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Exploring the Viability of Green Formic Acid as H2 Carrier

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To favour the implementation of hydrogen energy, H2 carriers are regarded as a reliable alternative for hydrogen transport. Common hydrogen carriers include liquid organic compounds (as toluene, dibenzyltoluene or N-ethylcarbazole), ammonia, methanol, formic acid and chemical hydrides. These substances can release H2 upon demand through dehydrogenation or electrochemical reactions, offering a flexible way to integrate hydrogen into energy infrastructure. Among them, formic acid (HCOOH) is an attractive candidate due to its hydrogen content (4.4 wt.%) and straightforward dehydrogenation process. To explore the viability of green formic acid as H2 carrier, this work analyses all its possible production pathways from renewable energy, with a focus on the synthesis from captured CO2 as raw material. Advantages and disadvantages of this new process are presented, assessing its potential by means of the equivalent hydrogen methodology. The H2 delivery performance of formic acid, strictly related to its synthesis stage, is analyzed and then compared to other carriers (liquefied H2, ammonia, toluene, dibenzyltoluene), to discuss its practicality for industrial-scale implementation.

* 1. Introduction

While gaseous hydrogen low density and high volatility hinders its cost-effective transport, hydrogen carriers offer an attractive solution to connect green H2 production and utilization hubs (Restelli et al., 2023). These carriers are molecules, typically in liquid state at ambient temperature and pressure, in which hydrogen is chemically bonded and can be released upon need (Spatolisano and Restelli, 2024). A variety of hydrogen storage compounds have been proposed in literature: organic liquids derived from fossil feedstock, biomass-based substances or synthetic products obtained from captured CO2. The latter are of particular interest in the research panorama since they are able to conjugate CO2 utilization and H2 transport. Formic acid (HCOOH) is one of them. The physico-chemical properties of interest for its implementation as H2 carrier are listed in Table 1.

Table 1: Main physico-chemical properties of formic acid.

|  |  |  |
| --- | --- | --- |
| Property | Value | Reference |
| H2 density [gH2/L] | 53 | Gao et al., 2024 |
| Melting temperature [°C] | 8.4 | NIST Chemistry WebBook |
| Boiling temperature [°C] | 101 | American Chemical Society |
| Cost [$/ton] | 800 | chemanalyst.com |
| Dehydrogenation enthalpy [kJ/mol] | 31.2 | Patra et al., 2023 |

Formic acid, a colorless liquid with a pungent odor, is a simple carboxylic acid. It finds applications across various industries, thanks to its versatile properties: it is commonly used as a chemical precursor to produce a variety of substances, including formamide, esters and other derivatives, in turn used in the manufacture of plastics, textiles, pharmaceuticals and agrochemicals. It is a non-volatile liquid (normal boiling point around 100°C), less hazardous compared to some other hydrogen carriers like NH3, which is highly toxic, but corrosive in the concentrated form. Formic acid high H2 density allows, in principle, for an efficient storage and transport of hydrogen. As confirmed by the dehydrogenation enthalpy, it can undergo catalytic dehydrogenation at mild conditions (around 200°C), to release CO₂ and H₂. Dehydrogenation is less energy-intensive compared to other hydrogen carriers, such as NH3 or toluene, which often require more complex and energy-consuming processes.

Since CO2 is released during the dehydrogenation stage, in view of improving the carrier carbon footprint, research efforts are devoted to enable the synthesis reaction from renewable sources, such as biomass or CO₂ itself, through catalytic hydrogenation. This makes formic acid a sustainable option for hydrogen storage, unlike fossil fuel-derived hydrogen carriers. The H2 value chain with formic acid as hydrogen carrier, synthetized from captured CO2, is depicted in Figure 1.



*Figure 1: H2 value chain considering formic acid as H2 carrier. Long distance harbour-to-harbour scenario.*

Due to the straightforward nature of dehydrogenation stage, the tiebreaker of formic acid implementation at large scale is the effectiveness of the synthesis stage, which is deepened in section 1.1.

* + 1. Formic acid production

The state-of-the-art production method at industrial-scale is the well-established carbonylation of methanol, which is a two-stage process occurring via reactions (1) and (2) (Bulushev and Ross, 2018).

Reaction (1) is operated at high pressure (4 MPa), but at relatively low temperatures (80°C), with a selectivity

of 96% in the presence of a strong base (sodium methoxide). The second step is the hydrolysis of methyl formate to produce formic acid at high concentration (up to 98%) and methanol, which can be recycled back to stage (1).

|  |  |
| --- | --- |
| CH3OH + CO 🡪 HCOOCH3 | (1) |
| HCOOCH3 + H2O 🡪 HCOOH + CH3OH | (2) |

Despite the good process performance, formic acid production through methanol carbonylation is not a good choice for its implementation as H2 carrier. Since CH3OH is required as raw material, it would be more practical to consider CH3OH itself as H2 carrier, rather than HCOOH.

More sustainable approaches for HCOOH synthesis are being explored and summarized in Table 2, together with the related technology readiness level (TRL).

Table 2: Proposed formic acid production pathway and related TRL.

|  |  |  |
| --- | --- | --- |
| Production pathway | TRL | Reference |
| catalytic CO2 hydrogenation | homogeneous | 3-5 | Perez-Fortes et al., 2016 |
| heterogeneous | 3-5 | Chen et al., 2020 |
| electrochemical CO₂ reduction | 3-5 | Perez-Fortes et al., 2016 |
| biological  | 1-3 | Schwarz et al., 2022 |
| direct oxidation of biomass | 1-3 | Chen et al., 2020 |

The CO₂ hydrogenation methods can be broadly classified into homogeneous and heterogeneous catalytic processes. Álvarez et al. (2017) reviewed the state-of-the-art for the catalytic hydrogenation reaction, offering a summary of many catalytic complexes explored in literature.

As far as the homogeneous catalysis is concerned, transition metal complexes are typically used, as Rh, Ir, and Pd. Rh catalysts show high activity and good selectivity towards formic acid and typically operate at low to moderate temperatures (50–150°C) and moderate pressures (20–50 bar) with phosphine or carboxylate ligands. Similar concepts have been explored for Ir-based catalytic systems.

Pd-based catalysts, on the other hand, are known to be less effective than Ir or Rh-based: their activity and stability need improvement compared to Rh and Ir catalysts. Also, they often require higher temperatures and pressures than Rh and Ir systems.

Homogeneous catalysis can also involve bimetallic systems, where two metals (such as Rh/Ir or Rh/Pd) are combined to enhance the reactivity and selectivity for CO₂ hydrogenation. Different patents have been filed by BP and BASF. Anderson et al. (1989) proposed a process which occurs into different stages. In the first stage, CO2 reacts with H2 in the presence of a transition metal catalyst, with a high boiling solvent (e.g., polyethylene glycol, 1-phenyl-1-propanol, 3-phenyl-1-propanol, sulpholane) to produce a formate salt. Next, the catalyst is removed from the formate salt. The latter undergoes futher treatments in order to be thermally decomposed to formic acid.

Hladiy et al. (2004) patented a process comprising the following steps: a) hydrolysis of methyl formate to give a mixture of water, formic acid, methanol and excess methyl formate; b) removal of the methanol and excess methyl formate from the mixture of water, formic acid, methanol and excess methyl formate by distillation to give aqueous formic acid; c) extraction of the aqueous formic acid with at least one formic acid ester; d) separation of formic acid ester and formic acid by distillation.

The most recent invention is the one by Schaub et al. (2014), which proposed CO2 hydrogenation in the presence of a catalyst comprising an element of group 8, 9 or 10, a tertiary amine comprising at least 12 carbon atoms per molecule and a polar solvent as methanol, ethanol, propanols or butanols. Despite the promising catalytic performance, the major drawback of these homogeneous catalysts is their separation from the product, to be recycled back to the reaction stage.

As regards the heterogeneous catalysis, different alternatives have been proposed in literature. Transition and noble metals such as Ru (Park et al., 2020), Pd, Pt, Rh, Ni, Cu are commonly used (Chen et al., 2020).

However, lower selectivity is demonstrated for heterogeneous catalytic systems and complex reaction pathways are found in this case.

With reference to Table 2, other sustainable formic acid production pathways include:

* electrochemical reduction of CO₂, applying an electric current to CO₂ dissolved in an electrolyte, typically water, in the presence of a catalyst (often metals like silver, copper or tin). The reaction produces formic acid along with oxygen at the anode;
* thermochemical conversion of biomass, where lignocellulosic materials (such as wood, straw, or agricultural waste) are subjected to high temperatures in the presence of chemicals or steam. This can produce formic acid as a by-product, often as part of a broader bio-refinery process;
* microbial fermentation, that utilizes renewable biomass feedstocks like sugars (glucose or fructose) derived from agricultural waste, food scraps or algae. In this process, specific microorganisms are used to ferment these substrates into formic acid as a metabolic by-product under anaerobic conditions.

Despite these methods could seem viable at the laboratory level, they suffer from poor scalability.

The only realistic alternative for the green acid formic production, in view of its application as H2 carrier, is the catalytic hydrogenation of CO2. Although continuous homogeneous catalytic processes have been proposed at the laboratory scale, still the incomplete catalyst recovery from the reaction mixture hinders its scale-up. As for the heterogeneous catalysis, many studies in literature are focused on the tuning of the catalytic complex few of them delve into the evaluation of process aspects of CO2 hydrogenation, also discussing the separations downstream the reaction section. After a preliminary literature analysis, the work of Park et al. (2020) is assumed as the reference. The authors tested the Ru-based heterogeneous catalytic complex in a continuous fashion and proposed a process flow diagram for formic acid synthesis stage.

With reference to the work of Park et al. (2020), Figure 2 shows the block flow diagram (BFD) of the formic acid production stage.



*Figure 2: Block flow diagram (BFD) of the formic acid production stage, according to Park et al. (2020).*

CO2 and H2 are fed to the formic acid formation reactor, together with the recycled gases, water and triethylamine. In the first stage, a carbonate complex is formed which is routed to the formate formation reactor, the latter operated at very high pressure (120 bar) and moderate temperature (120°C). The liquid product undergoes evaporation to concentrate the adduct formed in the reaction stage and, then, the latter is introduced into the amine exchange column. This unit makes the separation of the strongly non ideal mixture possible by replacing triethylamine with a heavier homologue. The triethylamine is routed back to the reaction stage, while the new amine formate complex is further processed in another separation unit, which allows the recovery of formic acid as the top product.

Pressure and temperatures levels are specified in Figure 2, for each stage of the process. Considering the operating conditions of Figure 2, high energy consumptions are expected because of the low pressures but, mostly, because of the high temperatures needed in the separation downstream the reactor.

Starting from Figure 2 and in view of preliminarily exploring formic acid viability as H2 carrier, its production stage is assessed by means of equivalent hydrogen methodology, described in section 2, and then compared with others H2 carrier. In this way, opportunities and weaknesses are pointed out, to understand whether further deepening is needed or not.

* 1. Methodology

The equivalent hydrogen methodology is useful to compare and assess different hydrogen carriers based on their ability to store, transport and release hydrogen. According to this concept, the H2 delivered at the utilization hub is evaluated by equation (2).

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| --- | --- |
| $$\dot{m}\_{H\_{2,net}}=\dot{m}\_{H\_{2,in}}-\dot{m}\_{H\_{2,consumed}}$$ | (2) |

All the electric and thermal energy consumptions are expressed as equivalent H2 consumed which must be subtracted in equation (2) to account for the net H2 quantity delivered upon arrival.

The following contributions are considered in the calculation.

1. Cooling duty produced by a proper refrigeration cycle, for cooling down to temperatures lower than the ambient one (cooling above the ambient temperature is neglected in the present analysis).

The theoretical Coefficient Of Performance (COP) of the refrigeration cycle is evaluated according to equation (3), where *TH* and *TL* are the two constant temperatures, respectively, of the condenser and of the evaporator in the refrigeration cycle. The temperature of the hot reservoir is set equal to 25°C, whereas the one of the cold reservoir is determined as the temperature of the process stream to be cooled down (from simulations) minus a temperature approach of 5°C.

|  |  |
| --- | --- |
| $$COP\_{R,Carnot}=\frac{1}{\frac{T\_{H}}{T\_{L}}-1}$$ | (3) |

From the ideal *COP* of equation (3), the real *COP* can be calculated through equation (4), taking into account the rational efficiency *ηII* and the amount of hydrogen equivalent to the cooling duty *Q* can be determined according to equation (5), from the value of the efficiency of the combined cycle *ηCC*.

|  |  |
| --- | --- |
| $$COP\_{R}=COP\_{R,Carnot}⋅η\_{II}$$ | (4) |
| $$\dot{m}\_{H\_{2}}=\frac{Q}{COP\_{R}⋅η\_{CC}⋅LHV\_{H\_{2}}}$$ | (5) |

1. Mechanical work required by compressors, evaluated according to equation (6), recalling that the *COPR* represents the ratio of the provided cooling duty and the electrical energy consumed, *WEL*, by the cycle (equation (6)).

|  |  |
| --- | --- |
| $$\dot{m}\_{H\_{2}}=\frac{W\_{EL}}{η\_{CC}⋅LHV\_{H\_{2}}}$$ | (6) |

1. Heating above the ambient temperature, calculated as in equation (7), where *ηB* is the boiler efficiency.

|  |  |
| --- | --- |
| $$\dot{m}\_{H\_{2}}=\frac{Q}{η\_{B}⋅LHV\_{H\_{2}}}$$ | (7) |

This methodology provides a standardized way of comparing hydrogen carriers based on practical and efficiency metrics, not just theoretical hydrogen content. Thus, the comparison allows for conscious decision-making in selecting the most suitable hydrogen storage and transport solutions.

* 1. Results and discussion

Based on the methodology described in section 2, energy consumptions of the production stages of different H2 carriers (liquefied H2 (LH2), ammonia (NH3), toluene (TOL), DBT (dibenzyltoluene), formic acid (FA)) are accounted for. The same H2 flow rate is considered for the synthesis of all these species, equal to 20000 Nm3/h, to take into account the land footprint of solar panels.

As regards ammonia, toluene, dibenzyltoluene and liquefied hydrogen, their detailed technical (Pellegrini et al., 2024) and economic assessment (Spatolisano et al., 2024) has been already published elsewhere and is not detailed in this work. For formic acid, the catalytic production process of Figure 2 is assumed. Energy consumptions have been evaluated from Park et al. (2020) and referred to the considered H2 capacity.



*Figure 3: Energy consumptions in terms of equivalent H2 for the production stage of different H2 carriers: liquefied H2 (LH2), ammonia (NH3), toluene (TOL), dibenzyltoluene (DBT), formic acid (FA).*

As can be observed in Figure 3, formic acid production stage is very energy intensive with respect to the other carriers, consuming even more H2 than the one needed by gaseous hydrogen liquefaction. Indeed, the production stage of Figure 2 is quite complex: it involves a huge quantity of amine diluted in water which act as the reaction medium. This amine undergoes a reactive distillation, in which it is substituted by a heavier homologue to enable the product separation. Also, the system is strongly non ideal: a heterogeneous ternary azeotrope is present, formed by water, formic acid complex and amine.

Liquefied H2 (LH2), ammonia (NH3), toluene (TOL) and dibenzyltoluene (DBT) only require electric energy for their production stage. On the other hand, formic acid needs a huge amount of heat for the separation downstream the reaction section to occur. This is another drawback of the analyzed production stage, as heating by a hot utility as stream is associated with indirect CO2 emissions release.

Due to the energy-intensive reaction and separation stages, green formic acid production of Figure 2 is far from the industrialization target.

* 1. Conclusions

This work discusses the potential of formic acid (FA) as green H2 carrier, focusing on its production stage from CO2 and H2 . Referring to the studies reported in literature, FA catalytic synthesis is analysed by means of the equivalent hydrogen methodology described in section 2. Due to the low maturity of the synthesis stage from CO2, as well as the lack of effective heterogeneous catalysts, formic acid is proved to be an unrealistic alternative for hydrogen transport.

Research efforts should be devoted to the identification of more active and selective catalysts, also considering the process design aspect. In the present case study, despite the good catalytic performances, product separation from the reaction medium is not straightforward and calls for energy-intensive unit operations.

In addition, it must be pointed out that the HCOOH melting point is not very low (around 8°C). This is a practical drawback for its implementation as H2 carrier on a large scale: during winter, it must be stored in heated vessels to hinder solid deposits formation.

By the way, green formic acid production, in view of its application as a chemical rather than energy vector, also from methanol, still could be an interesting topic to focus on.

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