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An overview on sustainable hydrogen supply chain using the carbon dioxide utilization system of formic acid

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ABSTRACT
The high hydrogen generation capacity is a safe and non-toxic substance that has made the formic acid a perfect hydrogen carrier candidate. This promising future caused substantial investments in formic acid production during the last decades. One of the essential developing methods is the chemical reduction methods in which the recent developments in the catalysts is the selective hydrogen production from acidic substances such as formic acid. These critical developments and characteristics of the formic acid and hydrogen fuel highlight the future of the formic acid in the transportation and fuel cell energy systems. In this research study, the future and the potential of the formic acid for the hydrogen generation was studied in terms of the full scale sustainable and green supply chain.

Introduction

Nowadays, climate change has become one of the main concerns in international scale, leading to development of carbon emission reduction techniques in all industrial and residential sectors. Fossil fuels have shown to contribute significantly to green house gas emissions (GHGE). For instance, among all oil and gas suppliers, Iran is the world’s seventh-largest dirty industry in 2017 [1]; however, more than 93% of Iran’s electricity is generated by gas-fired power plants. Although natural gas contains the least GHGE among fossil fuel portfolios, there is still great potential for GHGE recording to the country, equivalent to the capacity of more than 600 million tons of CO₂ in the country [2].

Figure 1 demonstrates the trend of the Iranian GHGE trend throughout the past decades [3]. In parallel, the diagram in Figure 2 illustrates the critical role of Power (31.3%) and industrial (24.1%) sectors in this rapid incremental trend [4, 5]. The residential (23.4%) and transportation sectors (21.2%) are the following contaminant sectors of the society, respectively. Due to the scattered nature of emission in residential and transport sections, and appropriate CO₂-capturing procedure like direct air capture (DAC) is costly and difficult, against to power and industry section which can
be easily used. The recoverable capacity of CO$_2$ in Iran is estimated at 55.4% of the total carbon emissions [6, 7].

Numerous carbon capture technologies (CCTs) have been reviewed by Mattison et al. indicating that most of them (CCTs) consume a tremendous amount of energy during the process. Adanez et al.

**Figure 1.** Iran CO$_2$ emissions by year (tons)

**Figure 2.** CO$_2$ emissions by sector in 2016 [2]
introduce a novel chemical looping combustion method (CLC), which is conducted mostly on gaseous fuels and reduces energy consumption considerably [8–10]. Cormos and Cristian Cormos evaluated various carbon capture processes implemented in the industries and power plants. In some cases, they have proposed the synthesis of formic acid from the mix of carbon dioxide and hydrogen as a promising candidate. They have developed a kinetic and thermodynamic limitation of synthesis reaction through the analysis of air, steam, and gas reactors. The process results revealed that, the CLC method has the potential to have the efficiency more than 90% CO\textsubscript{2} for the capture, which includes the post-processing, involving the treatment of the flue gas. The flue gas consists of nitrogen (about 78%), water vapor, and carbon dioxide, which the concentration depends on the type of fuel applied during the combustion process. Other contaminants in flue gas such as mercury, heavy metals, sulfur oxides (SO\textsubscript{x}), nitrogen oxides (NO\textsubscript{x}), and particulate matter being removed in the stack to meet the combustion standards [11]. The main problem and limitation of the carbon capture process is the low pressure of the flue gas in the stacks and post-combustion stages, as well as the considerable flow rate of the flue gas that makes the process more challenging [12]. The carbon concentration in the flue gas is 4% in the bryton cycle, 15% for coal-fired cycles, and 20-30% in the cement and steel production units [13].

The chemical absorption of CO\textsubscript{2} in an aqueous solution of amine-based organic such as, mono- or diethanolamine (MEA, DEA), is typical [13, 14] where the efficiency of this process is 85-90%, and the amine solvent highly defines its cost. Another proposed method for CO\textsubscript{2} capturing with the high efficiency of the carbon recovery (90%); however, still on the pilot-scale, is separation with membrane technology. Merkel et al. using the MTR membrane polaris (permeance 1000 GPU, CO\textsubscript{2}/N\textsubscript{2} selectivity a=50), and in their studies, they have found an optimal option (two-step counterflow/sweep membrane process). Against the amine-based solution, the process costs about 60 $/ton, the membrane process cast less than 20 $/ton, which presents a very prominent future for the membrane two-stage process in the carbon capture industry [15, 16]. Furthermore, recent researches stated that, capturing 90% of the CO\textsubscript{2} from the coal-fired system’s flue gas (containing 12-14% of CO\textsubscript{2}) is about 3.5% of the energy input of the system. However, the best commercial option increases this penalty to over 16%. The most prominent semi-industrial technology reduces this penalty to 6% and overall CO\textsubscript{2} capture cost to the 20 $/ton. This cost per ton of CO\textsubscript{2} capture is stated as the possible point of the CO\textsubscript{2} captured technologies. However, this possible point is highly dependent on the environmental restrictions, regulations, and policies implemented by the governments and international policymakers [17].

On the other hand, conventional methods to produce the hydrogen rely on the use of fossil fuels and electricity, which is not desirable due to the considerable quantity of carbon emission. Steam
methane reforming (SMR) is one of the most traditional hydrogen production methods. This method requires a large amount of heat due to its endothermic nature [18]. Coal gasification (CG) is also another traditional method of hydrogen production that is more complicated compared to the SMR. The CG process has lower feedback costs compared to the SMR, while its capital cost is higher instead [19]. In this method, the coal converted through steam/oxygen gasification or oxidation at a very high temperature and pressure to CO₂-rich syngas, which is containing hydrogen contents enhanced during the water-gas shift (WGS) reaction. The overall hydrogen production costs are 750 $/ton and 920 $/ton for the SMR and CG processes, respectively [20, 21].

One alternative suitable method for the large scale hydrogen production is the alkaline water electrolysis (WE). Compared to the other two above-stated processes, the cost of this process is higher due to applied materials, for instance catalyst. Its catalyst used as an electrode for the required purification of the water before the electrolysis and due to the price of the electricity. The commercially available systems produce hydrogen around 2000-3000 $/ton at a 0.05-0.06 $/kWh electricity price. In this case, the electricity can be easily provided by the solar photovoltaic systems (PV) to reduce the electricity generation emissions out of the table. There are many other alternative methods such as polymer electrolyte membranes (PEM), solid oxide electrolyzer (SOEC), and the carbon assisted water electrolysis (CAWE), which at the moment are not in the financial status [22].

To reduce the environmental impact of modern societies and limit the limitations of fossil resources, the projected increase in global energy demand must be accompanied by the implementation of carbon-neutral and energy production systems [23]. The most important and most essential candidates for such technologies are renewable or energy fuels for nuclear power plants, solar, wind power, and power plants. Although competition with food production and CO₂ imbalances is uncertain, the global replacement of fossil fuels with biofuels seems unlikely [24], the law and the industry are slowly pressing for the generation of renewable electricity [25]. The current electricity grid makes this technology attractive as initial investment in infrastructure is moderate, and market entry is low. However, electrifying the transportation sector faces severe challenges as electricity storage requires large batteries, which have low gravity and bulk density for the foreseeable future (Figure 1). Hydrogen (H₂) is a promising alternative to intermediate the energy storage. It is expected to play an essential role in the new energy system as a transporter of fuel and secondary energy [8–13]. H₂ has a high gravitational energy density of 34 kWh and can be converted to an internal combustion engine or fuel cell by producing water as the sole by-product. However, it is anticipated that the hydrogen economy will not be realized unless significant advances in technology are made in H₂ production, storage, and delivery systems [13]. In particular, creating a safe and efficient system for storing hydrogen is a significant challenge. Conventional H₂ storage in
high pressure compressed gas cylinders or cryogenic liquid tanks is pure but suffers from excessive energy losses (H₂ compression, liquefaction, and welding) and low volume energy capacity [14, 15]. The art of storing hydrogen on a base plate (700 bar) weighs 6%, which translates into the energy of 2 kWh and 1.5 kWh/L [16]. Alternative approaches through the physical absorption of H₂ in high-level materials such as, organometallic frameworks, zeolites, and nanostructured carbon materials, limit the range of temperature and pressure and generally provide less heat and volumetric energy. Bring they find density [17–19], while chemical hydrides (CH) can carry a high H₂ gravitational capacity of up to 22.3% by weight, and they prohibit weak reversibility factors.

FA is compatible with other reversible hydrogen storage options (data for Toyota Mirai 15 and BMW 5 GT36 taken from company publications). Dashed lines indicate DOE 2010 targets.

The FA compares well with hydrogen or a medium internal combustion vehicle (ICV) (engine power: 100 kW; range: 600 km). Recent advances in commercial fuel cell technology have led to significant weight loss trains, with 15 H₂-powered H₂ FCVs competing with ICVs for overall weight. While consuming H₂ only eliminates minor mass loss, it releases FA CO₂, and so the power train's energy density is more than an H₂ FCV and even an ICV to fill the medium and low fuel tank.

Carbon dioxide utilization (CDU) considers CO₂ as raw material to synthesize carbon-based marketable products. Among them, formic acid (HCOOH, synthesized from CO₂+H₂) is considered as an efficient H₂ carrier that improves H₂ storage as a non-toxic, liquid, and easy-to-store chemical. Hosseinpour et al. [26] worked on developing a reversible and fully renewable thermochemical process of formic acid synthesis. In turn, decomposition of formic acid (HCOOH ↔ CO₂ + H₂) provides the needed H₂ to power the fuel cell operation (electricity generation) or directly applied in the heavy oil upgrading process [25]. Thus, the process first transforms H₂ into formic acid to restore H₂ in a liquid form whenever it is needed, making the CO₂ again available to be reused or directly used in the petrochemical refineries [27].

Unlike other carbon dioxides conversion methods, such as electrolysis and photoelectrochemical processes, it involves converting energy for production, heat to chemical energy. It is used that raising the temperature to 1100 °C, which improves the efficiency of these processes in chemical heat treatment; fuel is produced by chemical heat through two steps. In these steps, the heat loss of metal oxides is produced at high temperatures, followed by re-oxidation, reduced metal oxides by CO₂ or water to produced CO or H₂ [28]. In this process, the time required for the production of O₂ and monoxide is relatively slow. It is increasing the temperature in the heat transfer pathways for the thermochemical production of the synthesized gas from water and CO₂. This reaction results in improved heat transfer action, which ultimately increases the efficiency of these CDU processes. Thus it can be converted into liquid fuels or used for the chemical synthesis [29].
\[ MO_{2-\delta L} \rightarrow MO_{2-\delta H} + 1/2(\delta_{H} - \delta_{L})O_2 \]  
(Eq. 1)

\[ MO_{2-\delta H} + (\delta_{H} - \delta_{L})H_2O \rightarrow MO_{2-\delta L} + (\delta_{H} - \delta_{L})H_2 \]

If reacted instead of \( H_2O, CO_2 \)

\[ CO_2 \rightarrow CO + 1/2O_2 \]

Another method is photocatalytic technology. Photocatalytic conversion for the use of semiconductors at the presence of light is also known as artificial photosynthesis [30]. Since the \( CO_2 \) hydrogenation requires high temperatures and pressures. Therefore, the photoelectrochemical and photocatalytic conversion methods are important due to the use of sunlight as a low-energy-available energy source. Photocatalytic conversion involves a combination of photophysical and photochemical processes. Photocatalytic degradation exhibits high potential carbon dioxide utilization efficiency. In this process, some key factors, including the disproportion between semiconductor absorption capacity, light spectral power, lack of reduced \( CO_2 \) solubility in water, and competitive water molecule reduction reaction limits the efficiency of these processes [31].

The basic processes in this method are divided into three stages including, charge carrier generation, photon absorption with appropriate energy, charge carrier separation and their transfer, and finally, chemical reactions between the surface species and charge carrier [32]. For evaluating the \( CO_2 \) reduction process, it is important to consider possible reactions after the absorption of photons with equal or greater energies than the bandgap at the catalyst surface [33]. The excitation of the crack band results in formation of the conductive electrons and valence cavities, which act as sites for oxidation and reduction of light, respectively. The cavities of the valence band are followed by hydroxyl radicals that produce oxygen and produce \( H^+ \) ions by the electrons of the hydrogen conduction band [33, 34]. This formula is as follows:

\[ TiO_2 + h\nu(\text{UV}) \rightarrow TiO_2(e_{cb}^- + h_{cb}^+) \]  
(Eq. 2)

\[ TiO_2 (h_{cb}^+) + H_2O \rightarrow TiO_2 + H^+ + ^0OH \]

\[ TiO_2 (e_{cb}^-) + O_2 \rightarrow TiO_2 + O_2^- \]

\[ HCO_3^- + 2e_{cb}^- + 2H^+ \rightarrow HCO_2^- + H_2O \]

\[ HCO_3^- + ^0OH \rightarrow ^0CO_3^- + H_2O \]
For this method, we should use a catalyst for the photocatalyst scenario and use enzyme and methyl viologen for the bioelectrochemical method. The catalyst can be used, such as, GaP, ZnO, TiO$_2$, CdS, and WO$_3$ [35].

The other method is the hydrolysis of formamides. At this stage of methanol, carbonylation, to purify the feed, the CO gas passes through the V-101, and V-102 adsorbent bed and the moisture in it is fully absorbed, then increased to 65 atmospheric pressure by the K-101 compressor. Furthermore, it transferred to the R-101 carbonylation stirred reactor [22]. The methanol feed is then mixed with the sodium catalyst along with the return methanol stream and sent to the reactor. This return current is cooled by the E-103 converter. The reactor output stream contains compounds such as methyl formate, methanol, and carbon monoxide that are sent to the C-101 distillation column to separate the methyl formate product.

It should be noted that, the return stream from the methyl formate hydrolysis section is also sent to the tower. Operating pressure is atmospheric tower and exits from the top of the tower with light methyl formate and co compounds and after cooling in two steps by E-104 and E-105 partial converter and condenser carbon monoxide gas is sent to the atmosphere and part of the methyl liquid (Fu, 2018). The formats are returned in the form of a reflux flow at a specified ratio to the tower. Then the remainder is transferred to the next step. The liquid methanol with the catalyst is removed from the bottom of the tower and then returned to the carbonylation reactor. Its formula is as follows [17].

$$\text{CH}_3\text{OH} + \text{CO} \leftrightarrow \text{HCOOCH}_3$$  \hspace{1cm} (Eq. 3)

The hydrolysis of the methyl formate method is one of the main processes in the hydrolysis of formamides technology. The methyl formate will exit from the top of the tower after being warmed in the E-201 converter with the return water flow from the process into the R-202 hydrolysis reactor. The liquid effluent from the reactor consists mainly of formic acid, methyl formate, and water, which is sent to the C-201 distillation tower to purify the product [15].

Operating pressure is atmospheric in the light compounds tower such as methyl formate. In this process, the wet methanol is removed from the top of the tower, and after passing the E-203 condenser, part of it is returned to the column by reflux flow and the remainder sent to the C-202 dryer column [19]. Its formula is as follows:

$$\text{HCOOCH}_3 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{CH}_3\text{OH}$$  \hspace{1cm} (Eq. 4)
Furthermore, one of the other leading technologies is the chemical electrical electrolyze method, which is discussed in further sections [18]. In this work, the electrochemical methods are being implemented for the system analysis. Considering the literature review of the previous studies in carbon capture, green hydrogen production, and formic acid synthesis, the dynamic formic acid synthesizes never studied in the previous researches. Jin et al. evaluated the flow modeling in a review article; in this research, all recent papers and researches in this field are being studied. But no dynamic model nor a capture-electrolyze-synthesis simulation never conducted for the power plants or the steel or cement factories in the previous papers. Xu et al. studied a chemical looping combustion approach of the formic acid synthesis over a coal-fired power generating system using a bulk model for simulation. Nandakumar et al. studied formic acid synthesis using a two-step CO₂ hydrogenation inflow. Although previous studies considered energy and thermochemical performance quality of the carbon utilization electrochemical process; however, neither considered the process as a dynamic supply chain [27].

This study aimed at conducting a comprehensive performance analysis with a unique approach to the dynamic hydrogen supply chain by the use of FA renewable production, which is called solar fuel for the fossil fuels synthesized using the CDU and PV energy sources [28].

A general assessment of FA. The high gravitational capacity of FA has been recognized, and its potential application as a secondary fuel in direct FA fuel cells (DFAFC) has been suggested and explored [35]. While, early models suffered from the poor performance of platinum catalysts, palladium could achieve better performance [33]. The commercial feasibility of the DFAFC technology with investment of an industrial sector (Tekion and Motorola in collaboration with BASF) for the design and manufacture of power packs was investigated [20]. Probably, since the issue of catalyst poisoning, in the long run, could not be resolved, there was no further update on these advancements, and Tekion’s approaches were used by Neah power cooperations by 2013 [12].

While DFAFCs are facing significant challenges, fuel cells are a mature technology, commercializing in fuel cell vehicles (FCVs) with more than 140 kW and a range of more than 590 km (Toyota Mirai, Hyundai Tucson, Honda Clarity). Therefore, the selective synthesis of H₂ from FA to hydrogen fuel cells using a promising approach with a short path to the market. As with conventional fuel, energy depletion means consuming FA, which results in significant CO₂ release. In combination with light electric motors and fuel cells, an FA-based power plant train can achieve more energy-to-mass than current combustion engines with fossil fuels (Figure 3). Besides, costs related to the construction and maintenance of distribution infrastructure constitute a significant obstacle to large-scale consumer applications of H₂ gases. As the FA is a non-toxic, environmentally benign
liquid and has low flammability under ambient conditions, the existing gasoline infrastructure may be easily adapted for FA distribution [10].

The central gap of the literature reviewed in this research study is that the recent papers are all experimental or theoretical modelings, and applicable references are rare in this field. Moreover, previous studies evaluated the design and operational modeling of synthesis units and plants, not the entire supply chain modeling for hydrogen using the FA as the hydrogen carrier. This work aimed to develop the sustainable hydrogen (green) energy supply chain for the fuel cells or other kinds of hydrogen-demand points (Figure 3).

![Figure 3. The schematics of the FA carbon utilization system](image)

**Experimental**

Considering catalytic systems. Optimal catalyst properties. An FA catalytic converter system, which produces a fuel cell in a vehicle at a hydrogen power plant, introduces certain requirements that must be considered during catalyst development. The main factors (1) are the choice for H₂ production, (2) the catalytic activity of the catalyst, which uses the frequency of the catalyst rotation (TOF) at the specific reaction temperature, (3) the durability or longevity of the catalyst, commonly known as the catalyst. Turnover number (TON) S), and (4) catalyst costs. Economic considerations
for consumer access to new technology are of particular importance. Selected for H₂ production. Because FA mediates the WGS response, FA damage can occur in two low-consumption enthalpy pathways in the absence of a suitable catalyst (Figure 4). Dehydrogenation (decarboxylation), extracting H₂ and CO₂ (ΔG° = −32.9 kJ/mol⁻¹, ΔH° = 31.2 kJ/mol⁻¹, and ΔS° = 216 J/mol⁻¹/K⁻¹).

1) dehydration (decarbonylation), given H₂O and CO (ΔG° = −12.4 kJ/mol⁻¹, ΔH° = 29.2 kJ/mol⁻¹, and ΔS° = 139, J/mol⁻¹/K⁻¹).

When FA acts as a chemical carrier of hydrogen, any production process must be suppressed as the CO formation not only reduces the overall performance of H₂ but also leads to fuel cell catalyst poisoning. CO poisoning of platinum catalyst in a proton exchange membrane fuel cell (PEMFC) is one of the severe obstacles in the construction of commercial fuel cells with a typical critical CO concentration of >10 ppm [19, 20]. Therefore, any suitable sewage disposal catalyst should provide a choice of dehydrogenation/dehydration 105, assuming that the cortin C diet is as high as ΔG high=34.7 kJ at 90 °C. So, cantilever catalysts, which include reducing the metal species [21] to encourage decarbonization and strong acidic components for dehydration [22], are therefore not desirable. The heterogeneous metal nanoparticle catalyst offers very few options and typically produces more than 1000 ppm of hydrogen at a significant CO [10]. Alloy nanoparticles [23] may show improved hydrogen selection. However, they do not meet the target selection [24] provided by homogeneous counterparts to recent advances [25]. Therefore, a high level of control over the body’s dehydration pathway makes homogeneous catalysts currently more suitable for use. From an engineering point of view, a homogeneous converter system requires nothing; however, a small reactor, where the FA is pumped at the speed at which it is used, while the catalyst dissolved in the reactor remains. Such a system can quickly regulate the hydrogen production, meeting the needs of transportation programs. As the evolved gas is made up of hydrogen and carbon dioxide with a molar ratio of 1:1, it may be necessary to separate the two gas membranes to prevent CO₂ from accumulating on the anode and achieve high energy efficiency of the catalyst activity. The maximum fuel cell output power directly determines the amount of the H₂ evolution catalyst required in the FA converter. Assuming the energy efficiency of the high fuel cell (58%) at the maximum power, the hydrogen fuel cell consumes r_{FC}(H₂)=0.713 mmol/(s/kW)⁻¹. Since there is no tank on H₂ gases in an FCV equipped with FAV, the converter must be able to maintain this hydrogen flow. According to the design coefficient of the sample RF=200%, the amount of catalyst required can be used (Figure 5).

\[
n_{cat} = \frac{r(H)RF}{TOF_{cat}} = 1.43 \frac{mmol}{kW \ TOF_{cat}} \cdot [s^{-1}]
\]
Accordingly, the lowest value of the catalyst in the converter is the interaction of the catalyst with the specified operating temperature. The stability of the applied catalyst directly determines the driving distance of the catalyst loading and, thus, the service intervals. The driving distance is directly accessible by the TON value, and the catalyst, which is accepted to be demolished until loss of performance is observed. Therefore, the length of a service interval of the FA converter catalyst from Equation 2.

**Figure 4.** Formic acid volumetric capacity of being a hydrogen carrier

**Figure 5.** The energy density of power train vs. tank filing status
\[ d_{\text{service}} = \frac{\text{TONcat}}{\text{TOFcat}} \cdot \frac{n_{\text{cat}}}{n_{H_2}} \left( \frac{\text{mmol}}{\text{kW-km}} \right) \] (2)

The minimum amount of catalyst in the converter is counterbalanced with the TOF catalyst (Equation 1), and therefore the service intervals depend on the TON/TOF ratio.

\[ d_{\text{service}} = \frac{\text{TONcat}}{\text{TOFcat}} \cdot \left( r_F C(H_2) \cdot (R_F - 100\%) \right) \] (3)

For the average molar hydrogen consumption of \( n_{H_2} = 36 \text{ mmol/(kW-km)} \) and the assumptions stated above, the service intervals are directly proportional to the TON/TOF ratio: (Equation 4).

\[ d_{\text{service}} = 0.2 \text{ km/s} \cdot \frac{\text{TON}}{\text{TOF}} \left[ \text{s}^{-1} \right] \] (4)

Stability against water and acid. Since FA contains water from commercial sources, a homogeneous catalyst in the market must perform well at the presence of water.

To eliminate the problems associated with the disappearance of a volatile organic solvent and additives such as amines in the hydrogen production process, the reaction in an aqueous mixture is desirable. Therefore, catalysts that can perform well in aqueous solutions are predicted to play an essential role in the early stages of development [19–26]. A catalyst that demonstrates reasonable stability and activity at high concentrations or appropriate FA in the absence of a primary promoter is a crucial opportunity. This not only features the full volumetric density of 53 hydrogen-phosphorous 53 grH\textsubscript{2}/L, but can also trigger the direct high-pressure production of H\textsubscript{2} from FA under acidic conditions. Due to the fact that, the conversion of FA to H\textsubscript{2} and CO\textsubscript{2} is an equilibrium, the highest theoretical pressures of H\textsubscript{2} and CO\textsubscript{2} that can be obtained are estimated to be 225 megapascals (2,250 times) more than the washed FA. A remarkable system has recently been implemented to produce continuous high pressure (>120 MPa) from FA using an iridium catalyst at 80 °C [27]. This is a significant improvement as it can open up more opportunities for increased H\textsubscript{2} use of High pressure, even at the H\textsubscript{2} service station. Existing technology to supply high-pressure H\textsubscript{2} power supplies for FCV is costly, primarily due to the need for widespread use of mechanical and power hydrogen compressors in connection with H\textsubscript{2} compression, lubrication, and welding processes [9, 10]. Although FA has several advantages as a hydrogen carrier, the adoption of new technologies for consumption purposes is usually very sensitive to prices. The infrastructure costs for adding FA tanks and pumps to conventional service stations should be relatively low, which would facilitate the launch of the FA distribution network. However, a significant factor in the initial investment and operating costs of a proposed power plant will be compared to other options. As seen in Figure 6, FA market prices are
approximately 400-650 USD/kg, according to the H\textsubscript{2} selling price at the US hydrogen stations. Prices below 300 $/ton of the FA is comparable to the price of gasoline in the United States of 190 $/barrel at a DOE target price of 4 $/kg H\textsubscript{2}. An increase in the scale of the world's current production capacity (8*10\textsuperscript{5} ton/year) to the required amount of factor 10\textsuperscript{4} can be expected to lead to a sharp decrease in production costs. While evaluating the fuel ratio of a vehicle's operating costs is relatively clear, a comparison of catalyst economy requires more detailed analysis. Since catalysts are generally identified by their TON and TOF, we use these two parameters without normalizing the critical dimension to normalize the cost of the catalyst. This approach must be applied to each catalyst. However, the price of a standard catalyst to TON (CON) or the cost of a catalyst normalized to average values (TOF) of a catalyst is always a particular process. CON (Equation 5) describes the share of the catalyst in operating costs. CON is part of the cost of fuel that can be attributed to the catalyst. The COF (Figure 8) demonstrates the share of the system in the cost (capital) expenditure of the system due to the catalyst.

\[
\text{CON} = \frac{P_{\text{cat}}}{TON} \cdot K_{\text{prod}} \tag{5}
\]

\[
\text{with } K_{\text{prod}} = \frac{(P_{\text{prod}}^{-1})M_{\text{cat}}}{M_{\text{prod}}}
\]

\[
\text{COF} = \frac{C_{\text{cat}}}{TOF} \cdot K_{s} \tag{6}
\]

\[
\text{with } K_{s} = \frac{TFC(H_{2})}{C_{s}} \cdot \frac{M_{\text{cat}}}{M_{\text{prod}}}
\]

Therefore, if the H\textsubscript{2} product price targets \((P_{\text{prod}}^{o})\) and the system cost target of the \(C_{s}^{o}\) process are known, the CON and COF values allow the economic evaluation of different catalyst systems. As demonstrated in Figure 7, the defined thresholds for a product (in this case hydrogen) and the entire reactor system (tank, converter, controller) allow economic comparison with existing technologies. For each process, there is an area in the CON/COF diagram that meets the cost of the catalyst meeting the relevant cost threshold criteria. Catalysts with higher CON or COF values result in higher prices than the targeted product (CON>CON\textsubscript{b}) or system cost (COF>COF\textsubscript{b}). So, the green space in the graph represents the target for catalysts that meet all the defined criteria such as FAV/FCV competing with hydrogen fuel prices.
Figure 6. Comparison of the prices of hydrogen, FA, [17] and gasoline has been normalized to the energy available for "energy wheels," which takes into account the different tank-to-wheel efficiency [23].

Figure 7. According to Equations 5 and 6, the price of the catalyst is generally normalized to TON (CON), and the cost of the catalyst normalized to TOF (COF) numbers represents the deficit that the catalyst price contributes to the target product price (CON) or capital. System Costs (COF). Products: Price of all raw materials; CS, empty: Catalyst-free system costs (here fuel tank, pumps, FA converter, and controller) [22].
Results and Discussion

In this work, eight homogeneous catalyst systems evaluated from which TOFs and significant amounts were reported (Table 1). In system 1, the addition of 6 equivs of 1,2-bis(diphenylphosphino)-ethane (DPPE) in N,N-dimethylhexylamine (HexNMe₂) effectively reduced the TOF and TON of Ru catalysts compared to those of 5HCO₂H 4HexNMe₂ at ambient temperature. Ru₂ cation system lives for several million cycles in HCOOH/HCOONa aqueous solution systems [28, 29]. However, the result and output TOF of 230 h⁻¹ at 100 °C is more than 100 times smaller than the performance for Ir systems at 80 °C. With a well-defined PNP-Ru catalyst (3) when the less volatile trioxylamine (NHex₃) base was used, the TON advanced from 326500 (NEt₃) to 706500 with similar high TOF [17].

Estimates were based on the commercial prices of raw materials available in 100 gr or less, assuming a similar reaction yield in the literature without counting solvent and workforce costs. These values are intended for initial economic evaluation only. According to the authors present at ICEF 2016 with average lifetime over catalysts.

Figure 8. The illustration of the results of Table 1 [35]
While significantly slower, the PN3P-Ru (4) catalyst had a long catalyst lifespan of 150 h in DMSO/NEt₃. Cationic pentamethylcyclopentadienyl (Cp*) Ir complexes 5 and 6, showing excellent reactions in HCOOH/HCOONa aqueous solution. One notes that the initial TOFs of 158,000 h⁻¹ for 571 and 487500 h⁻¹ for 672 are approximately 3 to 6 times faster than the average TOFs, indicating the apparent degradation of the catalysts in 12-14 h. It is exciting to see base metals, such as iron, [27, 30] that exhibit similar or superior activities to their precious metal counterparts; however, the cost of the ligand for practical investigation seems to be the dominant factor. System 8 also revealed that, the presence of Lewis acid, such as LiBF₄, significantly increased the TOF. Unfortunately, with a very low catalyst load of 0.0001 mol%, [31–33], the rate of total hydrogen production is limited. Due to the fact that the specific activity of these catalysts is not available under the same reaction conditions (solvent, base additives, and temperature), our analysis was reported based on the results, which assume that these values work best under certain conditions [33]. Figure 8 depicts that, the cheapest iron pendant system currently meets the two assumed cost criteria, while the Ru system/complexes one and three, and Ir chelate 6 complexes meet the COF threshold (0.5). The low price is calculated, and TON places the catalyst Ru catalyst four below the allowed limit (0.35) [34]. Under the minimum catalyst requirement calculated from Equation 1, the service distance is proportional to the TON/TOF ratio of the corresponding catalyst. Therefore, in Figure 8, the catalysts are divided into three groups: those with low TON/TOF ratios (complexes 3 and 8) generally require short switches, possibly filling the station at each stop. However, the costs are

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Operation conditions</th>
<th>Cost [$/mol]</th>
<th>TON</th>
<th>TOF [h⁻¹]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>in HexNMe₂ at 25 °C</td>
<td>60000</td>
<td>80000</td>
<td>47970</td>
<td>[31, 35]</td>
</tr>
<tr>
<td>2</td>
<td>HCOOH/HCOONa in H₂O at 100 °C</td>
<td>250000</td>
<td>3000000</td>
<td>230</td>
<td>[21, 28]</td>
</tr>
<tr>
<td>3</td>
<td>in DMF/ HexNMe₂ at 90 °C</td>
<td>150000</td>
<td>706500</td>
<td>256000</td>
<td>[13]</td>
</tr>
<tr>
<td>4</td>
<td>in DMSO/NEt₃ at 90 °C</td>
<td>35000</td>
<td>1100000</td>
<td>7333</td>
<td>[30]</td>
</tr>
<tr>
<td>5</td>
<td>HCOOH/HCOONa in H₂O at 80 °C</td>
<td>98000</td>
<td>308000</td>
<td>25700</td>
<td>[32]</td>
</tr>
<tr>
<td>6</td>
<td>HCOOH/HCOONa in H₂O at 80 °C</td>
<td>125000</td>
<td>2400000</td>
<td>171000</td>
<td>[33]</td>
</tr>
<tr>
<td>7</td>
<td>in propylene carbonate at 80 °C</td>
<td>62000</td>
<td>92417</td>
<td>9425</td>
<td>[35]</td>
</tr>
<tr>
<td>8</td>
<td>in dioxane at 80 °C</td>
<td>11000</td>
<td>983642</td>
<td>196728</td>
<td>[34]</td>
</tr>
</tbody>
</table>
initially low [35]. Catalysts with higher estimated service intervals can be replaced by each service (1, 5, 6, and 7). Catalysts 2 and 4, which have a high TON/TOF ratio, can last the entire life cycle of the vehicle; however, the initial cost of filling the catalyst is significant enough to increase the FCV sales.

Conclusions

FA is known to be material available for the implementation of hydrogen storage technology, which avoids the costly infrastructure required to fill the hydrogen-based FCVs. Conventional hopper pumps can generally provide another pump that supplies FA, and can also utilize the HCOOH storage tank to produce the hydrogen on-site, and use HCOOH technology as a catalyst to reduce the barriers of global implementation in FCV. The working group meeting after the G7 Energy Ministers Meeting (G7WG) at the ICEF cooling innovation forum 2016 will be followed by scientists, industry representatives, and policymakers to discuss possible connections, efforts, and research on CO₂-based hydrogen carrier systems. Catalysts and technology have made significant strides, and everyone should now be able to demonstrate the technology. For instance, linear CO₂-H₂ reaction systems have been implemented in acidic environments. An encouraging prototype of a Ru-catalyzed hydrogen generator using FA was developed, successfully satisfying 1 kW of output power (30 L/min H₂/CO₂), and a similar system is available on a larger scale. Additionally, a group of researchers in Eindhoven is building buses that have fueled using the FA. In 2019, a 400-watt car was shown to be able to carry 45 kg at an approximate speed of 8 km/h. To create a cost-effective economic system for initial marketing, specifying the activity of the catalyst and selecting the best option to produce the required hydrogen is an essential stage of the design process. The best option significantly reduced the cost of the catalyst under the operational conditions, minimizing the absorption of resources and energy and improving the CO₂ capture efficiency. While resource constraints and regulatory measures strongly affect the future of transportation, the FA’s strategy as an energy carrier to release the hydrogen to generate electricity through fuel cells is promising. Furthermore, many mobile applications and fixed power plant bases are predictable. With global research efforts in the field of renewable hydrogen production, this storage and distribution concept will undoubtedly play a vital role in the future of the hydrogen economy.

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