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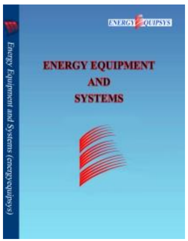

Economic assessment of solar-based hydrogen for methanol production

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ABSTRACT

The climate change crisis has urged societies to take action for mitigating greenhouse gas emissions. Carbon neutral fuel is one of the proposed solutions to achieve this goal. Carbon neutral fuel is the product of captured CO_2 *with different methods such as direct air capture, sea water-absorbent, and power plant chimneys, and reformed through reactions with hydrogen under high temperatures and pressures. Methane, Methanol, E-diesel and Dimethyl Ether are some fuels that can be made through these processes. With this renewable fossil fuel, there will be no need for building new infrastructures, and it saves tons of money and mitigates greenhouse gas emissions resulting in higher GDP and life quality in the long term. Since there must be no added* CO_2 *emissions within the whole process of carbon-neutral fuel production, to fulfill carbon neutrality, the hydrogen component should be produced from renewable energy sources like solar, wind or geothermal. This paper presents an economic assessment of the solar-based hydrogen for green methanol production. The results show that the levelized cost of solar-based hydrogen is dramatically higher than fossil-based hydrogen due to lack of investments in the renewable energy section in Iran. With a solar-based hydrogen price of $28.1/kg, green methanol price is evaluated $19159/mt.*

Keywords: Carbon Neutral Fuel, Solar-Based Hydrogen, Greenhouse Gases, Renewable Energy, Green Methanol.

1. Introduction

Global energy demand is estimated to be doubled by the year 2050 concerning an increase in economy sizing and population growth [1]. Eighty-two percent of the energy demand is met by fossil fuels [2]. The issues regarding fossil fuels, including climate change, global warming, and limited sources, encourage energy researchers to investigate alternative and renewable energy sources, energy-efficient technologies, carbon capture systems, and new storage methods [3].

Iran will confront a significant increase in electricity demand in the near future [4]. Iran has signed a new climate action plan to the UN Framework Convention on Climate Change.

Sternberg et al. [5] studied CO_2 based production of methane and methanol and assessed the environmental impact reduction in comparison with fossil-based production. The result showed that CO_2 based production has more environmental impact reduction regardless of the environmental impact of used hydrogen.

El-Shafie et al. [6] overviewed both fossil-based and non-fossil based hydrogen production technologies. Hydrogen production using a concentrated photovoltaic

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(CPV) system is investigated by Boundaries [7]. Cost-effective CPV field for small scale operations and hydrogen production is investigated by Burhan et al. [8]. Thermoeconomic analysis of a hybrid PVT solar system for hydrogen production was presented by Behzadi et al. [9]. The results show that by decreasing the PV cell's temperature from 100 °C to 160 °C, the total product unit cost is decreased by about $1.94/GJ. Economic optimization of solar systems under uncertain economic conditions was presented by Kasiri et al. [10]. The probability function of the life cycle solar saving (LCS) is then estimated by the Monte Carlo method. A solar-based multi-generation system is assessed by Ghasemkhani et al. [11]. The total cost rate is evaluated at $9.63 per hour.

Karapekmez investigated hydrogen production using solar and geothermal combined energy system [12]. These technologies are cost-competitive and differ in production capacity and electricity usage. Bhandari et al. [13] reviewed 21 studies addressing the LCA of hydrogen production technologies, mostly electrolytic. From an LCA point of view, electrolysis using wind and hydropower is one of the best hydrogen production methods with the lowest carbon footprints. Symes et al. [14] decoupled reactions in electrolytic hydrogen production to improve efficiency and durability. By dividing the simultaneous reactions into two electrochemical (reduction of water at cathode and oxidation of anode) and chemical (reduction of anode back to its starting state) reactions, water splitting is enabled at 1.44-1.60 V. Table 1, sorts main parameters of dominant electrolyzers.

Carbon dioxide is captured directly from the atmosphere, power plant chimneys and other large sources like cement factories and heavy industries. Fasihi et al. [15] have investigated the techno-economic assessment of direct air capture of CO_2. In this study, low temperature and high-temperature direct air capture are compared and concluded that low-temperature capture due to lower heat cost is more favorable. Berstad et al. [16] reviewed the application and potential of low-temperature carbon capture technologies with respect to energy consumption and CO_2 capture ratio. Results showed that for specific applications like synthesis gas from coal gasification, low-temperature capture has high potential and is highly competitive to baseline technologies. Raza et al. [17] studied significant aspects of carbon capture and storage. In this study CO_2 properties, capture and separation, CO_2 transport, storage, monitoring for safety and economics are reviewed. Lawal et al. [18] developed a dynamic model and simulated operation of a full-scale 500MWe coal-fired power plant. The result showed that with taking absorber height as 27m, there would be a balance between column cost and heat requirement. Another result of this study indicated that the CO_2 capture plant is slower than the power plant, and by increasing the capture level, the thermal efficiency has decreased. On the other hand, Rifka et al. [19] assessed low-temperature post-combustion capture in three different CO_2 concentrations and showed with higher CO_2 intensity energetic efficiency increases and a decrease in CO_2 cost and energy penalty is observable. Liang et al. [20] reviewed recent progress and developments in post-combustion carbon capture technology with amine-based solvents. Results showed that the main challenge of carbon capture is energy consumption, and by reducing down to 30% still, 2.6 GJ energy is required per tonne of CO_2 capture. Captured CO_2, then have to get compressed to store or mix in the mixing chamber. The compressor component can be optimized in order to lower energy consumption. Jackson and Brodal used MATLAB utilized with the TREND package for optimizing the multi-stage compressor used for compressing CO_2. Results showed that a range of 292 to 406 kJ/kg CO_2 with 8 to 9 compression stages is an optimum solution for this goal [21]. Subramanian et al. [22] compared four different post-combustion capture technologies for the exact NGCC. Results showed that low-temperature sorbent electric efficiency is good enough for further researches, and using exhaust gas recirculation (EGR) is a good option for CO_2 capture in NGCC. The comparison showed that low-efficiency polymeric membranes, as a result of high energy usage, are good for streams with high CO_2 concentrations. Jiang et al. [23] studied post-combustion CO_2 capture from NGCC power plant using activated carbon adsorption. The net efficiency of NGCC increased from 50.8% to 51.1% as a result of lower regeneration temperature at 85 degrees Celsius.

Methanol can be used directly as a fuel [24]. Methanol is a vital feedstock for dimethyl ether (DME), which can be used as a clean high-efficiency fuel with less NOx and SOx itself. Liu et al. [25] reviewed advancements in the conversion of methane and CO2 to methanol. This study admits that the process of methanol production through methane is mature, but it has a long way to improve the efficiency and performance of catalysts used for hydrogenation. Sheldon [26] reviewed a 100-years record of methanol production. This study shows that the scale of methanol plants is growing with demands. Zhen and Wang [27] systematically studied different methanol production methods. They introduced the potentials of methanol as renewable fuel by considering supply and demand, economic benefits and climate change mitigation. In this study, 13 methods of methanol usage in internal combustion engines for mitigating emissions are reviewed. Ham et al. [28] designed a systematic process for hydrogenating CO_2 with a capacity of 10 kt/y. catalysts used in this design are $Cu/ZnO/Al_2O_3$. The process has high net CO_2 reduction but not economically feasible at current CO_2 tax conditions. Matzen et al. [29] analyzed and compared the economic and sustainability aspects of green methanol and ammonia. They assessed potential environmental impact by using the Aspen Plus software package. The economic assessment revealed that the cost of hydrogen production is a key parameter for green methanol.

The objectives of this paper are to:

- investigate the methanol production processes using captured CO_2 and solar-based hydrogen
- conduct an economic assessment of the green methanol production
- investigate the feasibility of green methanol production in Iran
- perform a sensitivity analysis to assess the impact of key parameters

Nomenclature

$C_{fom.a}$	Annualized fixed operation & maintenance cost
C_{mc}	Maintenance of compressor cost
C_{cont}	Cost of the service contract
C_{rep}	replacement cost
CRF	Capital recovery factor
$C_{rep.a}$	Annualized replacement cost
i	Interest rate
$C_{cap.a}$	Annualized capital cost
$C_{vom.a}$	Annualized variable operation & maintenance cost
C_e	Cost of electricity
C_w	Cost of water
LCOH	Levelized cost of hydrogen
$C_{LCC.a}$	Annualized life-cycle cost
$M_{h.a}$	Annualized mass of hydrogen

Abbreviations

DAC	Direct Air Capture
CNF	Carbon-Neutral Fuel
LCA	Life-cycle Analysis
GHG	Greenhouse Gas
PEM	Proton Exchange Membrane
SOE	Solid Oxide Electrolyzer
RWGS	Reverse Water Gas Shift
NVP	Net Value Present
IRR	Internal return rate
NGCC	Natural Gas Combined Cycle
O&M	Operation and Maintenance
SPAC	Substituted Price of Avoided CO_2

2. Solar-based hydrogen production

Solar-based hydrogen production methods include thermochemical cycles, photovoltaics, and electrolyzers.

Thermochemical cycles are made of two water splitting and reduction reactions and use solar energy as heat source to increase the temperature to the point that reactions start [30]. In these cycles, first, higher valance oxide is reduced to lower-valance by losing oxygen, and second, the reduced oxide turns to high-valance oxide by taking oxygen from water and produces hydrogen. Examples of thermochemical cycles are sulfur-based cycles and two-step metal oxide cycles. Thermochemical cycles are not implemented in large-scale industries [30].

Another form of using solar energy is to convert it directly to electricity. Photovoltaic (PV) panels are packed solar cell modules that convert sunlight into electricity using semiconductors and their efficiency drops by increasing temperature. Larger PV installations have the advantage of economy of scale due to efficiency gain. Studies show that Iran has a high potential for a solar system with a wide range of areas and is economically worthy of investments [31]. The method of providing electricity in this study is solar, regardless of GHG emissions in PV modules production processes.

Electrolyzers include Alkaline, polymer electrolyte membrane (PEM), high-temperature solid oxide electrolyzers (SOE).

The Alkaline electrolyzer is a mature technology that contains two electrodes functioning in an alkaline electrolyte. This electrolyzer is widely used in hydrogen production industries and is optimized for large scale industrial use. The volume of electrolyte inside the electrolyzer is restricted by the gap between electrodes and is preferred to be an aqueous solution of KOH due to higher conductivity [32]. PEM electrolyzer uses a solid polymer electrolyte for conducting protons and separating anode and cathode. The advantage of the PEM electrolyzer is electrolysis in low current density. PEM electrolyzers are not suitable for large-scale plants and the catalysts used are expensive [10]. SOE uses a solid or ceramic as an electrolyte for hydrogen production. This electrolyzer works in high temperatures, and researchers are investigating the effects of adding external heat sources. SOE has long-term stability issues, and due to the high-temperature operation range, material selection is limited [11]. In this paper, an alkaline electrolyzer with an efficiency of 74% and a lifetime of 10 years is selected [12].

Electrochemical reactions in alkaline electrolyzer are described by

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \tag{1}$$

and

$$2OH^- \rightarrow \frac{1}{2}O_2 + 2H_2O + 2e^-. \tag{2}$$

3. Carbon capture and storage

The majority of CO_2 emissions are from two transportation and industrial sectors. To fulfill the CNF economy, we should focus on one sector. Focusing on two sectors at the same time will lead to an efficiency drop. DAC systems that are called artificial trees, seawater absorbent, and concentrated CO_2 plants like coal power plants and cement factories carbon capture, are examples of CCS technologies.

Capturing carbon in power plants includes pre-combustion, post-combustion, oxyfuel combustion and chemical looping combustion. Carbon capture in pre- and post-combustion is more mature. The main challenge in capturing CO_2 is to separate nitrogen from combustion products in post-combustion capture. There are mainly three post-combustion systems: advanced solvents, solid sorbents, and membrane systems. The solvent-based system absorbs CO_2 and by increasing temperature or decreasing pressure breaks the bond between absorbent and CO_2. This system takes high energy. Sorbent system uses low-cost sorbents and consumes lower energy. The membrane-based system uses a permeable material for separating CO2 from combustion products (See Fig. 1).

Table 1. Main parameters of electrolyzers

Electrolyzer type	Electricity to hydrogen Efficiency (%)	Hydrogen production rate (Nm^3/h)	Cell voltage (V)	Temperature range (^oC)	Lifespan	references
Alkaline	52-74	60	1.8-2.4	60-80	15-30	[33]
PEM	56-69	10	1.75-2.2	50-80	10-20	[33]
SOE	95-100	60	1.28	500-1000	10-20	[11]

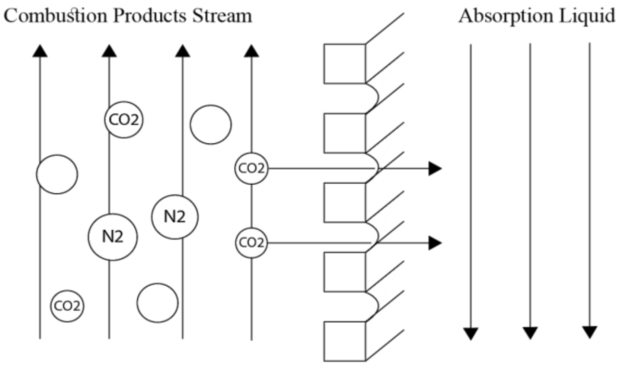

Fig. 1. CO_2 absorption membrane

On the other side of the membrane, absorption liquid absorbs the CO_2 molecules [34]. The intensity of carbon in post-combustion is higher; therefore, with lower energy consumption higher amount of CO_2 is captured. There are other processes like adsorption and cryogenic processes besides absorption that are not widely used [35]. Post-combustion carbon capture technologies have been commercialized. Post-combustion carbon capture can be deployed on nearly all power plants in Iran, and there is no need for new infrastructure design. Another method of capturing CO_2 is using activated carbons in high pressures.

4. Methanol production

In industries, methanol is produced mainly by hydrogenating carbon monoxide [36]. Methanol production from carbon dioxide is achieved mostly by two methods, direct synthesis and two-step synthesis. In two-step synthesis, CO_2 is converted to CO by reaction with H_2 and water as the second product in the reverse water gas shift (RWGS) reactor. In direct methanol synthesis, a mixture of CO_2 and H_2 at a ratio of 1:3 is injected directly inside the methanol reactor with the presence of proper catalysts. The direct synthesis method is more economically efficient but, in areas with cheaper abundant electricity potential, two-step synthesis is proven to be more efficient [37]. The chemical reaction of methanol production is given by

$$CO_2 + 3H_2O \rightarrow CH_3OH + H_2O. \qquad (3)$$

Key elements in reactions are catalysts, and researchers unveiled a high-efficiency catalyst, indium oxide, for methanol synthesis by CO_2 hydrogenation. This catalyst has 100% selectivity and high robustness [38]. The use of proper catalysts is important for overall methanol production system efficiency. The schematic of the green methanol plant is illustrated in Fig. 2. Storage conditions for H_2 are at 25° C and 33 bar and for CO_2 are at -25.6° C and 16.4 bar and in the liquid phase. A multi-stage compressor and pump compress H_2 and CO_2 to 50 bar and flows are mixed in a mixer. The stream goes inside the RWGS reactor. The produced water is separated in separator before methanol synthesis.

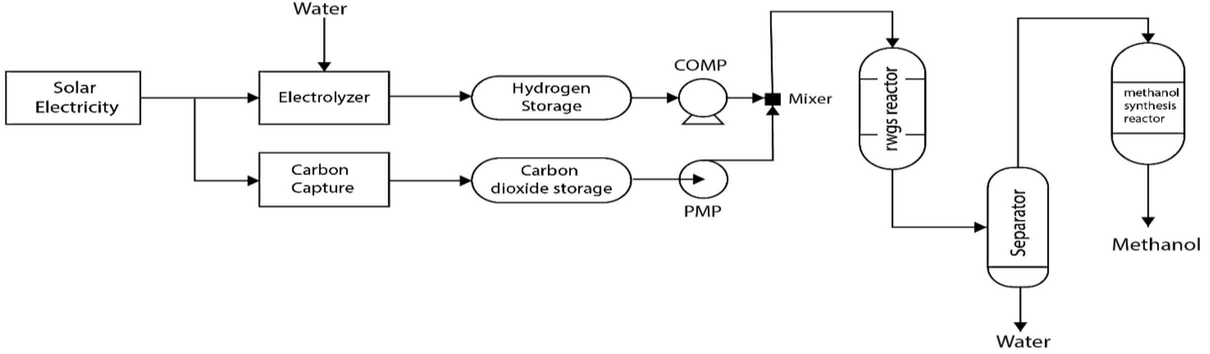

Fig.2. Schematic of the methanol production system

5. Economic modeling

The major costs for analyzing solar-based hydrogen are presented in Table 2 [39]. Operation and maintenance (O&M) costs are divided into two fixed and variable categories. Fixed O&M cost is presented by

$$C_{fom.a} = C_{mc} + C_{cont} + C_{rep.a}, \tag{4}$$

where C_{mc} indicates maintenance cost, C_{cont} accounts for service contract and $C_{rep.a}$ is the annualized replacement cost. $C_{rep.a}$ is evaluated by

$$C_{rep.a} = CRF \times \frac{C_{rep}}{(1+i)^t}, \tag{5}$$

where CRF is the capital recovery factor and is calculated as

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1}, \tag{6}$$

and

$$C_{vom.a} = C_e + C_w, \tag{7}$$

where C_w is the annual water cost and C_e is the annual electricity cost. The annualized life cycle cost (LCC) is evaluated by

$$C_{LCC.a} = C_{cap.a} + C_{fom.a} + C_{vom.a}, \tag{8}$$

where $C_{cap.a}$ is the annualized capital cost. Finally, the levelized cost of hydrogen (LCOH) is assessed by

$$LCOH = \frac{C_{LCC.a}}{M_{h.a}}. \tag{9}$$

CCS costs are correlated with power plant costs and fuel prices and their capacity [40]. A large CCS investment is more feasible than a smaller one. Another important factor in CCS is the cost of transmission. The price for piping the captured CO_2 is considerable when the captured CO_2 is from an offshore source. The price for different distances for both offshore and onshore pipelines are discussed in [40]. For eliminating CO_2 transporting price and long pipelines, the CNF plant must be built near or beside an existing power plant. CCS cost is derived from the reference [41] based on the technologies that are used for post-combustion capture. If CCS is done far from the plant, the cost for CO_2 storage and transfer to the CNF plant must be added to the cost.

For measuring the benefit of renewable energy and attracting investments, the amount of avoided CO_2 is investigated. Feed-in-Tariff is determined by policymakers to pay factories and power plants for mitigating CO_2 emissions. This parameter boosts energy supply from renewable energy sources. Base Feed-in-Tariff for Iran in 2017-2018 for solar electricity is in range of \$0.09/kWh for above 30 MW, \$0.21/kWh for bellow 10 kW capacities, and mean value is \$0.155/kWh [42]. The substitute price of avoiding CO_2 emissions (SPAC) is an indicator to show how much countries pay to avoid 1 ton of CO_2 emission [43]. Table 2 shows different parameters for evaluating SPAC for different countries. For evaluating solar emission, different important factors like location, technology are determinants. SPAC values in Table 2 are corrected by more reliable solar emission data. Eq. (10), shows how SPAC is evaluated as [43]

$$SPAC = \frac{1000 \times \text{Tariff rate}}{\text{Avoided } CO_2}. \tag{10}$$

For a 30-year plant operation with 5-year construction time, the levelized cost of green methanol is assessed. At present, the annual inflation rate in Iran is 34%, but a forecast for inflation indicates that it will stabilize at 13.5% [44].

Transmission and distribution of electricity have a considerable contribution to the expenses. Two main scenarios for providing electricity are one, off-grid solar power, and second, renewable contracts.

Table 2. Countries payment for avoiding CO2

Country	Tariff rate (US\$)	CO_2 emission (kg CO_2/kWh)	Solar emission (kg CO_2/kWh)	Avoided CO_2 (kg)	SPAC (US\$/ton CO_2)
Iran	0.155	0.309	0.049	0.260	596
Germany	0.388	0.553	0.049	0.504	769
Ontario (Canada)	0.780	0.220	0.049	0.171	4561
Vermont (US)	0.300	0.630	0.049	0.581	516

Data sources: [43, 45]

Renewable contracts, due to transportation and distribution, cost more, and are not viable. On the other hand, off-grid solar power stations are founded to be entirely surplus electricity. The majority of costs, about 65%, in the CNF economy are to buy electricity [46]. Fossil based economy leads to momentum in migration into cleaner energy and CO_2 cut down. In all scenarios for the CNF economy, the government plays a key role by allocating subsidies. In other words, without the government's supports, CNF production will not be viable. Iran spends $45 billion annually on fossil fuel subsidies, and this amount increases year to year, equal to about 10% of Iran's annual GDP [42]. Fortunately, the country is going to reform its targeted subsidy plans. With these reforms, the share of renewable energy sources in Iran's energy sector will increase from 0.02% at present to 10%. Due to these decisions, solar power generation will cost 30% less in upcoming years, around 2030 [47].

6. Results and discussion

Policy analysis for IRR and NVP shows that a green methanol production plant is not feasible in Iran for current conditions due to the high price of solar-based hydrogen production as a key input parameter. The payback period is longer than useful operational years. Using solar-based hydrogen and eventually producing green methanol will cut 0.5Mton of CO_2 emissions annually. With multiplying CO_2 by SPAC, total payment for avoiding CO_2 is estimated to be way less than fossil fuel subsidies. With migration into green methanol, energy demand and GHG emission rate will stabilize as a long-term outlook. Table 5 presents the final cost results for green methanol production. As is shown, the high price of electricity caused hydrogen to be very expensive, and eventually, the price of one metric ton of green methanol is dramatically high. Other alternative ways to achieve feasibility include increasing CO_2 tax and price up to $250/t for commercial use, decreasing in hydrogen cost up to $2/kg by high investments in clean and renewable energies. Figure 3 is visualizing the comparison of the levelized price of hydrogen and CO_2 capturing price between Iran and the global median price. The dramatic price of methanol is shown in Fig. 4.

One kg of hydrogen produces 141.8 MJ energy, while this amount for methane is 50.1 MJ. At present, the price for 1kg of methane is 1% of the same amount of solar-based hydrogen produced in Iran. For large-scale plants, the electricity price drops to 0.14 $/kWh, leading hydrogen price to be 19.6 $/kg, and as a result, the final methanol price of 13363 $/mt. The price of capturing carbon is not way off the chart comparing with other countries like Germany and Belgium. With a considerable difference in the cost of fossil-

Table 3. Cost factors for solar-based hydrogen

Cost factor	Cost per unit	References
Water cost	$0.06 /m^3	[45]
Electricity cost	$0.2 /kWh	[45]
Cell stack change	$76222 per stack	[39]
Service contract	7.1% of WE investment	[39]
Fixed maintenance	6% of investment	[39]

Table 4. Fundamental parameters for financial modeling of carbon-neutral fuel [48]

Parameter	Value
Plant Lifetime	30 years
Construction Time	5 years
Inflation Rate	13.5%
Depreciation Method	Straight line
Depreciation Rate	5%
O&M	7% of capital cost

Table 5. Results for the levelized cost

Utility	Unit Cost	World Median Price
Hydrogen	\$28.1 /kg	\$5.7/kg [49]
CO_2 Capturing	\$95 /ton	\$80 /ton [41]
Methanol	\$19159 /mt	\$600 /mt [46]

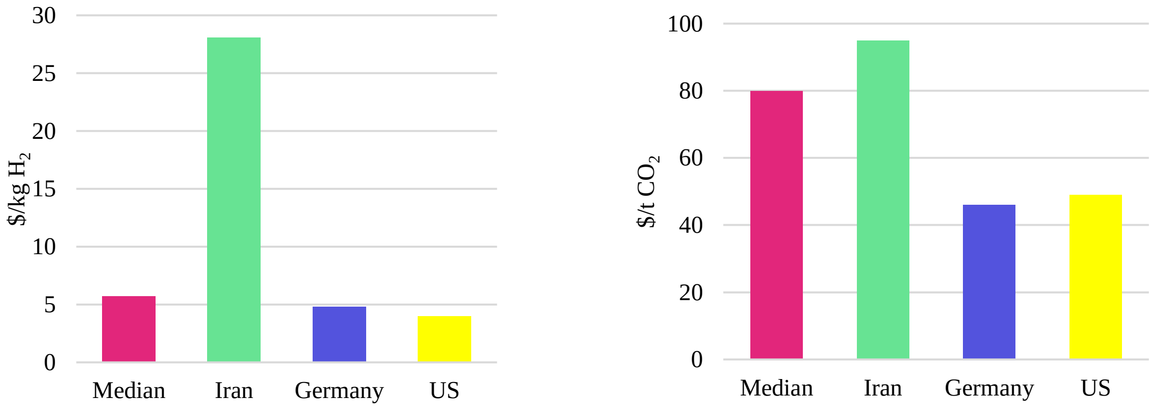

Fig. 3. Comparison of levelized cost of hydrogen and captured CO2

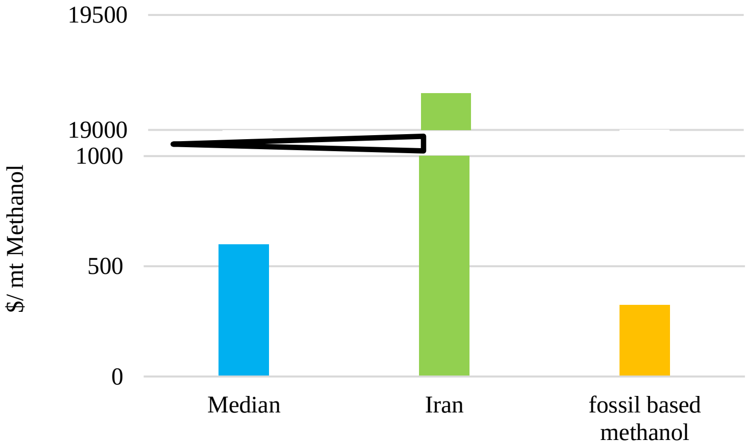

Fig. 4. Methanol cost comparison

based methanol and green methanol, major action for reducing green methanol price is the government's new subsidy plan, and an increase in CO_2 tax or green methanol production will not be economically feasible in the near future. A sensitivity analysis is performed to measure the effect of variation in electricity price on hydrogen Levelized cost. By investing in solar power and lowering the price for PV modules, the electricity price is assumed to reduce down to half of the current price, and the LCOH will be reduced to \$13.6 /kg shown in Fig 5. As the price for water is extremely low by considering new policy changes in water consumption, a hike in water price is predictable. This increase is slight and, on the other hand, helps with better subsidy planning. To increase the efficiency of the system, using hybrid (wind and solar) electricity is suggested [40].

7. Conclusion

This study investigates Iran's opportunities as a developing country for CNF plants supplied with solar-based hydrogen considering important parameters. Iran is one of the best countries for investments in solar-based technologies due to its geographical location,

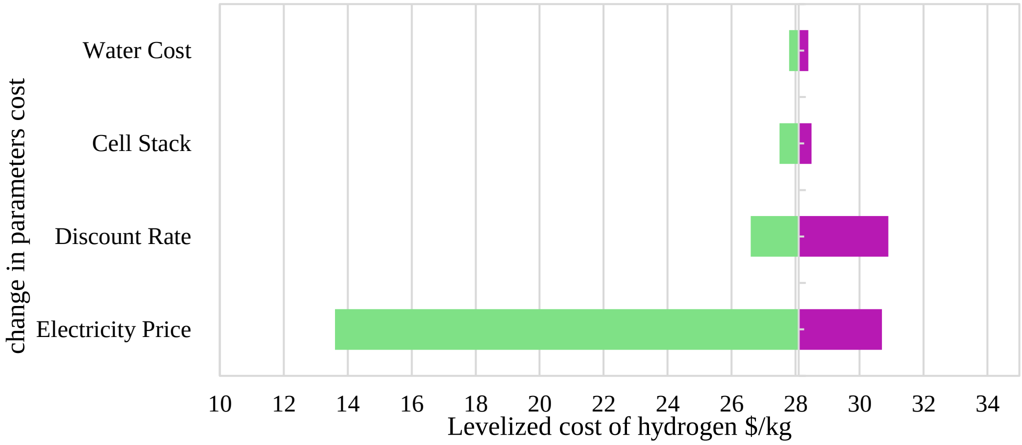

Fig.5. Sensitivity analysis

and integrating solar energy stations with other renewable sources can decrease the total annual cost by about 25% in comparison with the stand-alone solar station. Government policies are one of the most important factors in any new technology, and feasibility in solar-based hydrogen for cheaper hydrogen production and carbon-neutral section is dependent on direct decisions of government and its policies on tax, subsidy, and legislation. Iran as a developing country is not ready to jump into the CNF economy due to the high electricity price generated from solar energies and have to invest more in renewable section, to lower the output electricity price to compete with global markets. Green methanol production in Iran with current conditions is highly dependent on solar-based hydrogen price, which optimistically can be decreased to $13.6 /kg, which is still higher (about 3 times) than hydrogen price in developed countries. For further research, emission reduction from migration to the CNF economy for Iran is considered.

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