

Review Article

Hydrogen storage by liquid organic hydrogen carriers: Catalyst, renewable carrier, and technology – A review

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ABSTRACT

Hydrogen has attracted widespread attention as a carbon-neutral energy source, but developing efficient and safe hydrogen storage technologies remains a huge challenge. Recently, liquid organic hydrogen carriers (LOHCs) technology has shown great potential for efficient and stable hydrogen storage and transport. This technology allows for safe and economical large-scale transoceanic transportation and long-cycle hydrogen storage. In particular, traditional organic hydrogen storage liquids are derived from nonrenewable fossil fuels through costly refining procedures, resulting in unavoidable environmental contamination. Biomass holds great promise for the preparation of LOHCs due to its unique carbon-balance properties and feasibility to manufacture aromatic and nitrogen-doped compounds. According to recent studies, almost 100% conversion and 92% yield of benzene could be obtained through advanced biomass conversion technologies, showing great potential in preparing biomass-based LOHCs. Overall, the present LOHCs systems and their unique applications are introduced in this review, and the technical paths are summarized. Furthermore, this paper provides an outlook on the future development of LOHCs technology, focusing on biomass-derived aromatic and N-doped compounds and their applications in hydrogen storage.

1. Introduction

As living standards around the world improve, there is an increasing reliance on energy, which exacerbates the global energy challenge. Renewable energy has developed into a clean and efficient alternative to existing energy sources. Furthermore, the worldwide focus on “Emission Peak and Carbon Neutrality” and the adoption of numerous legislations have made renewable energy the unavoidable path for the transformation of the current energy system [1–3]. Therefore, it is an inevitable trend to accelerate the development of renewable energy. At present, the use and storage of hydrogen is a potential route to the current development of renewable energy, as hydrogen is a clean energy source that does not produce any pollutants [4]. “Hydrogen economy” is also a hot topic of sustainable development, and it is necessary to determine the direction and strategy of future development based on the conditions of the world. Technical methods for hydrogen production and consumption are reasonably established and well-developed in the supply chain. Hydrogen energy storage, hydrogen-powered automobiles, and hydrogen-powered ships are common applications [5,6]. Due to low volumetric density (0.0899 kg/m³), volumetric energy density

(0.003 kW·h/L), and gravimetric energy density (33 kW·h/kg), hydrogen energy usage faces significant storage and transportation constraints. The flammable and explosive qualities of hydrogen at normal temperature and pressure have also hampered large-scale and commercial hydrogen energy uses [7–9]. For on-board hydrogen sources, the US Department of Energy (DOE) has proposed objectives of 5.5 wt% and 62 kg/m³ for gravimetric and volumetric hydrogen capacity, respectively [10].

Hence, the development of efficient hydrogen storage technology is currently a popular focus of research. Improving hydrogen storage capacity and rate while reducing energy consumption are major characteristics of hydrogen storage technology. Compressed hydrogen storage (CH₂), liquid hydrogen storage (LH₂), liquid organic hydrogen carriers (LOHCs), liquid ammonia hydrogen storage (LAH₂), metal alloy hydrogen storage (MAH₂), and carbon material hydrogen storage (CMH₂) have all been the subject of much investigation to address above problems [11,12]. Among them, LOHCs technology is recognized to be excellent for long-distance and large-scale hydrogen storage and transportation due to its high hydrogen storage capacity, environmental friendliness, safety, and efficiency [13,14]. According to previous research, hydrogen storage liquids are generally high-purity single

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Nomenclature	
<i>Abbreviations</i>	
2-MID	2-Methylindole
4H-NECZ	Tetrahydro-N-ethylcarbazole
8H-NECZ	Octahydro-N-ethylcarbazole
8H-2-MID	Octahydro-2-methylindole
12H-NECZ	Dodecahydro-N-ethylcarbazole
12H-NPCZ	18H-DBT Dodecahydro-N-propylcarbazole Perhydro-dibenzyltoluene
BTX	Benzene, toluene, and xylene
CFP	Catalytic fast pyrolysis
CH ₂	Compressed hydrogen storage
CMH ₂	Carbon material hydrogen storage
DOE	United States Department of Energy
LAH ₂	Liquid ammonia hydrogen storage
LH ₂	Liquid hydrogen storage
LOHCs	Liquid organic hydrogen carriers
MAH ₂	Metal alloy hydrogen storage
MCH	Methylcyclohexane
MTA	Methanol-to-aromatics
NECZ	N-ethylcarbazole
NPCE	N-propylcarbazole
TCC-A	Thermal catalytic conversion and ammonification
TOL	Toluene
USA	United States of America

aromatic or N-doped compounds. Complex refining methods are often used to create these compounds from nonrenewable fossil energy sources. For instance, aromatic compounds can be made through naphtha reforming and petroleum cracking. Potentially, LOHCs can be obtained from biomass been turned into valuable liquid fuels and aromatic compounds through a variety of conversion methods. The lignocellulosic biomass is composed of cellulose (40%-50%), hemicellulose (25%-30%), and lignin (15%-20%) [15,16]. Take lignin as an example, it is a unique, renewable natural polymer with aromatic structures. Through the thermochemical conversion pathway, lignin can be depolymerized into aromatic compound intermediates, and can also be used to produce small molecular compounds such as biomass fuels and light aromatics [17]. Theoretically, these compounds can be used for the storage and release of hydrogen via a pair of reversible reactions in LOHCs technology. Thermal conversion conditions of biomass are expected to optimize the target product as a major component of organic hydrogen storage liquids, including targeted deconstruction, nitrogen doping, better catalysts, reaction condition, etc.

In all, this article provides an overview of LOHCs technology, including basic principles, technical approaches, and applications. This

review also proposes the concept of biomass-derived renewable LOHCs to demonstrate the potential of biomass as a carbon-neutral energy carrier for hydrogen storage. Combined with the current thermochemical conversion technologies of biomass, the preparation and development of aromatic hydrocarbons and N-doped compounds are briefly summarized and exhibited. In addition, the technological route, feasibility, and challenges of biomass-based LOHCs were evaluated.

2. Existing hydrogen storage materials including LOHCs

Based on the reaction principle, the categories of hydrogen storage are mainly composed of physical hydrogen storage, physical adsorption hydrogen storage, and chemical adsorption hydrogen storage. CH₂ [18] and LH₂ [19] are two types of physical methods. The physical adsorption of hydrogen [20] is usually composed of carbon materials, zeolite, and metallic organic framework materials. LOHCs, LAH₂ [21], electrochemical hydrogen storage [22], and MAH₂ [23] are examples of chemical adsorption storage methods. It is worth mentioning that hydrate hydrogen storage is also a physicochemical method, where H₂ capture occurs via the formation of a hydrate shell with hydrogen bonds

Table 1
Comparison of different hydrogen storage technologies.

Types of technology	Key parameters	Hydrogen storage capacity	Advantages	Disadvantages	Current main applications	References
CH ₂	20 MPa 70 MPa	11 kg H ₂ /m ³ 39 kg H ₂ /m ³	1) Mature 2) Simple structure 3) Fast process	1) Low volumetric hydrogen storage capacity 2) Increased safety risks and transport costs as pressure increases	1) Common cylinders 2) Lightweight high-pressure hydrogen storage tanks	[18]
LH ₂	<-253 °C	70.8 kg H ₂ /m ³	1) High hydrogen storage capacity 2) Safe	1) High vessel insulation requirements 2) High energy consumption in the liquefaction process	1) Mass- and long-distance transport 2) Rocket cryogenic propulsion	[19,33]
LOHCs	Toluene/ Methylcyclohexane Dibenzyltoluene/ Perhydro-dibenzyltoluene	w _{H2} = 6.16 wt % 47.4 kg H ₂ /m ³ w _{H2} = 6.2 wt% 57 kg H ₂ /m ³	1) High hydrogen storage capacity 2) Closed carbon cycle 3) Long-cycle storage and transportation	1) High energy consumption for dehydrogenation 2) Difficulty in developing dehydrogenation catalysts 3) Short cycle life	1) Transoceanic transport 2) Bulk storage and transportation	[34] [34]
LAH ₂	NH ₃	w _{H2} = 17.8 wt%	High hydrogen storage capacity	1) High toxicity 2) Trace amounts of ammonia tend to remain in the hydrogen gas	Proton exchange membrane fuel cells	[21]
MAH ₂	LiH MgH ₂	w _{H2} = 12.5 wt% w _{H2} = 7.65 wt%	1) High volumetric hydrogen storage capacity 2) Safe	1) Lack of technical maturity 2) Low efficiency of hydrogen storage and discharge 3) Low density of hydrogen storage per mass 4) High energy consumption	Laboratory research stage	[23] [35]
CMH ₂	Activated carbon Carbon nanotubes	w _{H2} = 3.8 wt% w _{H2} = 6.5 wt%	Fast process	1) Easily influenced by reaction conditions and material preparation processes 2) The hydrogen storage capacity is related to cryogenic conditions	Laboratory research stage	[29] [36]

between water molecules, with H₂ being kept by the topology of the cavity [24]. The characteristics, advantages, and disadvantages of several common types of existing main hydrogen storage technologies are summarized in Table 1. Pure steel metal (17.5–20 MPa), steel liner fiber wound (26.3–30 MPa), aluminum liner fiber wound (30–70 MPa), and plastic liner fiber wound (>70 MPa) are the four pressure categories for gas cylinders [25]. The application of some countries is relatively mature. For instance, the all-steel bottle container produced by JFE in Japan and the carbon fiber-wound hydrogen storage container with steel liner developed in the USA have been used for hydrogen refueling stations. Currently, bottle leakage, liner and interface sealing, and the design of transportable hydrogen cylinders for transportation are all issues that researchers are grappling with.

CH₂ technology is relatively easy to industrialize and offers fast charge and discharge rates, it is widely used for onboard hydrogen storage in new energy vehicles. Compared with CH₂ technology, the storage capacity of LH₂ technology has been greatly improved. LH₂ technology has a density of 70.85 kg/m³, which is 1/800 of the volume of gaseous hydrogen, making it easier to transport large volumes over long distances, considerably improving transport efficiency [26]. This type of technology is universally used for cryogenic rocket propellants [27,28]. Although LH₂ technology has sufficient advantages in terms of storage and transport capacity, it is based on a liquid-phase state formed at extremely low temperatures (<−253 °C). As a result of its peculiar working conditions, LH₂ technology has some drawbacks. On one hand, energy consumption is extraordinarily high as a result of the need to transform gaseous hydrogen into liquid through a series of technical means. Liquid hydrogen, on the other hand, absorbs heat continuously to form evaporative gases, which necessitate high insulation in storage facilities [29]. LAH₂ technology tends to utilize ammonia as the hydrogen carrier, and a high hydrogen storage capacity is obtained (17.8 wt%), 1.7 times higher than that of LH₂. Due to the high stability, liquid ammonia can meet the need for energy storage in time and in space [30]. However, LAH₂ technology should be considered for the need of high energy input and toxicity, and potential hazards to equipment, the human body, and the environment during long-term and long-distance storage and transportation [31].

In contrast with traditional hydrogen storage technologies, LOHCs technology has following major advantages: (1) it has a prominent capacity for hydrogen storage, as well as excellent performance (meeting DOE index requirements); (2) most of the substances have a high boiling point and low melting point, allowing them to maintain a stable liquid phase at room temperature while remaining nonvolatile; (3) this system has stable catalytic hydrogenation and dehydrogenation processes, and the reactants and catalysts can be recycled; (4) the storage, transportation, and maintenance of hydrogen-storage materials are safer and more convenient, allowing for large-scale and long-distance distribution; (5) current gasoline and diesel delivery techniques and gas station buildings may be immediately implemented. However, there are also several disadvantages, mainly including: (1) the reaction requires professional hydrogenation and dehydrogenation equipment, which has high investment costs; (2) the dehydrogenation reaction must be carried out at high temperature, which is likely to result in catalyst coking and deactivation; (3) the reaction process consumes large amounts of energy, and the performance decreases after several cycles; (4) the hydrogen produced by the dehydrogenation reaction is not of high purity, and inappropriate conditions and reactants are more likely to induce side reactions; (5) the initial cost to purchase LOHCs materials is extremely high.

What's more, some studies have found a higher energy demand of LOHCs than CH₂, LH₂, MAH₂, and LAH₂ based on the 0-dimensional simulation [32]. However, in terms of energy storage of regenerative hydrogen in the cell system, LOHCs technology showed efficiency with the increase of the energy storage cycle, confirming the suitability for long-term hydrogen storage. Assuming that large-scale storage and transport across oceans are targeted for applications in the field of

hydrogen storage, then there will be a wider market for LOHCs technology. In addition to the characteristics of high hydrogen storage capacity, carbon cycle, and suitability for long-term utilization, the safety performance is also superior to that of other hydrogen storage methods. Since the concept of LOHCs was proposed, the technology has also been continuously optimized. In other words, LOHCs technology is exactly promising and marketable for hydrogen storage today.

3. LOHCs technology

3.1. Fundamental principle

LOHCs technology is based on reversible hydrogen storage and release reactions using unsaturated liquid organics (e.g., toluene, naphthalene, and N-ethylcarbazole) as hydrogen storage agents and the corresponding saturates (e.g., methylcyclohexane, decalin, and dodecahydro-N-ethylcarbazole) as hydrogen carriers [7,37]. The fundamental principle of the reactions in LOHCs technology is shown in Fig. 1. The hydrogenation process is an exothermic reaction in which the organic hydrogen storage liquid is mixed with raw hydrogen in the reactor. The system is then heated to a specific temperature under the influence of the catalyst to form the corresponding saturated hydride. The products of the hydrogenation reaction are called hydrogen carriers (H_x-LOHCs). Essentially, it is a catalytic mechanism that uses hydrogen to transform unsaturated bonds into saturated ones [14,26]. From the perspective of chemical equilibrium, both low temperatures and high pressures are more favorable to hydrogenation. As the inverse of hydrogenation, dehydrogenation is an endothermic reaction. In the presence of the catalyst, hydrogen is extracted from H_x-LOHCs in the dehydrogenation device. The process involves continual absorption of external heat due to the energy difference between the energy required for the dissociation of hydrogen atoms and the activation energy of the C-H bond [38]. It is necessary to focus on the large energy consumption caused by the difference in temperature during the reaction, as well as the reduction of catalytic activity. Then, for long-distance transportation of hydrogen carriers, existing liquid fuel transportation (pipelines, ships, trucks, etc.) can be employed. It was found that unsaturated aromatics and corresponding hydrides can be hydrogenated and dehydrogenated without destroying the main structure of the carbon ring [39].

To increase the conversion rate and selectivity, as well as the recycling efficiency and activity of the catalysts, the composition of the compounds and conditions can be tweaked. Consequently, a high-performance LOHCs system should have the following performance indices [40]: (1) low melting point and high boiling point; (2) large hydrogen storage capacity (volume: >56 kg/m³, gravity: >6 wt%); (3) high stability of ring chain during dehydrogenation and high purity of hydrogen discharged; (4) low heat uptake and mild dehydrogenation conditions; (5) cheap cost and readily available materials; (6) long cycle life and selective dehydrogenation; (7) enhanced stability during use and transportation, low toxicity, and environmental friendliness.

3.2. LOHCs systems

LOHCs technology was first proposed as a non-cryogenic approach in 1975. Such technologies are more inclined to use aromatic compounds such as benzene and toluene for vehicle fuels as hydrogen storage carriers. As research progressed, scholars discovered that the enthalpy and temperature can be effectively reduced when an appropriate number of heteroatoms, such as N atoms, intervene and replace C atoms. Furthermore, as the number of N atoms in an organic compound grows, the dehydrogenation temperature also increases [42–44]. The most investigated organic compounds at the moment are aromatic and N-doped compounds. Simultaneously, a growing number of organic compounds are being discovered. Table 2 lists the physicochemical parameters and reaction equations for several regularly used LOHCs systems. The main systems found in the literature are toluene (TOL)/methylcyclohexane

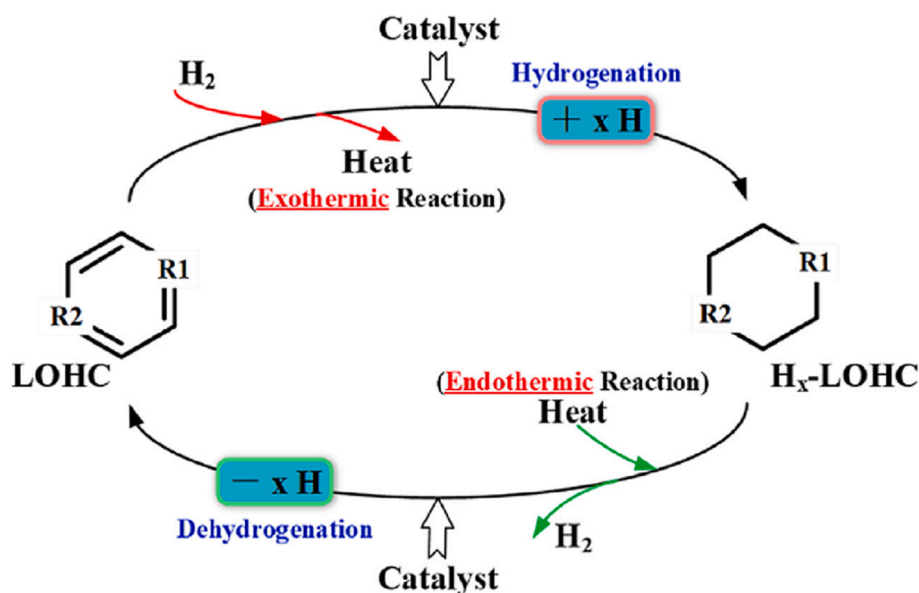


Fig. 1. Hydrogenation-dehydrogenation process of the LOHCs technology [41].

(MCH) [9], N-ethylcarbazole/dodecahydro-N-ethylcarbazole [45,46], naphthalene/decalin [47], dibenzyltoluene/perhydro-dibenzyltoluene [48], biphenyl/bicyclohexyl, and diphenylmethane/dicyclohexylmethane. Many scholars have studied the reaction mechanism of these hydrogen storage systems through molecular dynamics, nuclear magnetic resonance and other methods, which are summarized in Fig. 2. It is discovered that the steric effect will be strongly impacted by the existence of molecular size, methyl, heteroatoms, etc., thereby affecting the priority of bond hydrogenation and dehydrogenation.

Furthermore, a few corporations in wealthy countries such as Germany and Japan have already commercialized many systems. For example, dibenzyltoluene, which has a maximum hydrogen storage capacity of 57 kg/m³, has been the subject of research by the German business “Hydrogenious LOHC Technologies GmbH”. Japanese enterprises, such as “Chiyoda Chemical Construction”, have already integrated and developed in a variety of disciplines, including ocean-going hydrogen transport, miniaturization of hydrogenation and dehydrogenation, hydrogen refueling stations, and distributed energy delivery. Overall, Japanese industries have concentrated their research and development efforts on toluene/methylcyclohexane. Some Chinese firms have entered the LOHCs market. The most established company is “Hynertech” in Wuhan, where the N-ethylcarbazole/dodecahydro-N-ethylcarbazole system is the primary research focus. They have been concentrating on the creation of “hydrogen oil”, a liquid organic hydrogen storage solution that combines the benefits of safety and stability with high hydrogen storage capacity. It’s worth noting that “Hynertech” has demonstrated high-temperature waste gasification to “hydrogen oil” and the hydrogen energy business.

3.2.1. Systems of aromatic compounds

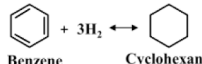
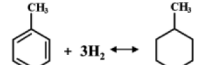
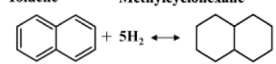
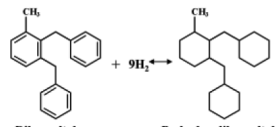
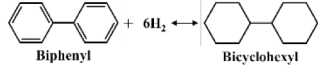
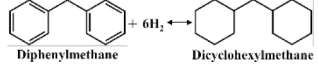
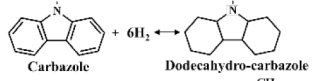
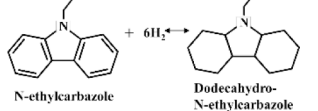
Although olefins, alkynes, and aromatic hydrocarbons can all be employed as hydrogen storage liquids, studies have confirmed that aromatic compounds are the best choice for hydrogen storage. Aromatic compounds can be applied as LOHCs because of the unique resonance interaction of aromatic rings which makes them more likely to hydrogenate and dehydrogenate than other organic molecules [65]. The first system studied was benzene/cyclohexane [65,66], which has a high gravimetric hydrogen storage capacity of 7.2 wt% and a volumetric hydrogen storage capacity of 55.9 kg/m³. The major disadvantage, however, is the high dehydrogenation temperature. The dehydrogenation reaction needs to be completed at a temperature of close to 300 °C, resulting in considerable energy consumption. Fig. 3a illustrates the

hydrogenation and dehydrogenation reactions of the benzene/cyclohexane system [65]. In a catalyzed hydrogenation process, benzene and hydrogen are introduced into the reactor at a pressure of 4 MPa and a temperature of 150 °C to create saturated cyclohexane. During the reaction, approximately 68.8 kJ/mol of energy is produced. At 300 °C and 0.1 MPa, cyclohexane absorbs roughly 68.8 kJ/mol of energy, with the gradual release of hydrogen and eventually dehydrogenates to benzene [67]. To find a better reaction system, Itoh et al. [68] used Pt/Al₂O₃ as the catalyst to compare the conversion and dehydrogenation temperatures of cyclohexane and methylcyclohexane, two types of hydrides: benzene and toluene. Because of the presence of methyl as an alkyl group, the dehydrogenation temperature was lower than that of cyclohexane. The mixture of methylcyclohexane and cyclohexane has also been shown to be a hybrid chemical hydride, which can be researched for hydrogen storage [68].

The reversible process of the toluene/methylcyclohexane system is shown in Fig. 3b, where a reduced storage capacity is accompanied by a lower dehydrogenation temperature. Overall, the benzene/cyclohexane and toluene/methylcyclohexane systems exhibited excellent hydrogen storage capacities. However, a higher dehydrogenation temperature remains a critical factor affecting the energy consumption of the reaction. Naphthalene, a cheap and simple condensed aromatic hydrocarbon with excellent hydrogen storage capacity, was shown to be equally suitable for hydrogen storage [69–71]. The naphthalene/decalin system reaction is shown in Fig. 3c [58]. As naphthalene is prone to many side reactions during hydrogenation, there are distinctions between the resulting naphthenic compounds such as *trans*-decalin and *cis*-decalin [72]. Many factors influence the rate of reaction, as well as the separation and purification of the product, such as the number of rings opened, organic solvents, and catalysts. Terribly, the high temperature and vapor pressure during the dehydrogenation of decalin will lead to ring-opening and cracking after several cycles. This will make more tar and coke adhere to the equipment which is difficult to remove [72]. In addition, to ensure the reactivity and state of the liquid phase, it is necessary to equip the transport with heating facilities, which increases the complexity and cost of storage and transportation.

Dibenzyltoluene (DBT) is the principal component of “thermal conductive oil” in daily production, in addition to the three systems mentioned above. The physical and chemical qualities of “thermal conductive oil” are stable, and it is distinguished by its high boiling point, low melting point, and low toxicity. The dibenzyltoluene/perhydro-dibenzyltoluene system has become a hot topic within

Table 2
Common LOHCs systems.

Hydrogen storage agents	Chemical formula	Hydrogen carriers	Chemical formula	Melting point/ $^{\circ}$ C	Boiling point/ $^{\circ}$ C	Hydrogen storage capacity/(wt%)/(kg/m ³)	Dehydrogenation temperature/ $^{\circ}$ C	Reaction equation	Reference
Benzene	C ₆ H ₆	Cyclohexane	C ₆ H ₁₂	6.5	80.7	7.2/55.9	300–320		[56]
Toluene	C ₇ H ₈	Methylcyclohexane	C ₇ H ₁₄	-126.6	101	6.2/47.4	300–350		[57]
Naphthalene	C ₁₀ H ₈	Decalin	C ₁₀ H ₁₈	-31	187	7.3/65.4	320–340		[58]
Dibenzyltoluene	C ₂₁ H ₂₀	Perhydro-dibenzyltoluene	C ₂₁ H ₃₈	-39	390	6.2/57	260–310		[48,59,60]
Biphenyl	C ₁₂ H ₁₀	Bicyclohexyl	C ₁₂ H ₂₂	3	227	7.27/-	310–330		[61]
Diphenylmethane	C ₁₃ H ₁₂	Dicyclohexylmethane	C ₁₃ H ₂₄	-18.6	153	6.66/-	340–360		[62]
Carbazole	C ₁₂ H ₈ N	Dodecahydro-carbazole	C ₁₂ H ₂₀ N	65	124	6.7/-	150–170		[63,64]
N-ethylcarbazole	C ₁₄ H ₁₃ N	Dodecahydro-N-ethylcarbazole	C ₁₄ H ₂₅ N	-84.5	-	5.8/-	170–200		[46]

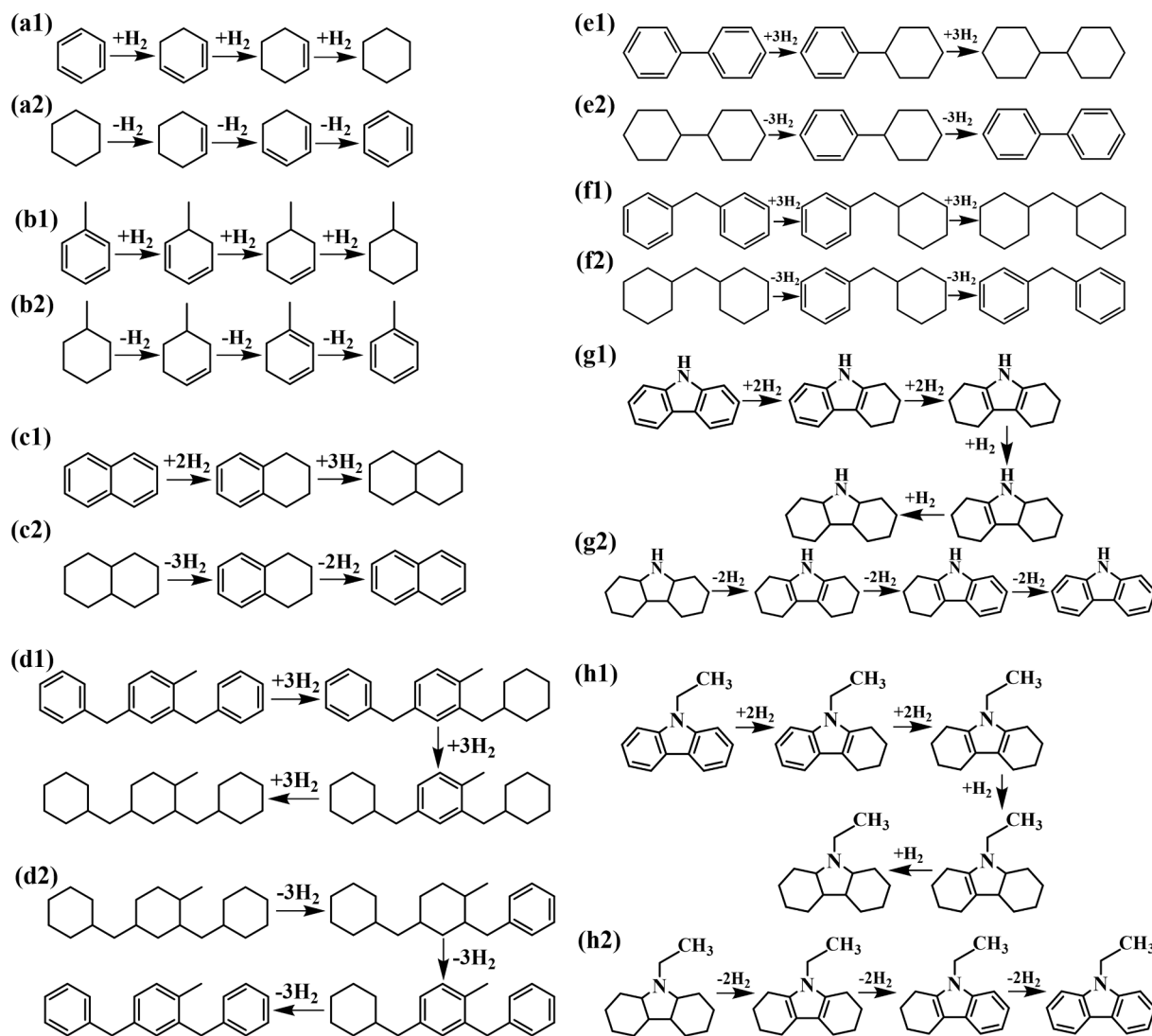


Fig. 2. Mechanism of hydrogenation [49–51] and dehydrogenation [52–55]. (a1), (a2) Benzene/Cyclohexane; (b1), (b2) Toluene/Methylcyclohexane; (c1), (c2) Naphthalene/Decalin; (d1), (d2) Dibenzytoluene/Perhydro-dibenzytoluene; (e1), (e2) Biphenyl/Bicyclohexyl; (f1), (f2) Diphenylmethane/Dicyclohexylmethane; (g1), (g2) Carbazole/Dodecahydro-carbazole; and (h1), (h2) N-ethylcarbazole/Dodecahydro-N-ethylcarbazole.

current aromatic hydrogen storage liquid compounds [59,73]. As illustrated in Fig. 3d, DBT interacted with hydrogen in the presence of the catalyst to produce perhydro-dibenzytoluene under certain conditions. What's more, DBT is a prominent research target for aromatic organic hydrogen storage liquids due to its exceptional physicochemical features. DBT may be recycled numerous times when used as the hydrogen storage carrier, and its fixed cost for hydrogen storage is lower than that of liquid chemical plants. However, the use of DBT has drawbacks of high energy consumption and slow reaction rate in dehydrogenation, and H_2 needs to be purified when released [42]. In addition, the technical bottlenecks in developing efficient and low-cost dehydrogenation catalysts also limit the application of DBT in liquid hydrogen storage to some extent.

In addition to the systems mentioned above, there are several studied on LOHCs utilizing biphenyl/bicyclohexyl and diphenylmethane/dicyclohexylmethane as the research subjects. Biphenyl and diphenylmethane are particularly popular as hydrogen carriers because of the excellent hydrogen capacity, stability and economic performance [74]. However, the solid physical state under ambient environment has limited the application for hydrogen storage. Hence, a growing number of studies have proposed the low-eutectic mixture (such as the combination of biphenyl and diphenylmethane) as potential hydrogen carrier,

realizing liquid state at room temperature and atmospheric pressure [75,76]. It has been demonstrated that an optimum composition of biphenyl ($C_{12}H_{10}$, 35 wt%) and diphenylmethane ($C_{13}H_{12}$, 65 wt%) can be formed and the hydrogen storage capacity can be maximized (6.9 wt % and 69.1 gL^{-1}) [77].

3.2.2. Systems of N-doped compounds

It has been confirmed that the incorporation of heteroatoms such as N, P, and O into aromatics can significantly affect dehydrogenation thermodynamics [43]. To better understand the relationship between the heterocyclic structure and the enthalpy of dehydrogenation, Clot et al. [63] investigated how the substituted positions of different heteroatoms affect the dehydrogenation reaction. They eventually discovered that substituting heteroatoms at the ring's 1-position can effectively lower the dehydrogenation temperature of the hydrogen storage carriers. In addition, the addition of heteroatoms to the five- and six-membered rings can reduce the enthalpy of dehydrogenation to a significant extent. Recently, an increasing number of studies have discovered that hydrides in N-doped systems of N heterocyclic compounds (e. g., indoles [78,79], pyridines [80,81], and carbazoles) exhibit lower dehydrogenation temperatures than cyclic olefins. N-ethylcarbazole (NECZ)/dodecahydro-N-ethylcarbazole (12H-NECZ) [63] is the most

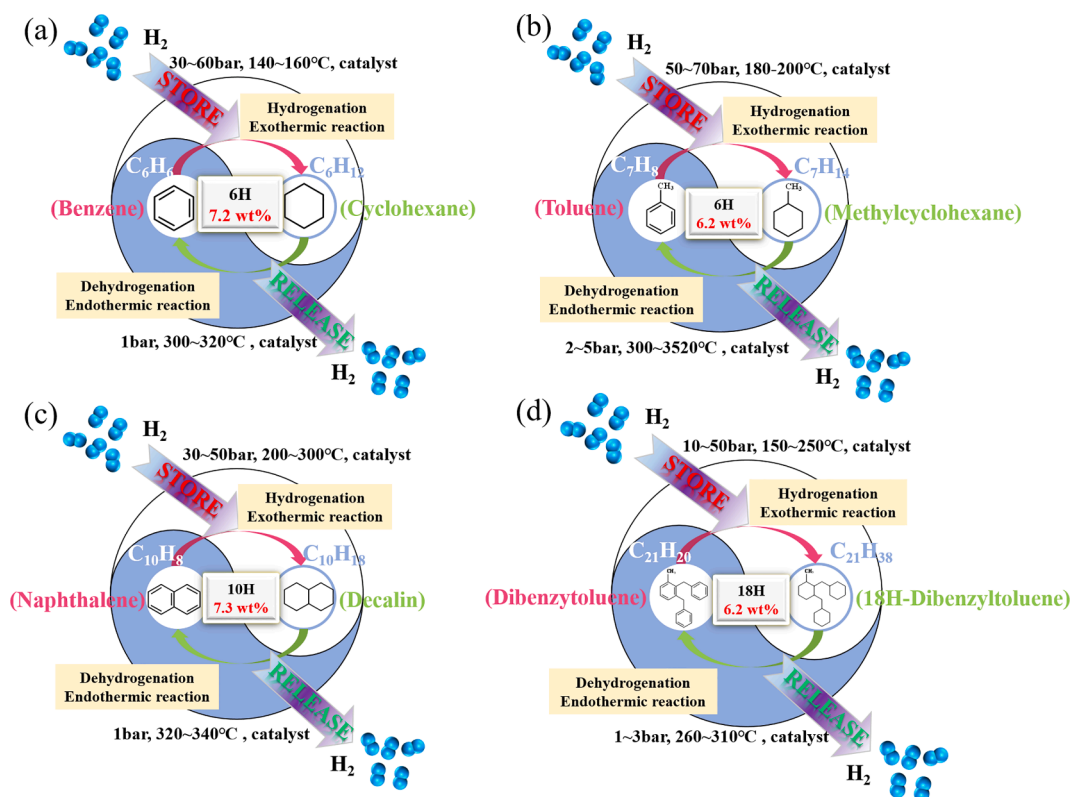


Fig. 3. Systems of aromatic compounds: (a) Benzene/Cyclohexane, (b) Toluene/Methylcyclohexane, (c) Naphthalene/Decalin, and (d) Dibenzyltoluene/Perhydrodibenzyltoluene.

frequent in this sort of system. The dehydrogenation temperature gradually lowered to around 200 °C as the number of heteroatoms in the organic matter increased. The hydrogen storage and release reactions of the NECZ/12H-NECZ system are shown in Fig. 4a. Under catalytic

action, hydrogenation of NECZ can be achieved within 150 °C–200 °C, resulting in the formation of 12H-NECZ. At a pressure of 0.1 MPa and a temperature around 200 °C, 12H-NECZ could be reduced to NECZ. When entirely hydrogenated, the gravimetric hydrogen storage capacity

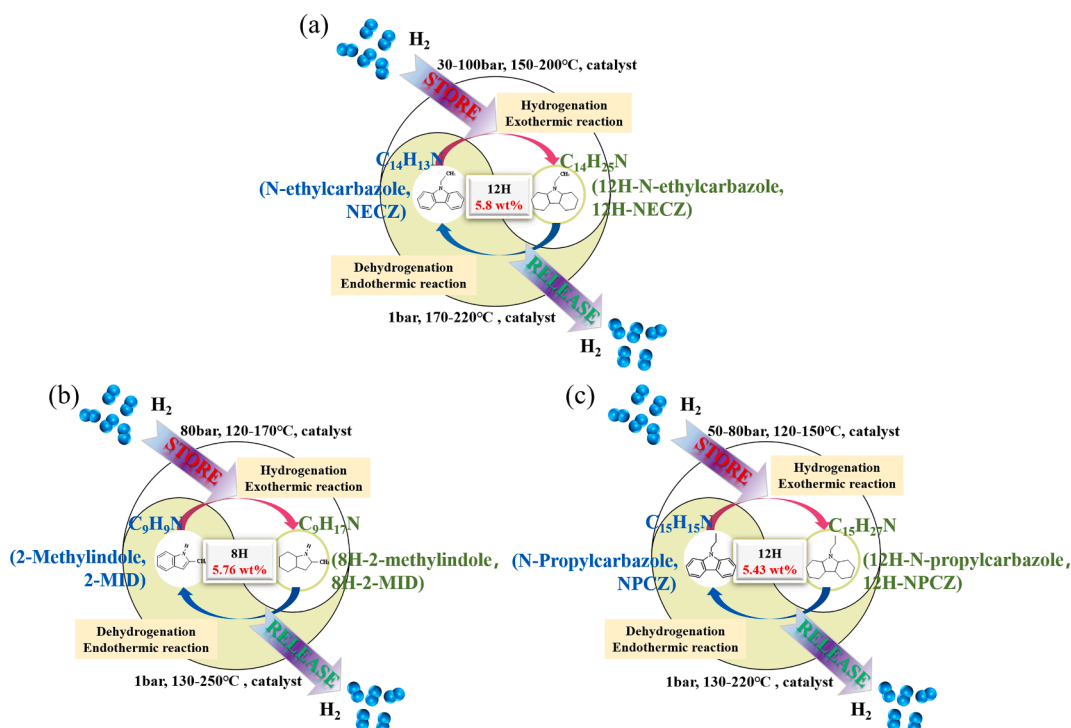


Fig. 4. Systems of N-doped compounds: (a) N-Ethylcarbazole/Dodecahydro-N-Ethylcarbazole, (b) 2-Methylindole/Octahydro-2-Methylindole, and (c) N-Propylcarbazole/Dodecahydro-N-Propylcarbazole.

of 6.7 wt% for carbazole and 5.8 wt% for NECZ are lower than that of the aromatic-alkane system. However, there was a significant decline in dehydrogenation temperature. The difference in temperature and enthalpy of the reaction between carbazole and NECZ is rather modest. The addition of ethyl in NECZ slightly decreases the hydrogen storage capacity. However, the passivation effect of N atom on the catalyst is effectively reduced to maintain the activity [82]. Moreover, the melting point of NECZ is just 69 °C, significantly decreasing the number of additional operating steps owing to the higher melting point. Because carbazole and NECZ are solids at room temperature, some organics, such as hot ethanol and ether, need to be added to dissolve the solid or lower the melting point to enable a smooth reaction. For the dehydrogenation of 12H-NECZ, an inadequate reaction produces additional by-products. Taking 4H-NECZ and 8H-NECZ as examples, these substances decrease the efficiency of transformation. In many cases, the presence of stereoisomers of semi-hydrogenated products with different reactivity results in reduced and incomplete conversion, even though the thermodynamic is favorable [83]. Accordingly, suitable catalysts for hydrogenation and dehydrogenation must be selected to address the problem of low efficiency.

In addition to carbazole, several N-doped aromatic heterocyclic derivatives (e.g., indole [79,84], pyridine [44,81], and pyrrole) can be hydrogenated and dehydrogenated. Despite the related studies being less frequent than those of carbazole, more studies need to be conducted. Fig. 4b and Fig. 4c show the relative reaction of 2-methylindole (2-MID)/octahydro-2-methylindole (8H-2-MID) and N-propylcarbazole (NPCZ)/dodecahydro-N-propylcarbazole (12H-NPCZ) systems [14]. When used as the organic hydrogen storage liquid, 2-MID has a hydrogen storage capacity of 5.76 wt% and can be hydrogenated to 8H-2-MID with catalysts such as Ru/Al₂O₃. Thus, 8H-2-MID can be completely dehydrogenated to form 2-MID. Similarly, NPCZ can be catalytically hydrogenated to 12H-NPCZ at 120 °C–150 °C with a hydrogen storage capacity of 5.43 wt%. The class of N-doped compounds has been the subject of much research, including the examination of some of the compounds produced during the hydrogenation process.

Similar to mixed aromatic systems such as biphenyl/diphenylmethane, owing to the limitations of the physical and chemical properties of pure substances, some studies have explored the effects of hybrid systems of N-doped compounds [68]. Compared to a single compound, the lower freezing point of the mixture made it more beneficial for use in colder climates. The melting points of combinations containing various alkyl compounds were examined by Stark et al. [85]. They realized that the melting points might be lowered by using the appropriate combination of N-alkylcarbazole. Shuang et al. [86] investigated mixed liquid hydrogen storage systems and the impact of mixing in different proportions on the performance of the system. Consequently, they discovered that the melting point of the mixture dropped to 25 °C when the system was mixed with 40 wt% 2-MID, 36 wt% NPCZ, and 24 wt% NECZ. With a solvent-free catalytic process and a high hydrogen storage rate, the hydrogen storage capacity could reach 5.64 wt%.

Taking various promising LOHCs as the research object, the dehydrogenation performance differs significantly in technical, economic, and environmental aspects [87]. For the production rate of H₂, TOL and DBT tended to be better than NECZ. For the economic feasibility, the use of NECZ took the higher investing cost to a large extent than DBT and TOL, with almost unit H₂ production cost of 264.47 \$ kgH₂⁻¹ while 54.94 \$ kgH₂⁻¹ for DBT, and 19.94 \$ kgH₂⁻¹ for MCL. Meanwhile, compared with DBT and MCH, the CO₂ emissions per produced H₂ were revealed to be showing environmental drawbacks of NECZ. Hence, the techno-economic performance of LOHCs should be comprehensively considered.

3.3. The developments of catalysts in LOHCs technology

When comparing the strengths and drawbacks of the LOHCs technology processes, it becomes obvious that a number of reasons can limit large-scale commercialization. The key obstacles include the high energy consumption, the difficulty of developing dehydrogenation catalysts, and the decrease of hydrogen storage performance as the number of cycles increases [88–90]. As a result, current research focuses on lowering energy consumption and developing high-performance catalysts. Major dehydrogenation catalysts are supported metal catalysts and tend to be prepared by impregnation [91], deposition precipitation [92,93], one-pot [94], and sol–gel methods [95], etc. Generally, these catalysts are loaded on carbon-based materials, Al₂O₃, TiO₂, zeolite, and other carriers [96,97]. Since the hydrogenation and dehydrogenation of hydrogen storage liquids are reversible reactions, catalysts with high hydrogenation activity also perform well in dehydrogenation reactions. Catalysts are often categorized based on how metals are mixed. Monometallic catalysts (noble metal catalysts, non-noble metal catalysts [98–100]), polymetallic catalysts [101], and other catalysts (such as boron nitride and metal complexes) are examples of different types of catalysts.

(1) Monometallic catalysts

Monometallic catalysts are normally categorized into metallic and non-metallic catalysts based on metal activity [89]. Palladium (Pd), platinum (Pt), ruthenium (Ru), rhodium (Rh), nickel (Ni), molybdenum (Mo), and copper (Cu) have all been extensively researched. The choice of the catalyst has a critical influence on the products and activity of the reaction. The proportion of different forms of d-electrons has been demonstrated to be related to the active component. In the case of noble metals, for example, Pd, Pt, Ru, and Rh all occupy 40% of the d-electrons in their atoms, and their activity is higher [102,103]. With high activity, Pd and Pt can significantly decrease the dehydrogenation temperature. The activity of Pd was maintained after a few cycles, demonstrating a distinct advantage in all types of LOHCs systems. Wang et al. [91] performed a comparative experimental study on the dehydrogenation of 12H-NECZ with graphene (rGO)-supported noble metal catalysts. The catalytic activity was found to follow the order Pd/rGO > Pt/rGO > Ru/rGO > Au/rGO in the experiments. The authors also compared Pd/rGO with the commercial catalyst Pd/Al₂O₃. Pd/rGO was shown to be superior to Pd/Al₂O₃ in many ways, and its catalytic activity remained unchanged within a certain range of reaction temperature. Sharma et al. [104] employed ruthenium metal as the active component of the catalyst. They discovered that at 120 °C and a partial pressure of H₂ of 60 atm for 2 hours, 100% conversion of benzene with 100% selectivity could be achieved. Despite the benefits of noble metal-supported catalysts in terms of activity, reaction rate, and service life, there is a demand for low-cost, high-efficiency catalysts for LOHCs.

For the storage and release of hydrogen from LOHCs systems, Ni-based catalysts also exhibit outstanding catalytic activity. These catalysts are generally utilized in the form of supported or skeletal Ni for reactions [105]. Raney-Ni is widely utilized for skeletal Ni and shows a high activity due to its large specific surface area. Nevertheless, the conversion rate tended to drop gradually as the number of catalytic cycles and time increase. When it comes to the supported Ni, the catalysts Ni/SiO₂ [67], Ni/Al₂O₃-TiO₂ [106], and Ni₂P/Al₂O₃ [67] are commonly utilized. In addition to some supported metals such as Ni, Mo have also been studied as a non-noble metal, and its loading effect has a significant impact on the surface properties of the catalyst. However, Mo frequently exhibits a decrease in activity and produces more coking materials. Generally, non-noble metals have disadvantages in terms of reactivity, temperature, and service life when compared with noble metals, but they offer a remarkable economic advantage.

(2) Polymetallic catalysts

For the features obtained by the different physicochemical qualities of single components of monometallic catalysts, the use of polymetallic or transition-metal catalysts can completely exploit the strengths of each

component. This sort of catalyst can be improved to stimulate the breakdown of C-H bonds, improve the activity of intermediates, speed up the reaction, and even increase the selectivity of products. The addition of Ni, Cu, Sn, and other second components to noble metal catalysts can take advantage of the involved synergistic effects, such as Au_xPd_y/rGO [107] and Pd-M/TiO₂ [92]. Doping with polymetallic materials can considerably reduce the number of noble metals and economic pressure, while maintaining high reactivity and cycle stability. Wang et al. [94] studied the dehydrogenation performance of 12H-NECZ by using rGO as a carrier to prepare Pd and Cu bimetallic catalysts via a one-pot method. The Pd_{1.2}Cu/rGO catalyst had the maximum catalytic activity, with 100% conversion of 12H-NECZ after 1 hour of reaction and 100% product selectivity after 7 hours. Yuki et al. [108] developed the binary alloy for the dehydrogenation of TOL/MCH, and they finally found that Pt₃Fe/SiO₂ acts as a highly active and durable heterogeneous catalyst with excellent toluene selectivity (>99%) and long-term durability. The core is that the excellent performance was derived from the synergy of each element (C-H activation of Pt, decoking of Fe, and toluene desorption of Zn). Numerous investigations have shown that the introduction of other metals into monometallic materials can result in positive synergy, improved catalyst activity and stability, and cost benefits [109–112]. However, the characteristics of the catalysts are strongly affected by the processing procedures and types of the carriers. For the hydrogenation and dehydrogenation of various LOHCs systems, the introduction of the second or third metal should serve as the reference object. Above all, it is necessary to consider whether the addition of metals and the preparation procedures can interact positively with the hydrogen carriers.

In addition to the active component, the metal-supported carrier is a crucial element that affects the performance of the catalyst. Several studies have discovered that catalysts with metal nanoparticles on the surface of carbon-based materials (e.g., activated carbon, graphene, and carbon nanotubes) can have strong hydrogenation and dehydrogenation activity [113,114]. Catalyst activity is increased when metal links are modified, allowing researchers to better regulate the reaction process and facilitate research for industrial applications. Above all, it is essential to assess whether the different metals and preparation processes used in the catalysts could lead to positive system synergy. Apart from supported catalysts, a growing number of other types of catalysts, such as boron nitride and metal complexes, have gradually become research hotspots in recent years. However, many of these catalysts have challenging production procedures and are difficult to apply in industrial settings.

Overall, the reactivity of hydrogen storage qualities is affected by the types of metal, support, and carriers. In both monometallic and bimetallic systems, noble metals exhibit excellent catalytic characteristics. However, it is still necessary to balance costs and benefits. Bimetallic and polymetallic catalysts are currently recognized as the most promising strategies to improve the process. The possibility of lowering the quantity of noble metals while retaining catalytic activity holds a lot of promise. In addition to changing the catalysts in terms of the active component, carriers, and supporting mode, many researchers employ sulfur in conjunction with catalysts modification techniques in the petrochemical industry to optimize the catalytic activity [115]. In order to prepare the Pt/Al₂O₃ dehydrogenation catalyst in the dibenzyltoluene/perhydro-dibenzyltoluene system, Wasserscheid's team added a specific amount of sulfide. They found that sulfur occupied a low coordination sites of the supported Pt nanoparticles, which significantly boosted the dehydrogenation efficiency and lowered the production of byproducts [116]. Furthermore, by increasing the dispersion of active components, lowering the surface charge density, and maximizing the H₂ spillover effect, the catalytic activity in the reaction of polycyclic aromatic hydrocarbons and heteroatom-doped compounds can be boosted [117–119].

3.3.1. Reactors for hydrogenation and dehydrogenation

Hydrogenation and dehydrogenation reactors are key components of the whole system, with dehydrogenation reactors receiving more research and development. The reactor has more rigorous pressure requirements since the hydrogenation process necessitates greater pressure. Stainless steel autoclaves, along with fixed-bed reactors and other laboratory equipment, are more commonly utilized for easy operation [65,83,120]. When the reaction is accompanied by tandem side reactions, the fixed-bed reactor allows continuous hydrogenation and effective interaction between the reactants and catalyst, resulting in high selectivity. Individual reactor units are utilized for batch hydrogenation in stainless steel autoclaves, which are relatively straightforward to operate. To maintain the reaction at a consistent pressure, a hydrogen reservoir was attached to the reactor during the reaction. According to the classification of reactants and reaction conditions, dehydrogenation reactors can be divided into two types: steady-state and non-steady-state [121,122]. Dehydrogenation reactions are typically categorized into three groups based on the phase of organic liquid hydride: gas-phase, liquid-phase, and “wet-dry” multi-phase dehydrogenation. The advantages and disadvantages of several types of reactors are listed in Table 3. Among what has been mentioned in the list, principal dehydrogenation reactors at the laboratory-research stage are “oil bath pot - three mouth flask” [114,123], fixed-bed reactor [47], pulse jet reactor, and membrane catalytic reactor [124]. The “oil bath pot - three mouth flask” apparatus is a batch reactor. The hydrogen-rich liquid is injected into the container after it has been heated to the temperature of the dehydrogenation reaction in the oil bath. The hydrogen removed by the reaction was cooled, separated by a serpentine condenser, and eventually collected. “Oil bath pot - three mouth flask” is a simple-structured device of the reaction which enables the effective separation of reactants and products. However, the temperature of the dehydrogenation reaction is frequently a limiting factor, and it is more commonly utilized in systems with lower dehydrogenation temperatures, such as NECZ. Fixed-bed [125–127], membrane reactors, and stainless steel autoclaves [128] are more often employed for systems with higher dehydrogenation temperatures and requirements for continuity. In a fixed-bed reactor, similar to hydrogenation, dehydrogenation is conducted by heating the catalyst to a given temperature and then transferring the organic hydrogen carrier into the unit. In the case of MCH, after being heated in the gasification chamber, it traveled through the catalyst bed in a gaseous condition and then reacted. Finally, the hydrogen was extracted and gathered.

Therefore, a suitable reactor must be selected for the phase states of different reactants and mechanisms of dehydrogenation. There are numerous methods for optimizing and upgrading the reactor on a regular basis. To improve the dehydrogenation rate and purity of the produced hydrogen, multiphase dehydrogenation can be used instead of single-phase dehydrogenation. Microreactors can also be utilized to keep a consistent dehydrogenation temperature [121]. Some bottleneck difficulties in pulse injection reactors [129] and membrane-catalyzed reactors remain addressed, and commercial applications are still a long way off. Fixed-bed reactors offer a high conversion efficiency and can be utilized for continuous feeding. However, the diffusion of gas, which easily causes coke production and catalyst degradation, currently limits the reaction rate of fixed-bed reactors. During the dehydrogenation, it is necessary to take into account the activity of the catalyst, temperature, and reaction efficiency to control completion of the reaction. When the reaction is insufficient, it is also critical to avoid a reverse reaction.

3.4. Integrated system of hydrogen storage and release processes

The development of several types of reactors for independent hydrogenation and dehydrogenation processes is progressing. Under ideal conditions, a high level of cycling performance can be reached by considering the full response system holistically. LOHCs technology is a

Table 3
Advantages and disadvantages of different types of reactors.

Type	Reactor/Reaction form	Key characteristics	Advantages	Disadvantages	Reference
Steady-state	Fixed-bed reactor	Continuous and sufficient contact between catalyst and reactants	Continuous operation	Prone to reverse reaction and liquid phase reaction	[125–127,130]
	Batch reactor	Catalyst particles suspended in a liquid hydrogen carrier	High conversion rate	1) Limited to liquid-phase reactions 2) Uncontrollable completion of the reaction	[114,123]
	Membrane reactor	Selective hydrogen-permeable membrane	Simultaneous reaction and separation	High cost and difficult maintenance	[124]
	Micro-structured reactor	Optimization of heat transfer by structural design	Compact structure to restrain heat transfer limitations	Complicated design	[131]
	Monolithic reactor	Structured catalyst reactor	1) High catalyst efficiency 2) Alternating wet-dry and liquid film states 3) Facile regeneration	Experimental data are not directly available	[130]
Non-steady-state	Liquid film state condition	Catalyst surface covered by liquid film	Effectively avoiding suspension of catalyst in liquid phase reactants	The catalyst is in a wet state for a long time	[132]
	Wet-dry multiphase system/Spray pulse system	The liquid evaporates and then condenses, thus spreading over the catalyst surface, reacting and vaporizing	1) Improved reactant contact 2) High catalytic temperature 3) Effective avoid of reverse reaction	1) Difficult commercial application 2) Limited scope of use	[129]

three-step closed-cycle reaction that includes hydrogenation reactions, hydrogen carrier conveyance, and dehydrogenation reactions. Among numerous nations with relatively advanced and widespread hydrogen energy development, Japan has essentially completed the demonstration project of hydrogen storage and release, addressing hydrogenation generation and Gas-to-Liquid technologies and benefiting from hybrid fuel cells [133]. The integrated system for hydrogen storage and release is depicted in Fig. 5, which is a flow chart at the level of laboratory or small and medium-sized hydrogenation and dehydrogenation equipment. As shown in the Fig. 5, when completely hydrogenated, the product is condensed by employing a condenser, which discharges the excess exhaust gas and produces hydrogen storage carriers. Fully hydrogenated organic liquids can be stored and transported efficiently

because of their high stability and cyclic performance. When the hydrogen is required, LOHCs are transferred by liquid storage tanks or other equipment to the dehydrogenation unit. The dehydrogenation is then carried out under the action of a specific condition. Finally, hydrogen is discharged from the hydrogen outlet of the unit and stored in a gas storage tank for later use. The organic liquid can be processed, transported, and recovered after dehydrogenation for further hydrogen storage.

3.5. Recent application of LOHCs technology

Owing to the advantages of safety, compatibility, and high hydrogen storage capacity of current liquid storage facilities, multiple energy

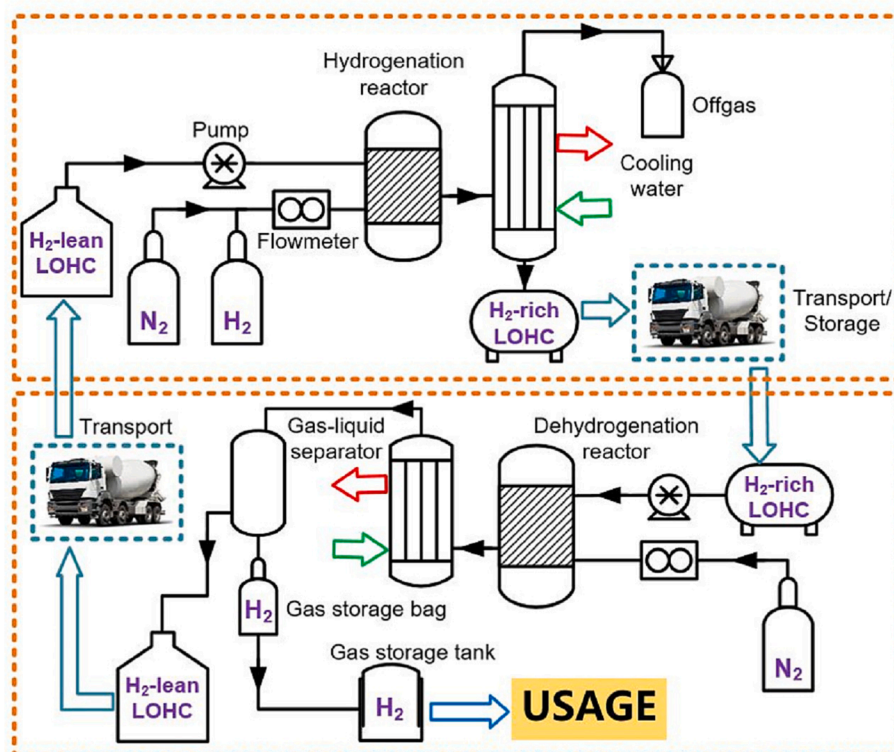


Fig. 5. Integrated system for hydrogen storage and release.

sources can be transported and preserved. These features distinguish LOHCs technology from conventional hydrogen-storage systems. This aligns with the present call for a firm guarantee for the development of clean, low-carbon, safe, and efficient energy systems. This is expected to alleviate the problem of uneven distribution of energy in space and time.

3.5.1. Large-scale storage and transportation of hydrogen

Since the reversible processes of LOHCs technology require specific reaction conditions, this ensures a high degree of stability for liquid organic hydrogen storage carriers. Because of the flammable and explosive characteristics and low density of hydrogen, its transport across oceans or other large-scale applications is particularly challenging. Liquid hydrogen, liquid ammonia hydrogen, and LOHCs are the three main technologies for bulk hydrogen transport now in use [10,134]. For the delivery of hydrogen, traditional LH₂ technology necessitates absolute temperature control. The storage vessel is insulated as a result of the conditions of use, which can will increase the cost greatly. In the case of LAH₂ technology, traces of ammonia remaining in the hydrogen after dehydrogenation cause severe degradation of the performance. In summary, high-pressure and liquid hydrogen are more suitable for short-haul transportation, but both systems have large upfront expenditures and administrative restrictions. As for LOHCs technology, hydrogen carriers can be stored and transported with existing oil and gas transmission pipelines, tankers, and storage tanks. The usage of LOHCs technology aims to store hydrogen through organic hydrogen storage liquids from raw hydrogen resources. Hydrogen storage tankers, tankers, pipelines, and ships are used to carry the carriers to their final destination [10,135,136]. Finally, catalytic dehydrogenation units release hydrogen for use in fuel cells, hydrogen refueling stations, and industrial production. At the same time, after cooling, the hydrogen-leaved liquids used for hydrogen storage can be recycled and stored for future use.

“Chiyoda Chemical Construction” in Japan has carried out the research and engineering test of large-scale LOHCs technology based on TOL/MCH, with the dehydrogenation conversion of MCH over 99.9%, selectivity of TOL over 99.9%, and catalyst life over 10,000 h. As the representative enterprise, “Chiyoda Chemical Construction” imported a total of 210 metric tons of hydrogen from Brunei to realize the transfer of hydrogen across the oceans in 2020. The first project of the worldwide hydrogen-energy supply chain has completed its demonstration phase. This chain was based on the production of hydrogen through natural gas reforming at the Brunei plant, employing a stable chemical as the carrier and then using conventional transportation to convey hydrogen to Japan across long distances. The goal of this project is to feed hydrogen to turbines to create electricity.

3.5.2. Hydrogen energy vehicle industry

In addition to being used for the bulk and transoceanic transport of hydrogen energy, LOHCs technology can also be applied to existing hydrogen energy vehicles [73,137]. It is possible to load hydrogenated cyclohexane straight into the vehicle and dehydrate it using an onboard dehydrogenation device in the case of hydrogenated cyclohexane. “Hynertech” in Wuhan, the representative firm among the LOHCs technology-related enterprises in China has demonstrated a project for 1,000-ton NECZ plant using “NECZ/12H-NECZ”. The business has proposed the world’s first fuel cell model that relied on liquid organic hydrogen as a source of energy in 2016. As mentioned in section 3.2, the hydrogen storage carrier developed in “Hynertech” of is known as “hydrogen oil”. Ultra-high-temperature gasification technology has been investigated for the production of “hydrogen oil” in accordance with Chinese policy. This technology makes use of municipal and industrial solid waste, which is gasified at extremely high temperatures to produce hydrogen gas and “hydrogen oil”. This not only reduces the environmental impact of hazardous waste, but it also improves energy efficiency and allows biomass to be combined with other emerging energy industries.

3.5.3. Renewable energy storage industry

In the context of carbon neutrality, the renewable energy industry in China is gaining traction and helping to lessen the reliance on imported energy. When it comes to long-distance transportation, conventional energy storage technologies (such as liquid fuels, electricity, and thermal energy) have limited by storage periods, high energy consumption, and low safety. As a result, positive energy storage technology research is required to realize the exploitation, transfer, and storage of important renewable energy supplies. In the case of hydrogen energy, the production and preparation of hydrogen usually consist of three categories: “blue hydrogen”, “grey hydrogen” and “green hydrogen” [138]. Hydrogen is a prospective energy carrier that can be employed as a conversion medium for a variety of energy sources. LOHCs technology allows for efficient hydrogen energy storage and transmission, and it can also be used to collect renewable energy, large-scale distributed generation, and hydrogen. This one-of-a-kind connection makes it suited for long-term and large-scale storage and usage, allowing collaborative connectivity between diverse components of the energy network [135]. For the production of hydrogen, there are an increasing number of studies on renewable energy methods such as water electrolysis/solar photolysis, biomass fermentation, bioethanol reforming, and biomass chemical cracking [139]. Electrolysis of hydrogen from renewable energy sources and the processing of biomass feedstock have been shown in a growing number of studies to be key sources of hydrogen for increasing the amount of hydrogen produced [41,135]. When comparing the investment expenses of CH₂, LH₂, and LOHCs, the latter is only 32% of the former [140]. Germany has proposed the “GET H₂” in 2020. The project seeks to develop industrial-scale green hydrogen production in regions with abundant wind and solar energy resources, and connect with downstream application. Fig. 6 shows one of the methods in which energy is stored in a renewable system by LOHCs technology in the form of a hydrogen supply chain.

4. Recent development of new LOHCs technology — biomass-based organic liquids for hydrogen storage

Aromatics and N dopants are the critical systems available for LOHCs technology. Existing hydrogen storage liquids are commonly prepared from coal and petroleum. Pure chemicals such as triphenylbenzene [benzene, toluene, and xylene, (BTX)] tend to be obtained from coal by thermal fractional distillation, and purification in turn [141,142]. When prepared from petroleum, the fractionated products contained fewer aromatic compounds and a large number of alkanes. As a result, numerous bond-breaking reforming and aromatization procedures must be used to transform them into aromatic hydrocarbons [143]. Traditional fossil energy sources utilized as raw materials are not infinite, and the cost is considerably large. To create aromatic and N-doped compounds for chemical or other applications, economical and sustainable sources must be investigated. Biomass resources, which are primarily made up of elements like carbon, hydrogen, and oxygen, offer a lot of promise for development as carbon-neutral renewable energy sources [144,145]. The three primary components of biomass, cellulose, hemicellulose, and lignin, have varied structural qualities and hence require different conversion methods and applications. Within cellulose and hemicellulose, equipped with a five-membered or six-membered cyclic polysaccharide structure, hemicellulose acts as a molecular binder bound between the cellulose and lignin [146]. Lignin, a three dimensional reticulated aromatic ring structure wrapping and reinforcing cellulose and hemicellulose, is a kind of nature organic compound made up of interlaced C-C and C-O bonds with a complex structure [147]. The aromatic and furan rings found in direct pyrolysis products of lignin can be exploited to make biomass fuels, light aromatics, and other small-molecule compounds [148,149]. Benzene is a basic carbon frame structure of biomass, consisting of a “benzene ring” encircled by six C atoms [150]. The basic structure of almost all of the products produced by various biomass conversion processes is benzene rings [151]. As a

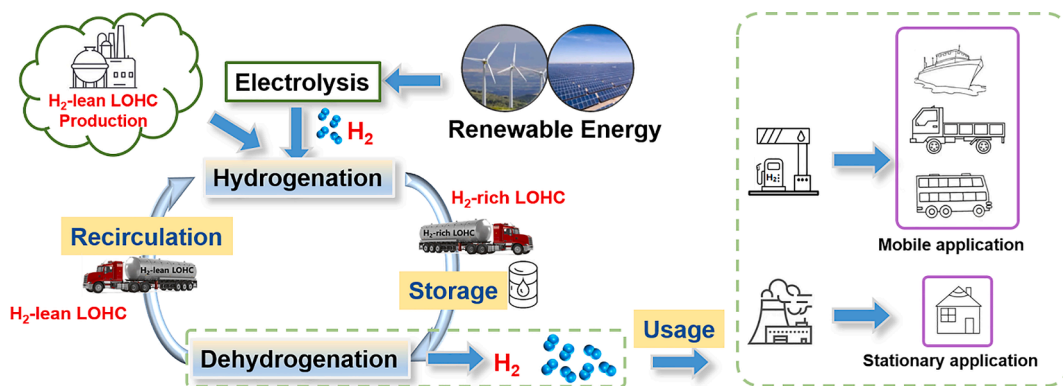


Fig. 6. Renewable energy storage using LOHCs technology [34].

result, using biomass as the source of reaction carrier in the LOHCs system has a certain amount of practicality and economic benefit.

4.1. Aromatic compounds hydrogen storage liquids from biomass

Based on the technical principles of aromatics extraction from biomass, it can be divided into direct and indirect routes for preparation. Direct preparation refers to the direct conversion of biomass into aromatic products in a reactor without further processing. This is the biomass-catalyzed thermal cracking method that is currently being explored and used the most. The conversion of biomass into intermediate products via a variety of techniques, followed by the manufacture of aromatics, is referred to as indirect preparation technology [152]. The second method has the benefit of allowing for the targeted conversion of intermediates to aromatics using existing conversion technologies with high yields and efficiency. However, the production method is lengthy, resulting in significant raw material waste and energy usage.

4.1.1. Processes for the indirect preparation of aromatics

When using intermediates in the form of syngas (CO , H_2), there are three major pathways for the preparation of aromatics: methanol/dimethyl ether, Fischer-Tropsch synthesis, and direct preparation using aromatization catalysts. Methanol-to-aromatics (MTA) technology [155–158] is one of the ways listed above that has been developed and applied in industry. The aromatic compounds were selective up to about 80% during the process, and the methanol is almost completely converted. The main products of syngas synthesis by Fischer-Tropsch are alkanes and olefins, with lesser yields of aromatics. Another technology for the direct preparation of aromatics from syngas is mainly obtained through improving the catalysts. The products can be directly converted to aromatics by selecting aromatized catalysts in the above two preparation procedures [157]. As indicated in Fig. 7, the synthesis of aromatic hydrocarbons entails various processes. First of all, through methods such as hydrolysis, hydrogenation, or fermentation of biomass, oxygenated compounds, such as sugars, aldehydes, and alcohols are

produced by the action of microorganisms. Subsequently, a series of operations including reform, dehydrogenation, and cyclization, were conducted to produce aromatics. This is attributable to the fact that the three primary components of biomass can be hydrodeoxygenated or enzymatically broken down into tiny molecules like alcohols, furans, and phenolic aldehydes. Under appropriate reaction circumstances, these molecules can be continually transformed into aromatic compounds [153]. Technologies of bioForming™ and bio-based isobutanol to aromatics, which produce aromatic compounds from 100% renewable plants and sugars, are already commercially viable in this field. Overall, the method of producing indirect aromatics from biomass is time-consuming, with additional intermediate steps in the reaction resulting in poorer product yields, higher reaction energy consumption, and feedstock waste. To put it another way, commercial applications are extremely tough to implement, necessitating further refinement and optimization.

4.1.2. Processes for the direct preparation of aromatics

Aromatic products like BTX and olefins can be synthesized from biomass feedstock (e.g., wood, agricultural products, organic solid waste, and fiber waste) via catalytic thermal cracking technology, which involves a series of complex reactions like depolymerization, isomerization, and polymerization. The products of catalytic pyrolysis of biomass include bio-oil, coke, and combustible gases. Depending on the reaction conditions, the proportion of products obtained varied. Catalytic slow pyrolysis mostly produces coke, while catalytic medium-speed pyrolysis generates combustible gas and catalytic fast pyrolysis (CFP) generates bio-oil [159–161]. The manufacture of aromatic compounds by direct catalytic pyrolysis is primarily performed through the CFP of biomass due to the high amount of aromatic products with the most basic benzene ring structure.

Owing to the different structures and types of biomass feedstock, the contents of the three main components vary accordingly. Lignin has a higher selectivity for aromatic compounds in catalytic cracking products than the other two primary components of biomass due to its high H/C

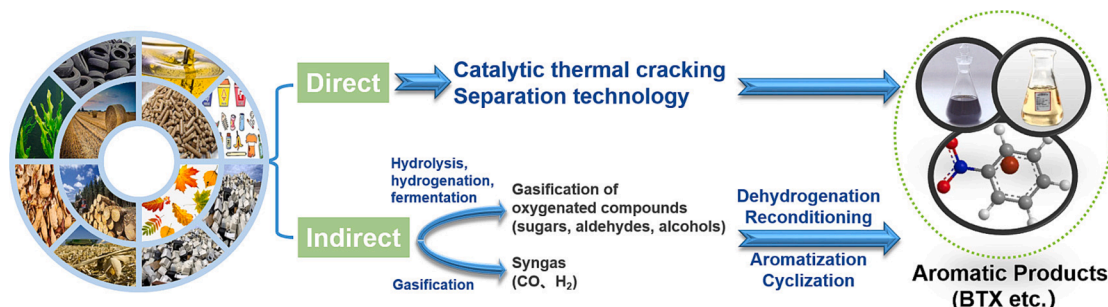


Fig. 7. Technical routes for the preparation of aromatics from biomass [153,154].

ratio. During pyrolysis, cellulose is the first to undergo bond breakdown, resulting in aromatic compounds and olefins with a high added value. As a result, biomass feedstock with high lignin and cellulose content offers a better potential for aromatic chemical production employing catalytic pyrolysis procedures [162]. It has been reported that the cellulose content of biomass feedstock affects the bio-oil content. More bio-oil can be produced with a greater cellulose ratio, which contributes to the generation of aromatics. Zhang et al. [163] chose ZSM-5 as a catalyst to evaluate the yield of CFP aromatic compounds products with varying pine-to-alcohol ratios. They discovered that the yield of aromatic compounds could be enhanced with the increase of the H/C ratio of the reactants. The conversion of organic matter to aromatic substances within the bio-oil can be facilitated by an increased amount of hydrogen. However, because the type of raw material has a considerable influence on the product, numerous studies have been conducted on model compounds or single components [164]. In addition, model compounds such as furan, furfural, and glucose are commonly employed to research pyrolysis mechanisms, products, and reaction routes. In the hydrodeoxygenation of lignin, Diao et al. [146] prepared $\text{MoCo}_9\text{S}_8/\text{Al}_2\text{O}_3$ as a catalytic material with a balance between economy and temperature stability. The easy deactivation of sulfide catalysts was focused on to achieve an efficient one-step conversion of lignin to aromatic compounds, with 99.8% conversion and 91.0% yield of benzene.

Alkali metals, alkaline earth metals, metal oxides, and molecular sieves are the most typical catalysts employed in biomass catalytic pyrolysis reactions. Molecular sieve catalysts are widely used in the field of catalytic pyrolysis of biomass to prepare aromatic compounds. Because of its unique internal aperture structure and acidic sites on the surface, ZSM-5, for example, can reduce the carbon build-up problem and promote selectivity of the target product to some extent [159]. The aperture structure, acidic sites, silica to aluminum (Si/Al) ratio, and particle size are also critical factors that affect catalytic activity. More studies on modification approaches, such as increasing metal supported [165,166], employing mesoporous catalysts [162,167], and modifying the acid-base treatment order, are needed in the future.

4.2. N-doped compounds hydrogen storage liquids from biomass

Thermal catalytic conversion and ammonification is the process of making N-doped chemicals from biomass using catalytic pyrolysis in the presence of a nitrogen donor (TCC-A). N-doped compounds include amines, nitro substituted, nitrile, and some N heterocyclic compounds with aromatic structures, such as indoles, pyridines, and pyrroles [149]. Nitrogen donors can be divided into three types: gaseous ammonia, high nitrogen biomass, and solid ammonia sources. Additionally, the ammonium salt is a nitrogen donor since it creates ammonia gas when heated. In LOHCs technology, N-heterocyclic aromatic compounds generated by heat catalysis and ammonification can be seen as hydrogen storage agents.

The indoles have a chemical structure that is similar to that of furans. Therefore, by introducing an external ammonia source, catalytic pyrolysis can be used to prepare indoles to catalyze the formation of furans from biomass. For the production of indoles, several furan derivatives such as 2-methylfuran and 2-methylfurfural can be employed as intermediates or source materials. TCC-A technology has been claimed to be capable of directly converting biomass-derived furans and furfurals to indoles for the manufacture of N-doped chemicals from biomass [168]. Xu et al. [149] experimentally discovered that TCC-A technology could transform raw biomass with complex compositions into N-doped compounds and N-containing biochar. By altering the reaction conditions, the percentage of pyridines and indoles could be selectively controlled. Yao et al. [169] exploited furfural, which is obtained from biomass, as the feedstock for thermal catalytic transformation and zeolite ammonification to convert furfural to indole compounds. Ultimately, they concluded that the conversion pathway was “furfural-furfural-imine-furan-pyrrole-indole”. Lactose, acetylation, and furan amination are the

most common processes for making pyrroles. Pyrroles prepared from biomass can be obtained by rapid *in situ* pyrolysis of cellulose under ammonia atmosphere using HZSM-5 [170–172]. In industrial settings, pyrrole is usually prepared from furans derived from petroleum under the catalysis of solid acid catalysts. Yao et al. [173] found that the catalytic fast pyrolysis of cellulose in a low-temperature ammonia atmosphere is an effective way to selectively prepare pyrroles. When the reaction temperature was controlled at 400 °C, they took $\gamma\text{-Al}_2\text{O}_3$ as the catalyst and a selectivity of up to 89.5% was achieved with a catalyst/cellulose ratio of 2. The classic method of “catalytic synthesis” was used to make pyridine compounds, and the raw material used was primarily glycerol. Pyridine tends to be synthesized by aldehydes, alcohols, and unsaturated hydrocarbons in an ammonia-rich environment. As a result, when pyridines are utilized as target products, biomass can be first converted into intermediate products such as aldehydes, ketones, and alcohols.

Therefore, by utilizing the current technologies of biomass conversion, suitable and prospective hydrogen carriers can be purposefully and selectively prepared for LOHCs technology in the future. Overall, the utilization of biomass in the synthesis of aromatic and N-heterocyclic compounds to be used as organic hydrogen storage liquids has a great prospect. However, further studies are required to create breakthroughs in terms of enhancing the stability and selectivity of the reaction.

4.3. The technical route and feasibility analysis for the preparation of biomass-based organic hydrogen storage liquids

The discrepancies between the raw biomass pyrolysis products and target carriers of the LOHCs system should be compared to directionally regulate the parameters of each process. Furthermore, according to the type of selected biomass, different catalytic reaction routes and pre-treatment modes are necessary to optimize the yield of the targeted product (Fig. 8). During the catalytic pyrolysis processes of biomass, it is important to focus on the pathways (e.g., purification and ammonification) that break bonds to form monomeric compounds for subsequent operations. On the basis of the positive or negative feedback of the reactions of biomass-based organic hydrogen storage liquids, it is necessary to adjust the conditions to optimize the characteristics within the operating range. At present, the technology for the catalytic pyrolysis of biomass for the preparation of aromatic and N-doped compounds is relatively advanced. Major studies are more likely to explore the influences of the feedstock type, reaction conditions, catalysts, and other factors. Meanwhile, the advancement of LOHCs technology has been steadily advancing, with more research currently concentrated on lowering the dehydrogenation temperature, improving catalysts, and reducing the energy consumption. In addition, certain businesses around the world have already succeeded in commercializing and trading LOHCs technology. This pattern suggests that the technology has reached a high level of maturity and usability. However, the technologies producing LOHCs have abundant disadvantages in terms of sustainability or material expense. Therefore, it is necessary to explore economic and sustainable renewable carriers. Through the review of previous researches, there are few studies on the generation of hydrogen carriers through biomass conversion technology. Combined with the reaction principles of the various LOHCs systems, biomass can be applied to LOHCs through existing methods of conversion. Future research in this field should improve the catalysts and other factors through targeted modifications to produce organic hydrogen storage liquids.

5. Summary and outlook

LOHCs technology can effectively avoid some of the shortcomings of conventional hydrogen storage technologies, which is aimed at meeting the requirements of long-term and large-scale hydrogen storage in an ambient environment. Fortunately, this technology possesses excellent

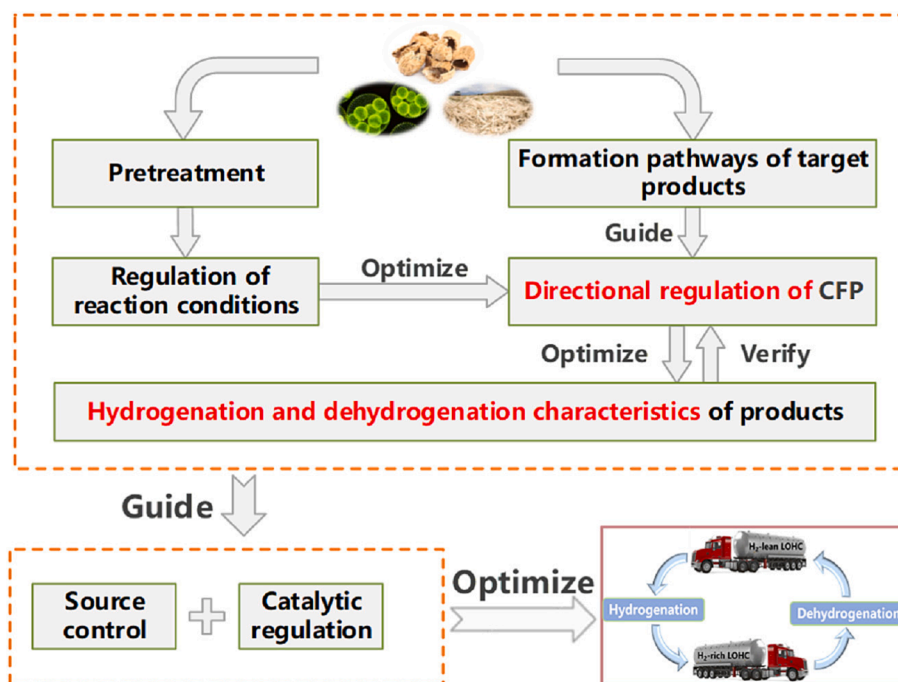


Fig. 8. Technical route for the preparation of biomass-based organic hydrogen storage liquids.

compatibility with existing equipment for oil and gas production, has tremendous development prospects, and is latent. Because of the unique feature of carbon neutrality and the structure of its basic components, biomass is widely used in the clean energy sector. The most common use of biomass is to make bio-liquid fuels with aromatics as the most basic structure, which can be prepared by a variety of depolymerization processes. The products can also be converted into other chemicals through advanced processes to realize high-value utilization. Petroleum, coal, and other raw materials are commonly used to make hydrogen storage liquids in existing LOHCs systems. However, because of the limited amount of traditional energy, newer manufacturing methods should be investigated. Based on the above review, there are still several challenges for the development LOHCs technology. (1) The temperature of dehydrogenation and the energy consumption are difficult to decrease. (2) Stable, efficient, and economic catalysts used for hydrogenation and dehydrogenation need further development. (3) The initial cost to purchase LOHCs materials is extremely high. (5) It is necessary to comprehensively consider the technical, economic, and environmental performance of the system.

Taking advantage of the fact that benzene is the fundamental unit in biomass, coupling LOHCs with technologies related to the catalytic pyrolysis of biomass is promising. Switching the orientation and research ideas is critical for biomass-based organic hydrogen storage liquids. To prepare this type of liquid according to the specific reaction equipment, appropriate technologies must be established. Therefore, there are numerous difficulties to solve in the utilization of renewable biomass-based hydrogen carriers.

- (1) According to the findings of this paper, there are numerous challenges to overcome when combining catalytic pyrolysis of biomass for the manufacture of aromatic and N-doped chemicals with LOHCs technology. Due to the coverage of active sites caused by coking, the blockage of channels, and the agglomeration of active metals, catalysts are easy to inactivate. Hence, it is necessary to prepare high-performance catalysts to ensure the directional, efficient and stable conversion of biomass pyrolysis.
- (2) Distinct components of biomass have different conversion processes. On one hand, Multifunctional catalysts should be designed

to achieve multiple conversion paths. On the other hand, to separate components without significantly affecting the structure, advanced pretreatment technology is necessary.

- (3) A few components in the products prepared by catalytic pyrolysis may not have the ability to store hydrogen, which requires to explore the technology of further separation and purification.
- (4) Most of the existing catalysts are used for LOHCs of single substance, which may not be applicable to the LOHCs prepared by catalytic pyrolysis of biomass. Therefore, it is necessary to design suitable and efficient hydrogenation and dehydrogenation catalysts according to the characteristics of the products.

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.

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