

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
H ₂ density [g _{H2} /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, synthesized from captured CO₂, is depicted in Figure 1.

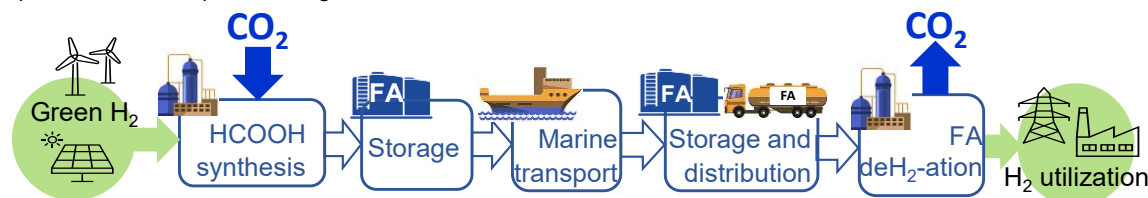


Figure 1: H₂ value chain considering formic acid as H₂ carrier. Long distance harbour-to-harbour scenario.

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.

1.1 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).



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 CO ₂ hydrogenation	homogeneous	3-5	Perez-Fortes et al., 2016
	heterogeneous	3-5	Chen et al., 2020
electrochemical CO ₂ 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 further 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.

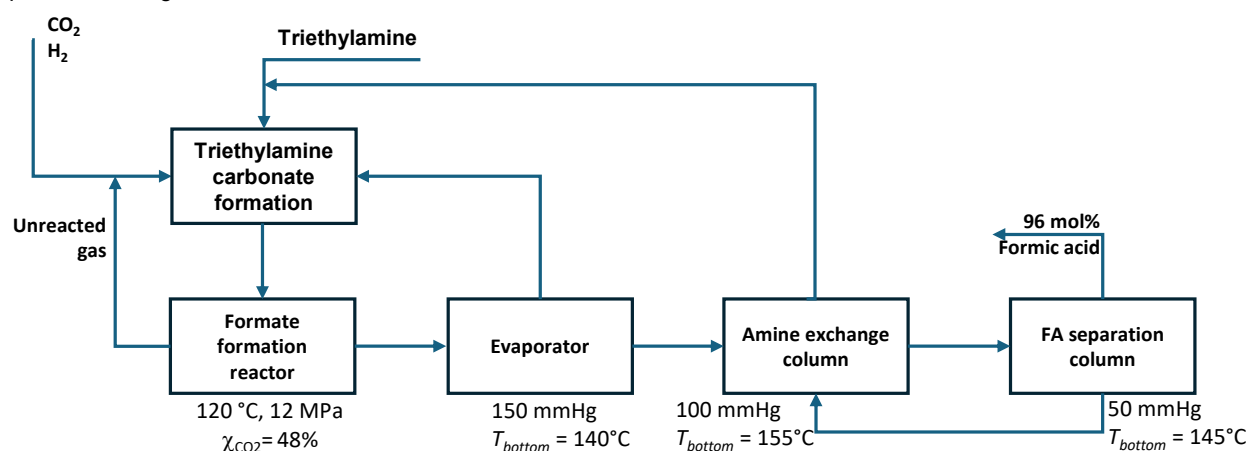


Figure 2: Block flow diagram (BFD) of the formic acid production stage, according to Park et al. (2020).

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.

2. 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).

$$\dot{m}_{H_2,net} = \dot{m}_{H_2,in} - \dot{m}_{H_2,consumed} \quad (2)$$

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 T_H and T_L 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.

$$COP_{R,Carnot} = \frac{1}{\frac{T_H}{T_L} - 1} \quad (3)$$

From the ideal COP of equation (3), the real COP can be calculated through equation (4), taking into account the rational efficiency η_{II} 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 η_{CC} .

$$COP_R = COP_{R,Carnot} \cdot \eta_{II} \quad (4)$$

$$\dot{m}_{H_2} = \frac{Q}{COP_R \cdot \eta_{CC} \cdot LHV_{H_2}} \quad (5)$$

2. Mechanical work required by compressors, evaluated according to equation (6), recalling that the COP_R represents the ratio of the provided cooling duty and the electrical energy consumed, W_{EL} , by the cycle (equation (6)).

$$\dot{m}_{H_2} = \frac{W_{EL}}{\eta_{CC} \cdot LHV_{H_2}} \quad (6)$$

3. Heating above the ambient temperature, calculated as in equation (7), where η_B is the boiler efficiency.

$$\dot{m}_{H_2} = \frac{Q}{\eta_B \cdot LHV_{H_2}} \quad (7)$$

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.

3. 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.

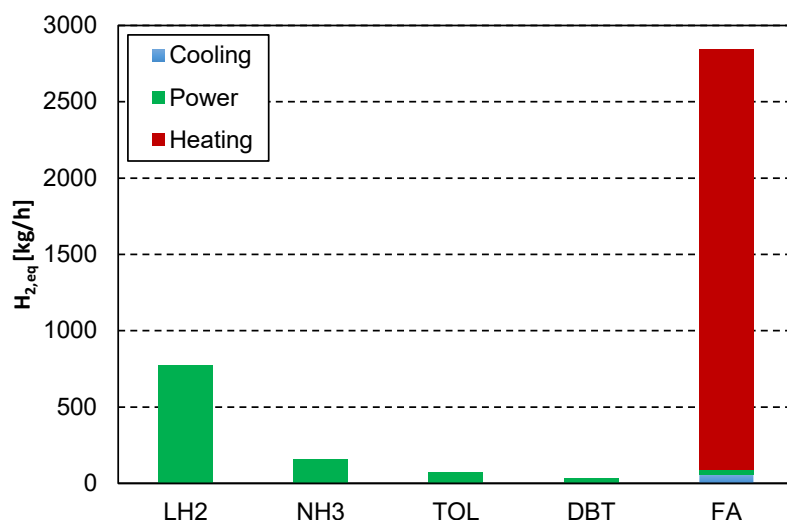


Figure 3: Energy consumptions in terms of equivalent H₂ for the production stage of different H₂ carriers: liquefied H₂ (LH₂), ammonia (NH₃), toluene (TOL), dibenzyltoluene (DBT), formic acid (FA).

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.

4. 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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