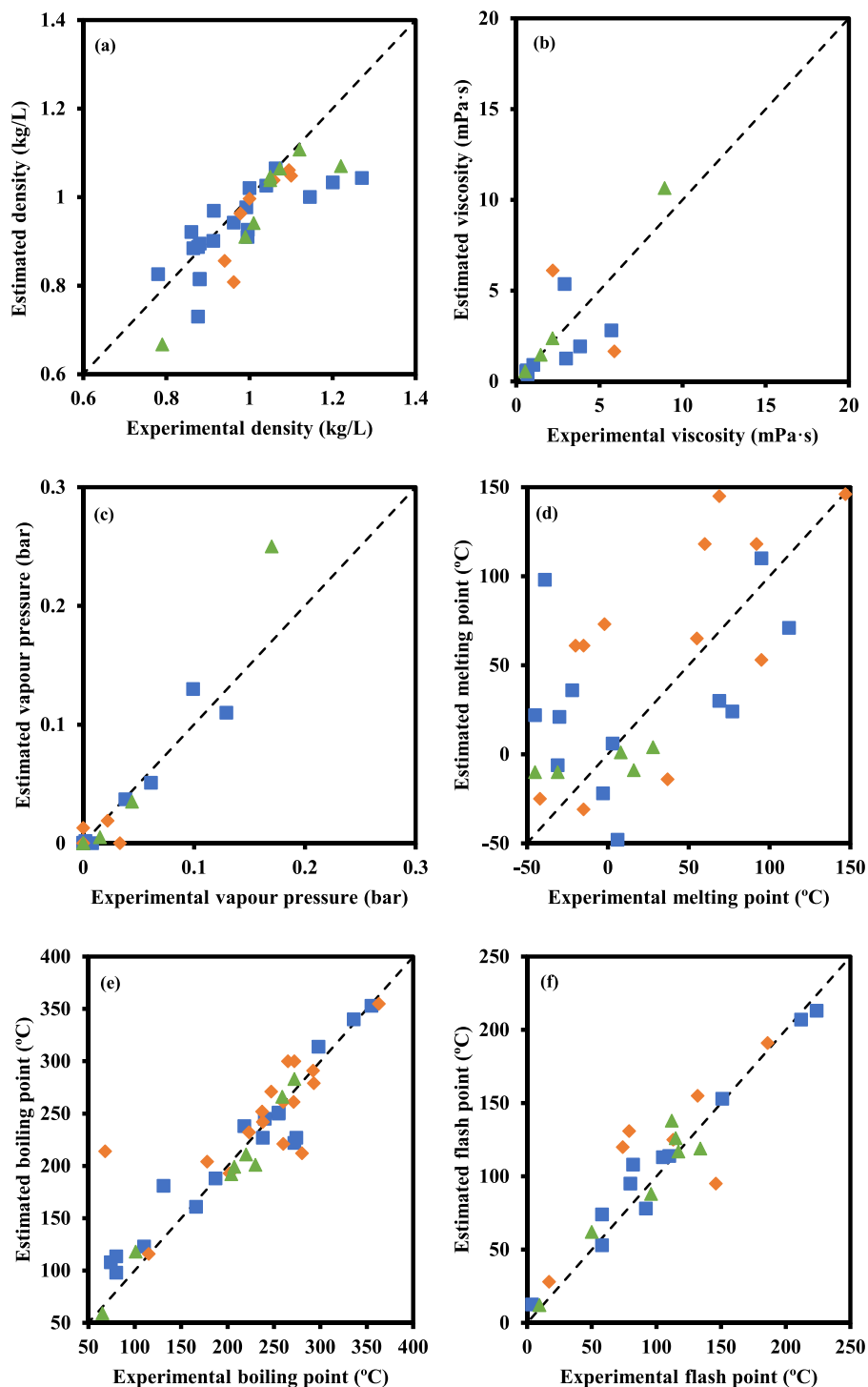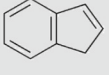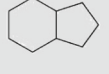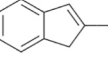
Fig. 1. Parity plots of estimated and experimental properties: (a) Density, (b) Viscosity, (c) Vapour pressure, (d) Melting point, (e) Boiling points, and, (f) Flash points. Represented compounds: homocyclic compounds, (■), N-heterocyclic compounds, (◆), and O-heterocyclic compounds, (▲).

Table 2A
Physical properties of pairs homocyclic compounds (sucessively ordered on their dehydrogenated/ hydrogenated form). Estimated data in brackets: A = *ASPEN HYSYS*, B = *COSMO-RS*. In parentheses, experimental values taken from the safety data sheets (SigmaAldrich, ThermoFisher, GroupChem, Carl Roth).

LOHC	State of matter	Formula	Structure	Density (g/cm^3)	Viscosity (mPa·s)	Vapour pressure at 25ºC (bar)	log Kow
Benzene	L	C_6H_6		0.887 [B] (0.876)	0.605 [A] (0.647)	0.13 [B] (0.1)	2.12 [B]
Cyclohexane	L	C_6H_{12}		0.826 [B] (0.780)	0.898 [A] (1.02)	0.11 [B] (0.13)	3.29 [B]
Toluene	L	C_7H_8		0.884 [B] (0.865)	0.546 [A] (0.590)	0.037 [B] (0.038)	2.67 [B]
Methylcyclohexane	L	C_7H_{14}		0.814 [B] (0.880)	0.683 [A] (0.679)	0.05 [B] (0.06)	3.73 [B]
Indene	L	C_9H_8		0.926 [B] (0.996)	2.450 [A]	0.002 [B]	2.93 [B]
Hydrindane	L	C_9H_{16}		0.815 [B] (0.88)	2.030 [A]	0.004 [B]	3.83 [B]
2-Methylindene	L	$C_{10}H_{10}$		0.815 [B]	2.030 [A]	<0.001 [B]	3.83 [B]

containing molecules. For each of the considered group, *LOHC* pairs were selected based on either published results about its use for this purpose or promising chemical properties, as discussed below. In all the cases, experimental data is taken from Materials Safety Data Sheets, when available, this data was also validated from published papers devoted to the study of physical properties. Although it could be considered that MSDS provide conservative estimations of the parameters, this data show very tight match with published values.
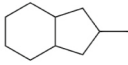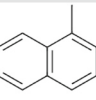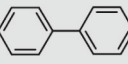
3.1. Aromatic and polyaromatic compounds
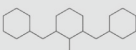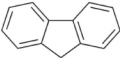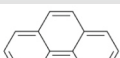
The first proposed *LOHCs* are monoaromatic compounds, because of their large availability. About 70 % of the total benzene, toluene, and xylenes production is obtained from petroleum naphtha, although these fractions also come from ethylene plants, as by-product of pyrolysis gasoline, from side liquid streams of coke ovens [29,30] and, more recently, from natural gas through aromatization reactions [29]. However, aromatic compounds can not only be obtained from non-renewable sources. In the last years, several manufacture strate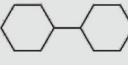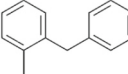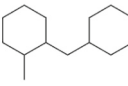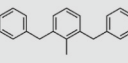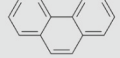gies have been proposed for obtaining aromatics from bioplatform molecules, aldol condensation/dehydration for obtaining benzene derivatives from

aldehydes and ketones [31] or Diels-Alders reactions between dehydrated bioethanol (ethylene, dienophile) and furanic compounds (dienes) [32]. Changing single bioplatform molecules by more complex biorefinery streams (as pyrolysis oils) lead to a plethora of different aromatic (both monocyclic and polycyclic) compounds [33–38].

3.1.1. Pure aromatic compounds used as LOHCs

First *LOHC* systems were based on the toluene/methylcyclohexane pair (Table 2A), with a 6.16 wt% H$_2$ and an enthalpy of dehydrogenation of 68.3 kJ/mol H$_2$, Table 2B. This high energy demand for carrying out the dehydrogenation requires working at high temperatures for releasing hydrogen, with the concomitant presence of cracking reactions, hindering the cyclic reuse of the organic carrier [2,39–41]. Likewise, the low flash point value of the compounds of this system represents an added difficulty. In spite of these disadvantages, Chiyoda Corporation developed a system for the massive H$_2$ storage and transportation technology based on toluene/methylcyclohexane system, using sulfided nano-sized Pt cluster on the Al$_2$O$_3$ catalyst [42]. With similar chemical structure, the benzene/cyclohexane system would be attractive from the point of view of the hydrogen loading capacity, 7.13 wt% and, although the dehydrogenation enthalpy of cyclohexane is high

Name	State	Formula	Structure				
2-Methylocta hydroindene	L	$C_{10}H_{18}$		0.864 **[B]**	0.747 **[A]**	0.003 **[B]**	4.76 **[B]**
Naphthalene	S	$C_{10}H_8$		1 **[B]** (1.08)	-	<0.001 **[B]** (<0.001)	3.19 **[B]**
Decalin	L	$C_{10}H_{18}$		0.895 **[B]** (0.880)	2.257 **[A]** (3.00)	0.002 **[B]** (0.002)	4.70 **[B]**
1-Methyl naphthalene	L	$C_{11}H_{10}$		1.020 **[B]** (1.0)	2.91 **[A]** (3.0)	<0.001 **[B]**	3.67 **[B]**
1-Methyldeca hydronaphtalene	L	$C_{11}H_{10}$		0.853 **[B]**	1.477 **[A]**	<0.001 **[B]**	4.96 **[B]**
Biphenil	S	$C_{12}H_{10}$		0.977 **[B]** (0.992)	-	<0.001 **[B]** (<0.001)	3.86 **[B]**
Bicyclohexyl	L	$C_{12}H_{22}$		0.921 **[B]** (0.860)	3.16 **[A]**	<0.001 **[B]**	5.82 **[B]**
Bencyltoluene	L	$C_{14}H_{14}$		0.91 **[B]** (0.995)	1.92 **[A]** (1.840)	<0.001 **[B]** (<0.001)	2.34 **[B]**
Perhydrobencyl toluene	L	$C_{14}H_{26}$		0.73 **[B]** (0.876)	2.805 **[A]** (2.720)	<0.001 **[B]**	6.60 **[B]**
Dibencyltoluene	L	$C_{21}H_{20}$		1.026 **[B]** (1.040)	14.39 **[A]** (14.92)	<0.001 **[B]** (<0.001)	6.64 **[B]**

Name	State	Formula	Structure				
Perhydrodibencyl toluene	L	$C_{21}H_{38}$		0.901 [B] (0.913)	24.32 [A] (25.5)	<0.001 [B] (<0.001)	9.70 [B]
Fluorene	S	$C_{13}H_{10}$		1.033 [B] (1.200)	-	<0.001 [B]	3.93 [B]
Perhydrofluorene	S	$C_{13}H_{22}$		0.940 [B]	-	<0.001 [B]	6.43 [B]
Phenanthrene	S	$C_{14}H_{10}$		1.065 [B] (1.063)	-	<0.001 [B]	4.19 [B]
Perhydro phenanthrene	S	$C_{14}H_{24}$		0.969 [B] (0.914)	-	<0.001 [B]	6.32 [B]
Pyrene	S	$C_{16}H_{10}$		1.043 [B] (1.270)	-	<0.001 [B]	4.62 [B]
Perhydropyrene	S	$C_{16}H_{24}$		0.942 [B] (0.962)	-	<0.001 [B]	5.13 [B]

(68.6 kJ/mol H_2), its value is very close to that of methylcyclohexane. However, it has two clear drawbacks: the melting and boiling temperatures and the hazards associated with the use of these compounds. By presenting melting temperatures of 5 and 6 °C for benzene and cyclohexane, respectively, they would become solids in the coldest seasons of even the Mediterranean countries of Europe, while the low boiling temperatures would make it necessary to work under pressure conditions such keep them liquid. As far as safety is concerned, benzene is considered a dangerous substance, since it presents mutagenicity in germinal cells, carcinogenicity and specific target organ toxicity, all of them in category 1. Add to this, it has and has been banned from commercial use [43].

To overcome these problems, several authors propose the system naphthalene/decalin, with tetralin as intermediate [44–51]. As advantages, the higher hydrogen loading capacity and the high flash temperature, similar to diesel (60 °C) [52], as well as the elevated boiling point for the three compounds. Hydrogenation of naphthalene is carried out on Pt supported catalyst at moderate conditions, 70–150 °C and 30 bar [45] with satisfactory results. Decalin dehydrogenation was widely studied, observing the outstanding performance of noble metal catalysts [46,53], whereas the supports do not seem to play any key role.

As a peculiarity of this reaction, it is noteworthy that decalin can be found in its cis- or trans-form. From the point of view of thermodynamics, the reaction of cis-decalin in tetralin is much more favoured than trans-decalin transformation [50]. Moreover, according to equilibrium constants, the conversion of cis-decalin into trans-decalin results in decreased rate. The next step, from tetralin to naphthalene presents a lower activation energy, thus the former dominates the overall reaction pathway [48], kinetics being described as a Langmuir-type rate equation, with inhibition due to naphthalene adsorption [48,54,55]. A drawback of this reaction is the solid state of naphthalene at room temperature ($T_{melting}$ = 80 °C).

The systems benzyltoluene/perhydrobenzyltolune and dibenzyltoluene/perhydrodibenzyltoluene present several advantages, as the high hydrogen capacity, low melting temperature and elevated both boiling and flash point [56]. The former is characterized by its high hydrogen storage density (6.23 %), and moderate dehydrogenation enthalpy (65.4 kJ/mol H_2), add to good toxicological and stability profiles. Benzyltoluene or dibenzyltoluene regioisomers combine very wide liquid ranges with thermal stability and favourable toxicological profiles [2]. The pair of compounds with three aromatic rings are highly viscous, this fact being especially relevant in comparison to both gasoline (0.6 mPa·s) [57] or diesel (<3 mPa·s) [52]. Both pairs where industrially adopted by the German company Hydrogenious to be used as hydrogen carriers [58]. These substances are already used at large-scale as heat transfer oils, being available at moderate price [2]. Regarding the value of log K_{OW}, although these compounds have values much higher than gasoline (3.5) and diesel (3.3- > 6) [59,60], there is consensus that superlipophilic compounds (log K_{OW} > 7.2) and substances of high molecular weight (>700) do not show significant bioaccumulation, being the range of log K_{OW} between 5 and 8 which present the main bioaccumulation hazard [61]. That is, we could consider as acceptable log K_{ow} values lower than 5 and higher than 8.

According to Table 2A and B, the systems whose dehydrogenated molecules are pyrene, fluorene and phenanthrene present as special difficulty their high melting temperature. In addition, fluorene was studied as a *LOHC*, showing a low rate of dehydrogenation [62].

Finally, 1-methylnaphthalene/1-methyldecahydronaftalene pair could be specially promising to be considered as *LOHC*. Several works in the literature deal with the hydrogenation of 1-methylnaphthalene on Co—Mo catalysts at temperatures between 300 and 400 °C and even 78 bar [63,64], observing a strong inhibition effect of 1-methylnaphthalene, being Pt evidenced as the best catalyst for the hydrogenation [41,65]. In fact, hydrogenation of 1-methylnaphthalene on Pt catalysts

Table 2B

Physical properties of pairs homocyclic compounds (sucessively ordered on their dehydrogenated/hydrogenated form). Estimated data in brackets: A = ASPEN HYSYS, B = COSMO-RS. In parentheses, experimental values taken from the safety data sheets (SigmaAldrich, ThermoFisher, GroupChem, Carl Roth).

LOHC	Melting point (ºC)	Boiling point (ºC)	Flash point (ºC)	ΔH rec (kJ/mol H_2)	wt% H_2
Benzene	(5)	113.6 [B] (80)	-5.2 [B] (-11)	68.6	7.13
Cyclohexane	(6)	98 [B] (80)	-2 [B] (-20)		
Toluene	(-95)	123 [B] (110)	12.5 [B] (4)	68.3	6.16
Methylcyclohexane	(-127)	108 [B] (101)	2.3 [B] (-3)		
Indene	(-3)	181 [B] (131)	74 [B] (58)	81.3	6.44
Hydrindane	-65 [B]	161 [B] (166)	28 [B]		
2-Methylindene	-32 [B]	199 [B]	70 [B]	81.3	5.8
2-Methyloctahydroindene	-17 [B]	182 [B]	44 [B]		
Naphthalene	(80)	238 [B] (218)	95 [B] (80)	66.3	7.29
Decalin	(-40)	188 [B] (187)	53 [B] (58)		
1-Methylnaphthalene	(-22)	245 [B] 240	108 [B] (82)	65.8	6.57
1-Methyldecahydro naphtalene	-54 [B]	186 [B]	42.3 [B]		
Biphenil	(69)	250 [B] (255)	114 [B] (110)	65.7	7.28
Bicyclohexyl	(3)	227 [B] (238)	78 [B] (92)		
Bencyltoluene	(-80)	222 [B] (272)	127 [B]	65.8	6.22
Perhydrobencyltoluene	(-30)	251 [B] (255)	93 [B]		
Dibencyltoluene	(-39)	385.6 [B] (406)	207 [B] (212)	65.6	6.25
Perhydrodibencyltoluene	(-45)	353 [B] (355)	158 [B]		
Fluorene	(112)	314 [B] (298)	153 [B] (151)	60.3	6.73
Perhydrofluorene	16 [B]	227 [B]	89 [B]		
Phenanthrene	(95)	340 [B] (336)	170 [B]	61.9	7.27
Perhydrophenanthrene	46 [B]	227 [B] (274)	113 [B] (105)		
Pyrene	(151)	382 [B] (404)	213 [B] (224)	61.1	7.33
Perhydropyrene	38 [B]	251 [B]	118 [B]		

was reported to be almost complete at 150 °C and 30 bar on Pt/alumina [45], whereas in mixtures of several aromatic compounds, with 1-methylnaphthalene among them at 10–36 bar and 250–300 °C, the reaction stops in 1-methyltetralin [66]. This pair presents other significant additional advantages: the dehydrogenated compound is liquid at ambient conditions (not usual in the bicyclic aromatic compounds), it is present in carbochemical streams (by-product from coke ovens) and can be manufactured from bioplatform molecules by Diels-Alders condensations.

3.1.2. Mixtures of aromatic or polyaromatic compounds

The use of mixtures of a given high-performance LOHC with a solvent for tuning their physical properties would allow the use of potential LOHCs not fulfilling the required physical properties (for example solid materials). The idea will be even more attractive if the solvent also has

hydrogen storage capacity. Obviously, the kinetics of the simultaneous hydrogenation/dehydrogenation of both molecules must be determined for these binary systems before further considerations.

The idea of using mixtures of polyaromatic compounds and other solvents as *LOHCs* was firstly proposed for biphenyl [67]. This chemical can be suitable as *LOHC*, but it is solid at room temperature, whereas bicyclohexyl would be liquid at these conditions. In this circumstance, working with a biphenyl solvent could be a valid option, being its solubility at 0 °C in toluene 305 g/L, while in 1-methylnaphthalene, 228 g/L.

In the same way, the high melting point of the naphthalene hinders its use as *LOHC*, as it is solid at ambient conditions. However, these aromatic compounds are very soluble in aromatic solvents. The solubility of naphthalene in different solvents in the temperature interval −25 to 25 °C is shown in Fig. 2. The selected temperature range aims to cover
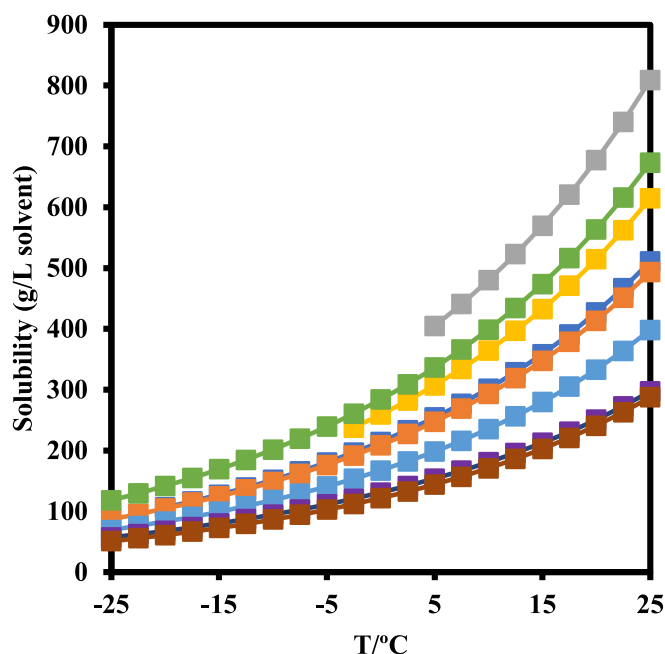
Fig. 2. Naphthalene solubility at temperature in the range −25 to 25 °C in several solvents: 1-Methylnaphthalene (▪); MBP (▪); Benzene (▪); Toluene (▪); Benzyltoluene (▪); Dibenzyltoluene (▪); 2-Methylindene (▪), and Indene (▪). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the most common temperatures at which *LOHCs* can be stored and transported. As it can be observed in the Fig. 2, the naphthalene solubility is maximum for benzene, however, the melting temperature of benzene rules out its use as a solvent. In a similar situation is indene, which melting temperature is −2.5 °C. Likewise, the solving capacity of naphthalene decreases in the order benzene > toluene > indene > 1-methylnaphthalene > 2-methylindene > methylbenzylpyridine > benzyltoluene > dibenzyltoluene. Therefore, the single aromatic rings favour the solubility, thus toluene seems an ideal solvent for naphthalene. Add to the solubility, it is worth mentioning that naphthalene is usually obtained both in petrochemical plants and biorefineries in combination with 1-methylnaphthalene, being in this solvent the solubility of naphthalene at −25 °C, 87 g/L, whereas at 25 °C, it increases to 510 g/L.

In addition to the use of common solvents, the use of mixtures of *LOHCs* for improving properties has been also reported. Therefore, the company Hydrogenious has recently proposed the use of binary mixtures of benzyltoluene and dibenzyltoluene for tuning the viscosity of the resulting *LOHC* [12].

3.2. N-heteroatomic compounds

Pyridine is the most common chemical of this family, being traditionally obtained as by-product carbochemical processes, but also by catalytic amination of aldehydes and ketones [68]. Other routes, from renewable resources, include catalytic cycloadditions of diynes and oximes using ethanol as an alternative green reaction medium [69] or even by bio-catalytic routes [70] and quinoline synthesis from aniline and glycerol [71], being aniline obtained via amination of phenol [72].
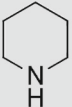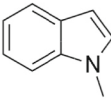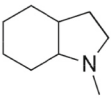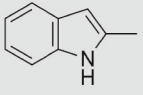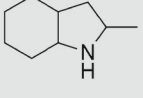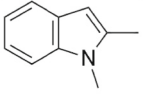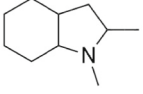
From these structural compounds, multiple derivatives can be obtained, such as quinaldine [73,74] or heterocycles [75,76], whereas phenazine derivates are synthetized by hydrogenolysis of lignin in presence of ammonia [77]. Other compounds in this group are N-ethylcarbazole/ perhydro-N-ethylcarbazole, 1,2-dihydro-1,2-azaborine/1,2-BN-cyclo-hexan, phenazine/tetradecahydrophenazine [6].

3.2.1. Single N-heteroatomic compounds

Substitution of N atom into the aromatic ring thermodynamically favours the hydrogen release, although the H_2 storage capacity slightly decreases [78]. As disadvantages in comparison to the polyaromatic *LOHCs*, are their lower availability (and therefore higher cost), as well as the toxicity or, even the lower chemical stability when working in charging/discharging cycles. N-ethylcarbazole (*H0-NEC*) was firstly proposed by Air Products and Chemicals as potential *LOHC* [79], mainly due to the H_2 content, 5.8 % (Table 3B) [4,14]. Pd catalysts were reported to be efficient in *H12-NEC* dehydrogenation, usually supported on alumina [79], whereas hydrogenation was carried out on Ru and Pd catalysts, at pressures up to 100 bar and temperatures between 130 and 180 °C [80]. Hydrogenation temperature was even reduced to 100 °C on Ru(Na)/Beta catalysts [81]. However, this chemical presents two important drawbacks: the high melting point, 69 °C, and the poor thermal stability by dealkylation to carbazole [78,80]. From the point of view of hazard, its log k_{OW} could be considered as potentially hazardous, whereas in the case of the hydrogenated pair, its n-octanol/water partition coefficient (6.15) represents a significant risk of bio-accumulation. A difference is highlighted between the rings of five- and six- membered ring. Whereas the unsaturated compounds of six-membered ring are in most cases liquid at room temperature, under

Table 3A

Physical properties of pairs of N-substituted compounds (sucessively ordered on their dehydrogenated/hydrogenated form). Estimated data in brackets: A = *ASPEN HYSYS*, B = *COSMO-RS*. In parentheses, experimental values taken from the safety data sheets.
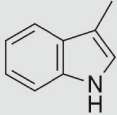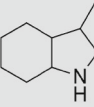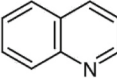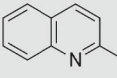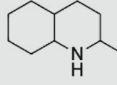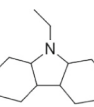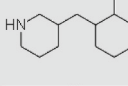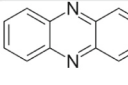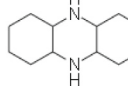
LOHC	State of matter	Formula	Estructure	Density (g/cm³)	Viscosity (mPa·s)	Vapour pressure at 25ºC (bar)	log Kow
Pyridine	L	C_5H_5N		0.963 [B] (0.978)	0.899 [A]	0.019 [B] (0.022)	0.82 [B]
Piperidine	L	$C_5H_{11}N$		0.882 [B]	1.288 [A]	0.034 [B]	1.94 [B]
1-methylindole	S	C_9H_9N		1.011 [B]	-	<0.001 [B]	2.77 [B]
1-methylperhydro indole	L	$C_9H_{18}N$		0.885[B]	0.672 [A]	<0.001 [B]	3.83 [B]
2-methylindole	S	C_9H_9N		1.052 [B]	-	<0.001 [B]	2.94 [B]
2-methylperhydro indole	L	$C_9H_{18}N$		0.896 [B]	1.011 [A]	<0.001 [B]	3.48 [B]
1,2-dimethylindole	S	$C_{10}H_{11}N$		0.996 [B] (1.000)	-	<0.001 [B]	3.27 [B]
1,2-dimethylperhydro indole	L	$C_{10}H_{20}N$		0.872 [B]	0.855 [A]	<0.001 [B]	4.27 [B]

these same conditions, unsaturated compounds with five-membered ring are solid. This general rule is not fulfilled for phenazine, however in this case the ring has two nitrogen atoms. On the other hand, decahydroquinoline is the only saturated compound solid at ambient conditions.

With similar structure than carbazoles, indole derivates were also the object of so many studies due to its availability and advantages like favourable thermodynamics (dehydrogenation enthalpies about 51–54 kJ/mol H$_2$, Table 3B) and kinetics [82,83]. Pd and Ru on alumina support catalysts were tested for hydrogenation and dehydrogenation reactions at mild conditions [5]. Likewise, Bachmann et al. [84] carried out a quantitative theoretical and experimental study focusing on the surface chemistry of indole molecules, deprotonation reaction as well as the decomposition temperature. A great influence of the substituents on the stability of molecules was reported, observing an increasing instability after the incorporation of 2-methyl group [84]. However, a drawback of these compounds is the melting points of saturated compounds.
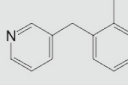
The phenazine/perhydrophenazine presents a remarkable hydrogen loading capacity (> 7 %), fact that has intensified its study as *LOHC* in the presence of solvents, due to its high melting point. Thus, dehydrogenation reaction has been carried out on Pd and Ru catalysts using diglyme as solvent at 190 °C, which reduces the hydrogen storage capacity to 2.4 wt %. In this case, the stability of the molecule and the reversibility of the reaction an important advantage. Concerning hydrogenation, the same catalyst is also active, working in this case at 50 bar [77]. A disadvantage of both phenazine and perhydrophenazine is the high energy demand (ΔH = 61.3 kJ/mol H$_2$, Table 3B). Similarly to phenazine, acridine was recently used as *LOHC* being advantageous its high hydrogen loading capacity (7.25 %) and the lower melting point than phenazine (111 °C), although it remains solid at room temperature [85].

Finally, it is remarkable the methylbenzylpyridine/perhydromethylbenzylpyridine potential with melting points of both molecules which ensures the liquid form at ambient temperature and boiling points of 291 and 293 °C (Table 3B), respectively. Oh et al. [78] studied the hydrogenation of methylbenzylpyridine on Ru/Al$_2$O$_3$ catalysts at

Compound		Formula	Structure				
3-methylindole	S	C_9H_9N		1.052 [B]	-	<0.001 [B]	2.96 [B]
3-metiperhydro lindol	L	$C_9H_{18}N$		0.888 [B]	1.010 [A]	<0.001 [B]	3.77 [B]
Quinoline	L	C_9H_7N		1.061 [B] (1.095)	4.726 [A]	<0.001 [B]	2.07 [B]
Decahydro quinoline	S	$C_9H_{17}N$		0.853 [B]	-	<0.001 [B]	4.96 [B]
Quinaldine	L	$C_{10}H_9N$		1.038 [B] (1.058)	5.930 [A]	<0.001 [B]	2.73 [B]
Decahydro-2-Methylquinoline	L	$C_{10}H_{19}N$		0.808 [B] (0.962)	1.420 [A]	0.002 [B]	5.52 [B]
N-Ethylcarbazole	S	$C_{14}H_{13}N$		1.048 [B] (1.100)	-	<0.001 [B] (<0.001)	4.40 [B]
Dodecahydro-N-Ethylcarbazole	L	$C_{14}H_{25}N$		0.856 [B] (0.940)	4.120 [A]	<0.001 [B] (<0.001)	6.15 [B]
Methylbenzyl piridine	L	$C_{13}H_{13}N$		1.025 [B]	1.65 [A] (5.90)	<0.001 [B]	3.87 [B]
Perhydromethyl benzylpiridine	L	$C_{13}H_{25}N$		0.926 [B]	2.977 [A]	<0.001 [B]	5.17 [B]
Phenazine	S	$C_{12}H_8N_2$		1.100 [B]	-	<0.001 [B]	3.59 [B]
Perhydro phenazine	L	$C_{12}H_{20}N_2$		0.991 [B] (1.000)	6.11 [A] (2.20)	<0.001 [B] (<0.001)	3.43 [B]

150 °C and 50 bar with almost complete efficiency, whereas dehydrogenation was achieved on Pd supported carbon at 250 °C. Oh et al. [14] prepared Pd/Al$_2$O$_3$ catalysts with improved performance in both hydrogenation and dehydrogenation reactions. Likewise, Lim et al. [86] observed improved dehydrogenation rates supporting Pd on MFI zeolites. Furthermore, the requirements of chemical reversibility without decomposition, chemical and thermal stability and appropriate handle characteristics are fulfilled in these compounds [78], thus, this compound could conform the most promising molecules in this group. As main drawback, it is the bioaccumulation trend of perhydromethylbenzylpyridine, with an octanol-water coefficient of 5.17 (Table 3A), as well as the energy demand ($\Delta H = 62.6$ kJ/mol H$_2$, Table 3B).

Table 3B

Physical properties of pairs of N-substituted compounds (sucessively ordered on their dehydrogenated/hydrogenated form). Estimated data in brackets: A = *ASPEN HYSYS*, B = *COSMO-RS*. In parentheses, experimental values taken from the safety data sheets (SigmaAldrich, ThermoFisher, GroupChem, Carl Roth).

LOHC	Melting point (ºC)	Boiling point (ºC)	Flash point (ºC)	ΔH rec (kJ/mol H$_2$)	wt% H$_2$
Pyridine	(-42)	116 **[B]** (115)	28 **[B]** (17)	65.6	7.04
Piperidine	-7 **[B]**	111 **[B]**	25 **[B]**		
1-methylindole	(95)	242 **[B]** (238)	112 **[B]**	51.9	5.80
1-methylperhydroindole	-23 **[B]**	212 **[B]** (280)	75 **[B]**		
2-methylindole	(60)	300 **[B]** (272)	155 **[B]**	51.9	5.80
2-methylperhydroindole	-29 **[B]**	204 **[B]** (178)	65 **[B]**		
1,2-dimethylindole	(55)	261 **[B]** (260)	125 **[B]** (113)	51.9	5.23
1,2-dimethylperhydro indole	(-15)	221 **[B]** (260)	73 **[B]**		
3-methylindole	(92)	300 **[B]** (265)	155 **[B]** (132)	51.9	5.80
3-metiperhydrolindol	-10 **[B]**	193 **[B]** (202)	65 **[B]**		
Quinoline	(-15)	252 **[B]** (237)	120 **[B]** (74)	61.9	7.18
Decahydroquinoline	(37)	214 **[B]** (68)	79 **[B]**		
Quinaldine	(-2)	271 **[B]** (247)	131 **[B]** (79)	64.0	6.58
Decahydro-2-Methylquinoline	-23 **[B]**	232 **[B]** (223)	95 **[B]**		
N-Ethylcarbazole	(69)	355 **[B]** (363)	191 **[B]** (186)	54.0	5.8
Dodecahydro-N-Ethylcarbazole	(-85)	261 **[B]** (271)	95 **[B]** (146)		
Methylbenzylpiridine	(-51)	291 **[B]** (292)	148 **[B]**	62.6	6.15
Perhydromethyl benzylpiridine	(-20)	279 **[B]** (293)	113 **[B]**		
Phenazine	(147)	403 **[B]** (357)	227 **[B]**	61.3	7.20
Perhydrophenazine	116 **[B]**	264 **[B]**	138 **[B]**		

3.2.2. Potential mixtures of N-heteroatomic LOHCs

In view of solid stated of *NEC* at ambient temperature, eutectic mixtures of N-alkyl carbazoles were essayed to decrease the melting point to 24 °C [87], and also super-critical CO$_2$ fluid was suggested to form a homogeneous phase [88]. Another possibility, it could be the solution of N-ethylcarbazole in another *LOHC*. From Fig. 3, the N-ethylcarbazole solubility is maximum for benzene, followed by toluene and indene. For toluene, the solubility varies from 60 g/L at −25 °C, to 651 g/L at 25 °C.

Similarly, to carbazoles, the saturated molecules of indole family, are also solid at operating conditions. In this way, Fig. S1 shows their solubility in other *LOHCs*, also observing the influence of the substituents. 1-Methylindole and 1,2-methylindole (Fig. S1A, S1C) are preferable dissolved in toluene, with maximum solubilities at 25 °C of 429 and 1334 g/L, respectively. However, 2-methylindole and 3-methylindole (Fig. S1B, S1D) are preferable dissolved in benzyltoluene, with

maximum solubilities of 1758 and 1082 g/L, respectively.

As in previous cases, phenazine solubility is plotted in Fig. S2, observing that phenazine presents low solubilities in most of the solvents with the exception of methylbenzylpyridine, and the solubility of perhydrophenazine in perhydro methylbenzylpyrine reaches 770 g/L at 25 °C, thus these molecules present difficulties to be used as *LOHCs*, whereas carbazoles and 2-methylindole and 3-methylindole exhibit more advantageous behavior at this point.

3.3. O-heteroatomic compounds

Although largely less studied than aromatics and organonitrogen compounds, oxygenated organics with unsaturated bonds can be promising *LOHCs*, especially considering that they can be obtained from renewable resources by different routes. For example, biomass acid hydrolysis yields furanic aldehydes, as furfural and 5-
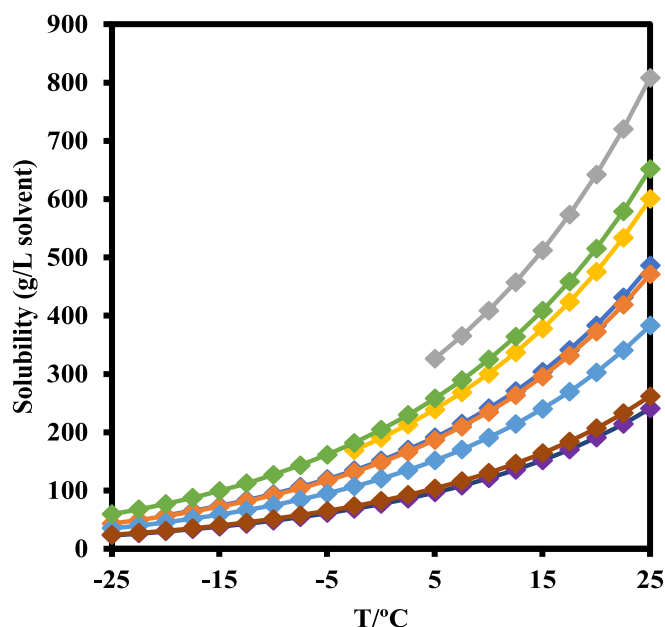
Fig. 3. N-ethylcarbazole solubility at temperature in the range −25 to 25 °C in several solvents: 1-Methylnaphthalene (■); MBP (■);Benzene (■);Toluene (■); Benzyltoluene (■); Dibenzyltoluene (■); 2-Methylindene (■), and Indene (■). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydroxymethylfurfural (5-HMF), which have O-containing heterocyclic compounds with two unsaturations. In addition, the presence of carbonyl groups enables the formation of oligomers and condensation adducts with larger hydrogen storage capacity [89–91]. From thermochemical conversion, and more specifically from pyrolysis, different kinds of compounds, such as anhydrosugars, phenols, furans, or small organic acids can be isolated to be used as biofuels or bioadditives [92,93]. Some of them, as the case of furfural can be used as *LOHC* [94]. Another interesting bioplatform molecule, levulinic acid, is produced by several alternative routes, being the via furfuryl alcohol one of the most promising [95]. Add to furan, (poly)alkyl furans, obtained from lignocellulose by hydrolysis, hydrogenolysis or dehydration, could be relevant reactants for obtaining renewable aromatic [32]. Similarly, but with a different approach, Ferlin et al. [3] explore the use of *LOHCs* as hydrogen source for biomass upgrading, with the purpose of the production of γ-valerolactone, 2,5-dimethylfuran, 2-methylfuran and phenols, among other compounds.
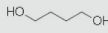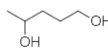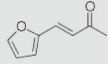
3.3.1. Single O-heteroatomic compounds

Use of oxygen containing molecules as *LOHCs* is nearly unexplored mainly due to their limited aromatic structures and chemically labile nature toward the hydrogenolysis, despite the apparent thermodynamic profit of heteroatom presence. In fact, by thermodynamic calculations, it was observed that the presence of an oxygen atom as an ether functional group could reduce temperature requirements for dehydrogenation [96,97]. In this way, FR3095203A1 patent [98] proposed the use of an aliphatic compound having at least two hydroxyl groups including at least one primary hydroxyl group as a hydrogenated organic liquid (*LOHC*). The invention consists of dehydrogenation between 110 and 300 °C and pressure from 1 to 2 bar on Cu, Zn or Cr catalysts, and further hydrogenation between 100 and 260 °C and pressure from 10 to 280 bar, of pairs such as γ-butyrolactone (*GBL*)/1,4-butanediol (*BDO*), succinic anhydride/1, 4-butanediol, γ-valerolactone (*GVL*)/1,4-pentanediol

(*PDO*), methyl levulinate/1,4-pentanediol, δ-valerolactone/1,5-pentanediol, furfuryl alcohol/1,5-pentanediol, 2 -hydroxytetrahydropyran/1,5-pentanediol, ε-caprolactone/1,6-hexanediol and 1,2,6-hexanetriol/1,6-hexanediol. Concerning the gamm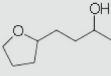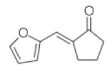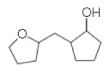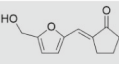a-butyrolactone/1,4-butanediol and gamma-valerolactone/1,4-pentanediol pairs, although it is known that the traditional way of conversion of diols into lactones is by a condensation reaction, a mechanism, which involves a dehydrogenation toward a hydroxyalcohol and further dehydrogenation toward the lactone is reported [99], showing in this way the possibility of the reaction. What is more, dehydrogenation could be predominant on the surface of metal sites [100]. Likewise, Tran et al. [101] evaluate the hydrogen release from ethanol to ethyl acetate and further dehydrogenation using an homogeneous Ru-catalyst, however, suggestion the performance of these catalysts is far from being optimal. In addition, the reverse hydrogenation reactions do not lead to the selective formation of the initial chemical. Jang et al. [96] experimented both hydrogenation and dehydrogenation of the commercial eutectic mixture of biphenyl and diphenyl ether to bicyclohexyl and dicyclohexylether on Pd and Rh catalysts. Hydrogenation was successfully accomplished without C─O bond scission with Pd/Al$_2$O$_3$ at 120 °C and 50 bar or Rh/C at 60 °C under 20 bar, whereas dehydrogenation was achieved with Pt/C at 300 °C under atmospheric pressure. According to Table 4A and B, the high hydrogen storage capacity and the low volatility, are interesting properties to consider these compounds as *LOHCs*. However, dehydrogenation enthalpy and the high melting temperature of most of the compounds are the main drawbacks. The high values of ΔH_{rec} (kJ/mol H$_2$), Table 4B, in many cases over 80 kJ/mol H$_2$, hinders the feasibility of dehydrogenation at acceptable temperatures. In the case of furfurylideneacetone / 4-tetrahydrofurfuryl-2-butanol pair, it exhibits an interesting H$_2$ content (5.56 wt%) and physical properties compatible with conventional *LOHCs*, however, the melting temperature cannot ensure its handling in the liquid state. A similar case is described for the pairs 1,5-bis(2-furanyl)-1,4- pentadien-3-one / 1,5-di(tetrahydrofuran-

Table 4A

Physical properties of pairs of O-substituted compounds (sucessively ordered on their dehydrogenated/hydrogenated form). Estimated data in brackets: A = *ASPEN HYSYS*, B = *COSMO-RS*. In parentheses, experimental values taken from the safety data sheets.

LOHC	State of matter	Formula	structure	Density (g/cm³)	Viscosity (mPa·s)	Vapour pressure at 25 ºC (bar)	log Kow
Gamma-butyrolactone	L	$C_4H_6O_2$		1.107 [B] (1.12)	2.37 [A]	<0.001 [B] (0.002)	-0.17 [B]
1,4-butanediol	L	$C_4H_{10}O_2$		0.941 [B] (1.01)	10.64 [A] (84.9)	<0.001 [B] (<0.001)	-0.36 [B]
Gamma-valerolactone	L	$C_5H_8O_2$		1.038 [B] (1.05)	2.37 [A] (2.18)	<0.001 [B]	0.31 [B]
1,4-pentanediol	L	$C_5H_{12}O_2$		0.91 [B] (0.99)	2.06 [A]	<0.001 [B]	0.19 [B]
Furfuryldeneacetone	S	$C_8H_8O_2$		1.098 [B]	-	<0.001 [B]	1.53 [B]
4-Tetrahydrofurfuryl-2-butanol	L	$C_8H_{15}O_2$		0.910 [B]	2.057 [A]	<0.001 [B]	2.34 [B]
(E)-2-(furan-2-ylmethylene)cyclopentan-1-one	S	$C_{10}H_{10}O_2$		1.126 [B]	-	<0.001 [B]	2.00 [B]
2-((tetrahydrofuran-2-yl)methyl)cyclopentan-1-ol	S	$C_{10}H_{18}O_2$		1.003 [B]	-	<0.001 [B]	2.76 [B]
(E)-2-((5-(hydroxymethyl)furan-	S	$C_{11}H_{12}O_3$		1.171 [B]	-	<0.01 [B]	1.50 [B]

2-yl) pentan-3-ol and (3Z,5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid/4-hydroxy-6-(oxolan-2-yl)-3-[(oxolan-2-yl) methyl]hexanoic acid.
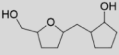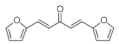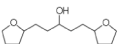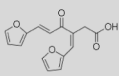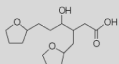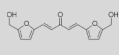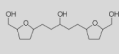
It should be noted that the use of oxygen-containing rings is largely more challenging than the use of their nitrogenated counterparts, larger research efforts being needed even assessing the real hydrogenation/dehydrogenation pathways. However, these compounds are still promising because they can be easily obtained from biomass and sustainable resources, within the framework of a biorefinery approach. On the other hand, although it is true that the dehydrogenation reactions are less favoured than in the other chemicals, there is an open field for the development of catalysts and processes based on these chemicals.

3.3.2. O-heteroatomic compounds mixtures

With these antecedents, Fig. S3a and S3b plot the solubility of furfuryldeneacetone and 4-tetrahydrofurfuryl-2-butanol on *LOHCs*, observing that the pair of molecules are preferentially soluble in benzene, toluene, indene or hydrogenated molecules, with very high solubilities in both

cases. The increase of molecule size to 13 carbon atoms leads to an order of magnitude reduction in solubility of 1,5-bis(2-furanyl)-1,4- pentadien-3-ona, 311 g/L in benzyltoluene (Fig. S3c), whereas this reductions is less pronounced for tri(furan-2-yl)methane (Fig. S3e). In both cases, saturated molecules are more soluble (Fig. S3d), being even completely soluble in the interval the pair of tri(furan-2-yl)-methane. Increasing the size of the molecule up to 15 carbon atoms reduces extremely the solubility of (3Z,5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid and its pair (Fig. S3f and S3g), therefore, its application is very limited. Also with a combination of properties that could be candidates to be used as LOHCs, (2E,5E)-2,5-bis(furan-2-ylmethylene)cyclopentan-1-one and 2,5-bis((tetrahydrofuran-2-yl)methyl)cyclopentan-1-ol pair. In this case, both molecules would be sol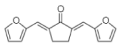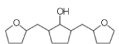id at working temperatures, thus, Fig. S3h and Fig. S3i show the high solubility of both molecules in toluene, indene and benzyltoluene.

At this point, it should be noted that even though some of these compounds with oxygen can be interesting to be used as *LOHCs*, and the thermodynamic properties, as well as the solubility of some of them in

2-yl)methylene) cyclopentan-1-one							
2-((5-(hydroxymethyl) tetrahydrofuran-2-yl)methyl)cyclopentan-1-ol	S	$C_{11}H_{20}O_3$		1.076 **[B]**	-	<0.01 **[B]**	2.63 **[B]**
1,5-bis(2-furanyl)-1,4-pentadien-3-ona	S	$C_{13}H_{10}O_3$		1.240 **[B]**	-	<0.001 **[B]**	2.83 **[B]**
1,5-di(tetrahydrofuran-2-il) penta-3-ol	L	$C_{13}H_{24}O_3$		0.960 **[B]**	27.56 **[A]**	<0.001 **[B]**	3.14 **[B]**
(3Z,5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid	S	$C_{15}H_{12}O_5$		1.267 **[B]**	-	<0.01 **[B]**	2.64 **[B]**
4-hydroxy-6-(oxolan-2-yl)-3-[(oxolan-2-yl) methyl]hexanoic acid	S	$C_{15}H_{26}O_5$		1.053 **[B]**	-	<0.01 **[B]**	4.23 **[B]**
(2E,5E)-2,5-bis(furan-2-ylmethylene) cyclopentan-1-one	S	$C_{15}H_{12}O_3$		1.204 **[B]**	-	<0.01 **[B]**	3.19 **[B]**
2,5-bis((tetrahydro furan-2-yl)methyl) cyclopentan-1-ol	S	$C_{15}H_{26}O_3$		1.002 **[B]**	-	<0.01 **[B]**	3.34 **[B]**
(1E,4E)-1,5-bis(5-(hy droxymethyl)furan-2-yl)penta-1,4-dien-3-one	S	$C_{15}H_{14}O_5$		1.288 **[B]**	-	<0.01 **[B]**	1.86 **[B]**
((3-hydroxypentane-1,5-diyl)bis (tetrahydrofuran-5,2-diyl))dimethanol	S	$C_{15}H_{28}O_5$		1.043 **[B]**	-	<0.01 **[B]**	-0.35 **[B]**

solvents that can be sustainable in addition to store hydrogen, it remains to be resolved their stability when subjected to the pressure and temperature conditions typical of hydrogenation / dehydrogenation reactions.

4. Future perspectives and conclusions

Hydrogen storage by *LOHCs* is a promising technology, although it still has many aspects that need to be investigated and, in view of the current geopolitical situation, this would be a pressing need. Most of the published works focus on *LOHCs* dealt with the experimental study (or simulations) of preselected pairs of compounds, with origin either in the petrochemical industry or, more recently, from biomass. In this context, this work provides a systematic evaluation of key parameters of potential *LOHCs* that must be taken into account in the selection of the best

pair of molecules for an efficient chemical hydrogen storage. Ideally, hydrogenation and dehydrogenation cycle should be carried out at the milder conditions and high stoichiometric hydrogen loading, with the highest yield and, simultaneously, keeping the stability of the organic molecules used as hydrogen receptors. Likewise, dehydrogenation reaction is endothermic restricted by equilibrium, so the optimization of reactions conditions is a major critical point for the development of these technologies. In addition, physical properties (ensure both forms of the pair are liquids, low vapour pressure, etc.) as well as toxicological data (taken oil-derived fuels as admissible references) must also been considered.

Taking these facts into account, the homocyclic pairs benzyltoluene / perhydrobenzyltolune and dibenzyltoluene / perhydrodibenzyltolune, already adopted by Hydrogenious to be used as *LOHCs*, present several advantages, such as the relevant hydrogen content and adequate
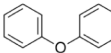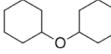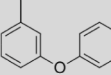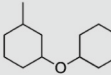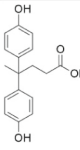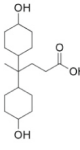
Name	State	Formula	Structure	Col1	Col2	Col3	Col4
di(furan-2-yl)methanol	S	$C_9H_8O_3$		1.176 [B]	-	0.002 [B]	2.18 [B]
bis(tetrahydrofuran-2-yl)methanol	S	$C_9H_{16}O_3$		1.021 [B]	-	<0.001 [B]	2.18 [B]
tri(furan-2-yl)methane	S	$C_{13}H_{10}O_3$		1.237 [B]	-	0.002 [B]	3.78 [B]
tris(tetrahydrofuran-2-yl)methane	L	$C_{13}H_{22}O_3$		0.993 [B]	5.46 [A]	0.0024 [B]	4.09 [B]
2,2´-({5-[(furan-2-yl)methyl]furn-2-yl}methylene)difuran	S	$C_{18}H_{14}O_4$		1.203 [B]	-	<0.01 [B]	5.34 [B]
2,2'-((5-((tetrahydrofuran-2-yl)methyl)tetrahydrofuran-2-yl)methylene)bis(tetrahydrofuran)	S	$C_{18}H_{30}O_4$		1.005 [B]	-	<0.001 [B]	5.43 [B]
5,5-bis(5-methylfuran-2-yl)pentan-2-one	S	$C_{15}H_{18}O_3$		1.08 [B]	-	<0.001 [B]	3.26 [B]
5,5-bis(5-methyltetrahydrofuran-2-yl)pentan-2-ol	L	$C_{15}H_{28}O_3$		0.939 [B]	24.25 [A]	<0.001 [B]	4.32 [B]
Diphenyl ether	S	$C_{12}H_{10}O$		1.064 [B] (1.073)	-	<0.001 [B] (<0.001)	3.98 [B]
Dicyclohexyl ether	S	$C_{12}H_{22}O$		0.949 [B]	-	<0.001 [B]	4.45 [B]
3-Methyldiphenyl ether	S	$C_{13}H_{12}O$		1.046 [B] (1.05)	-	<0.001 [B]	4.52 [B]
3-Methyldicyclohexyl ether	S	$C_{13}H_{24}O$		0.931 [B]	-	<0.001 [B]	4.93 [B]
Diphenolic acid	S	$C_{17}H_{18}O_4$		1.131 [B]	-	<0.01 [B]	3.71 [B]
4,4-bis(4-hydroxycyclohexyl)pentanoic acid	S	$C_{17}H_{31}O_4$		1.083 [B]	-	<0.01 [B]	4.87 [B]
Mesomandelide	S	$C_{16}H_{12}O_4$		1.168 [B]	-	<0.01 [B]	2.91 [B]
3,6-dicyclohexyl-1,4-dioxane-2,5-diol	S	$C_{16}H_{12}O_4$		1.083 [B]	-	<0.01 [B]	4.87 [B]

Table 4B

Physical properties of pairs of O-substituted compounds (sucessively ordered on their dehydrogenated/hydrogenated form). Estimated data in brackets: A = *ASPEN HYSYS*, B = *COSMO-RS*. In parentheses, experimental values taken from the safety data sheets (SigmaAldrich, ThermoFisher, GroupChem, Carl Roth).

LOHC	Melting point (ºC)	Boiling point (ºC)	Flash point (ºC)	ΔH rec (kJ/mol H$_2$)	wt% H$_2$
Gamma-butyrolactone	(-45)	192 **[B]** (204)	84.57 **[B]**	31	4.5
1,4-butanediol	(16)	201 **[B]** (230)	119 **[B]** (134)		
Gamma-valerolactone	(-31)	199 **[B]** (207)	88 **[B]** (96)	35	4.5
1,4-pentanediol	-17.96 **[B]**	211 **[B]** (220)	117 **[B]** (117)		
Furfuryldeneacetone	-5 **[B]**	190 **[B]**	84 **[B]**	83.75	5.56
4-Tetrahydrofurfuryl-2-butanol	2 **[B]**	218 **[B]**	100 **[B]**		
(E)-2-(furan-2-ylmethylene) cyclopentan-1-one	11.74 **[B]**	223.21 **[B]**	117.13 **[B]**	83.75	4.71
2-((tetrahydrofuran-2-yl)methyl)cyclopentan-1-ol	13.74 **[B]**	264.06 **[B]**	132.42 **[B]**		
(E)-2-((5-(hydroxymethyl)furan-2-yl)methylene)cyclopentan-1-one	81.03 **[B]**	373.26 **[B]**	191.71 **[B]**	83.75	4
2-((5-(hydroxymethyl)tetrahydrofuran-2-yl)methyl)cyclopentan-1-ol	81.33 **[B]**	367.67 **[B]**	234.10 **[B]**		
1,5-bis(2-furanyl)-1,4- pentadien-3-ona	58 **[B]**	267 **[B]**	166 **[B]**	89.43	6.54
1,5-di(tetrahydrofuran-2-il) penta-3-ol	2 **[B]**	334 **[B]**	172 **[B]**		

temperatures. But in this group, it is also convenient to point out the 1-methylnaphthalene / 1-methyldecahydronaftalene pair, with a 6.57 % of hydrogen content, and which melting and boiling temperatures ensure the liquid form of the compounds. Furthermore, the reaction was observed to be preferable on Pt catalysts, although inhibition effects could occur.

In the group of single N-heteroatomic cycles, the incorporation of N atom into an aromatic ring promotes dehydrogenation reactions, although decreases the H$_2$ storage capacity. With these premises, N-ethylcarbazole (*H$_0$-NEC*), proposed by Air Products and Chemicals, was the first compound widely studied. Although it completes the hydrogenation/dehydrogenation cycle, presents some disadvantages such as the high melting point, 69 °C, and the poor thermal stability by dealkylation to carbazole. In this group, the methylbenzylpyridine / perhydromethylbenzylpyridine pair presents an interesting combination of properties, since the hydrogen content exceeds 6 % and low melting point, although energy demand is over 60 kJ/ mol H$_2$, and both reactions were observed on Ru and Pd supported metals.

Many promising compounds from the point of view of the hydrogen storage and or the easiness of the hydrogenation/dehydrogenation reactions, present the problem of being solid at ambient conditions. Thus, the possibility to work with mixtures of *LOHCs* could be a valuable option. In this way, naphthalene and 1-methyl-naphatalne mixtures could be a promising option, both from the point of view of hydrogen content and molecular properties, but also since both compounds are usually obtained together in petrochemical plants and biorefineries, thus the previous separation would be eliminated. In the case of mixtures with N-heterocyclic compounds, the positive properties of indoles, could be used by solution on toluene or benzyltoluene, depending on the substituents.

Regarding oxygen-compounds, several sustainable compounds, such as furfuryldeneacetone / 4-tetrahydrofurfuryl-2-butanol, have been identified as of potential interest, due to their hydrogen storage capacity (5.56 wt%) and physical properties, competitive with conventional *LOHCs*. Although these molecules are solid at room temperature, they are soluble in many different solvents. However, the main limitation of these oxygenated molecules is their lower reactivity (inquired from the higher reaction enthalpies), and the lack of experimental evidences both on their stability and the feasibility of the hydrogenation and dehydrogenation steps.

That is why the study of the physical, thermodynamic and biocompatibility properties is outlined as an approach to the search for potential molecules used as *LOHCs*, trying to find the appropriate manageability and safety conditions. However, there is still a long way to go in terms of research, once specific interesting molecules have been identified, to carry out reaction studies that confirm their validity, as well as the catalytic conditions and stability of the compounds.

(3Z,5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid	174.25 **[B]**	409.59 **[B]**	240.61 **[B]**	83.75	5.56
4-hydroxy-6-(oxolan-2-yl)-3-[(oxolan-2-yl) methyl]hexanoic acid	112.12 **[B]**	630.78 **[B]**	248.08 **[B]**		
(2E,5E)-2,5-bis(furan-2-ylmethylene)cyclopentan-1-one	62.14 **[B]**	311.08 **[B]**	177.73 **[B]**	89.43	5.51
2,5-bis((tetrahydrofuran-2-yl)methyl)cyclopentan-1-ol	68.82 **[B]**	386.24 **[B]**	192.39 **[B]**		
(1E,4E)-1,5-bis(5-(hydroxymethyl)furan-2-yl)penta-1,4-dien-3-one	196.50 **[B]**	462.21 **[B]**	277.78 **[B]**	89.43	3.52
((3-hydroxypentane-1,5-diyl)bis(tetrahydrofuran-5,2-diyl))dimethanol	103.80 **[B]**	469.40 **[B]**	261.74 **[B]**		
di(furan-2-yl)methanol	71.12 **[B]**	303.27 **[B]**	190.08 **[B]**	86	4.65
bis(tetrahydrofuran-2-yl)methanol	13.18 **[B]**	315.74 **[B]**	173.91 **[B]**		
tri(furan-2-yl)methane	36.44 **[B]**	273.98 **[B]**	175.36 **[B]**	86	5.31
tris(tetrahydrofuran-2-yl)methane	-18.59 **[B]**	307.64 **[B]**	134.27 **[B]**		
2,2′-({5-[(furan-2-yl)methyl]furn-2-yl}methylene)difuran	124.54 **[B]**	435.60 **[B]**	238.63 **[B]**	86	5.16
2,2'-((5-((tetrahydrofuran-2-yl)methyl)tetrahydrofuran-2-yl)methylene)bis(tetrahydrofuran)	20.07 **[B]**	374.95 **[B]**	188.74 **[B]**		
5,5-bis(5-methylfuran-2-yl)pentan-2-one	28.29 **[B]**	378.07 **[B]**	176.48 **[B]**	77.6	3.91
5,5-bis(5-methyltetrahydrofuran-2-yl)pentan-2-ol	-3.65 **[B]**	352.34 **[B]**	170.71 **[B]**		
Diphenyl ether	(-31)	199 **[B]** (207)	88 **[B]** 96	69.3	6.59
Dicyclohexyl ether	6 **[B]**	242 **[B]**	93 **[B]**		
3-Methyldiphenyl ether	25 **[B]**	283 **[B]** (272)	138 **[B]** 112	69.3	6.12
3-Methyldicyclohexyl ether	6 **[B]**	248 **[B]**	96 **[B]**		
Diphenolic acid	(167)	509.99 **[B]**	282.44 **[B]**	68.5	4.03
4,4-bis(4-hydroxycyclohexyl)pentanoic acid	163.76 **[B]**	583.91 **[B]**	272.55 **[B]**		
Mesomandelide	57 **[B]**	326.12 **[B]**	188.63 **[B]**	62.5	5.63
3,6-dicyclohexyl-1,4-dioxane-2,5-diol	137.91 **[B]**	312.22 **[B]**	242.87 **[B]**		

CRediT authorship contribution statement

Eva Diaz: Data curation, methodology, writing original draft, **Pablo Rapado-Gallego:** Investigation, software, formal analysis, **Salvador Ordóñez:** Conceptualization, supervision, writing (review and editing), funding acquisition.

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.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.est.2022.106511.

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