Pathways for Low Carbon Hydrogen Production from Integrated Hydrocarbon Reforming and Water Electrolysis for Oil and Gas Exporting Countries

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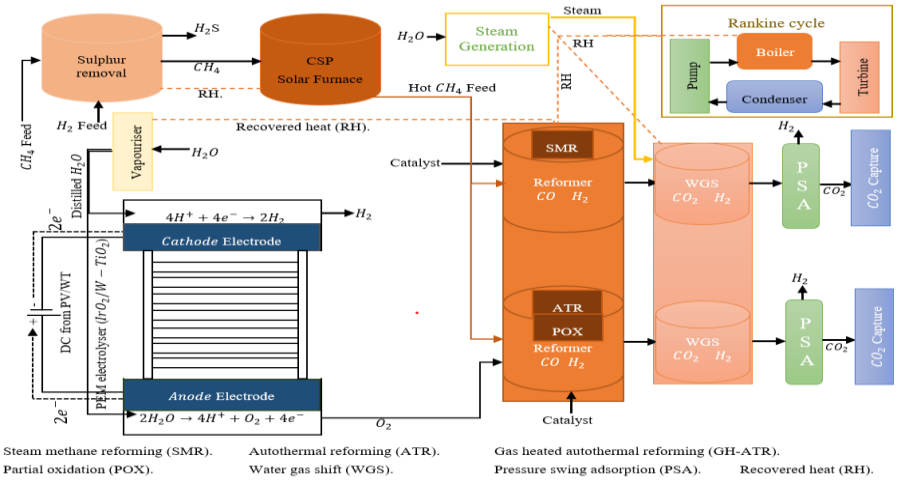
HIGHLIGHTS

- Integrated hydrocarbon reforming and electrolysis systems for higher efficiency.
- Electrolysis of H_2O powered by both solar and wind power systems.
- Parabolic dish concentrators for reformer and reactor heat source.
- O_2 from electrolysis used in GH-ATR, ATR and POX for partial oxidation reforming.
- Achieved below 4kgCO_2/kgH_2 and by-product CO_2 capture for carbon neutrality.

GRAPHICAL ABSTRACT



Abstract

To reduce GHG emissions in oil and gas exporting countries (OGEC), integrated hydrocarbon reforming processes coupled with H_2O electrolysis for H_2 production were developed and simulated. This hybrid system includes SMR, GH-ATR, ATR and POX. Each of these systems operates with PEMEC to increase the H_2 production rate and supply O_2 to the reformers. The hybrid systems use parabolic dish concentrators (PDCs), solar cells and wind turbine systems to produce thermal and electrical energy for endothermic and electrochemical reactions. The CO_2 by-product was captured by the adsorption process which releases heat. The result shows that using solar thermal energy with CH_4 as the working fluid at an exit temperature of 1050°C, between 526.78MJ/h – 1311.84MJ/h heat output is required to operate four of the hydrocarbon reforming systems. With the use of renewable energy sources and energy recovery units, the H_2 selling price for any of the proposed systems is expected to be <$2.9/kg. Furthermore, fuel cells application to any of these integrated systems can replace fossil fuel burning in power plants operating in OGEC for the reduction of carbon emissions. The provided method for the oil and gas rich countries will provide a high-value chain in the H_2 generation industry.

Keywords:

Parabolic dish concentrators (PDCs)

Solar cell and wind turbine system

Steam methane reforming (SMR)

Gas heated autothermal reforming (GH-ATR)

Proton exchange membrane electrolyser cell (PEMEC)

Nomenclature

Abbreviations and Symbols

%	Percentage
°C	Degrees Celsius
ΔH	Enthalpy
$m\mu$	millimicron
μm	micron
wt.%	Percentage by weight
ASU	Air separation unit
ATR	Autothermal reforming
CCS	Carbon capture and storage
CSP	Concentrating solar power
DNI	Direct normal irradiance
GHG	Greenhouse gas
GH-ATR	Gas-heated autothermal reforming
HRPs	Hydrocarbon reforming processes
HTF	Heat transfer fluids
HTS	High-temperature shift
HX	Heat exchangers
kg/hr	Kilo gram per hour
$kmol/hr$	Kilo mole per hour
kW	Kilowatt
LTS	Low-temperature shift
m^2	square metre
m/s	metre per second
MENA	The Middle East and North Africa
MW	Megawatt
NREL	National renewable energy laboratory
OGEC	Oil and gas exporting countries
PDCs	Parabolic dish concentrators
PEMEC	Proton exchange membrane electrolyser cell
PSA	Pressure swing adsorption
POX	Partial oxidation
PV	Photovoltaic
S/C	Steam carbon ratio
SAM	System Advisor Model
SMR	Steam methane reforming
WGS	Water gas shift
WT	Wind turbine
W/m^2	Watt per square metre

Introduction

Nowadays, reducing carbon emissions is still one of the most discussed topics in the global economy to limit the temperature increase above 1.5°C by 2030 [1]. Many researchers have recommended carbon pricing by taxing carbon-intensive products and switching fuels to low-carbon and renewable energy sources to mitigate the effects of climate change. For instance, it was evident that carbon dioxide (CO_2) emission from the burning of fossil fuels was the major cause of climate change [2]. As such that global warming is an international concern, most oil and gas exporting countries are largely concerned, even though more than 90 percent of greenhouse gas (GHG) emissions are related to downstream uses such as combustion. The role of hydrogen (H_2) in reducing the carbon footprint has received attention. On the contrary, most H_2 production processes use fossil fuels as feedstock and require the burning of fossil fuels in the decomposing furnace because of the endothermicity of the method. At present, hydrocarbon reforming with carbon capture and storage (CCS), gasification, pyrolysis, thermolysis, electrolysis, photocatalyst and fermentation are current methods to extract molecular H_2 from other elements such as water (H_2O) and methane (CH_4). Hydrocarbon reforming methods (HRMs) of H_2 production has been reported to account for 90% of global production because of cheaper H_2 selling price [3]. For example, the H_2 sale price of steam methane reforming (SMR) operating with 85% efficiency and carbon capture and storage (CCS) unit has been reported to be between $2.2/kg - $2.9/kg [4] [5]. While the electrolysis of H_2O which does not require fossil fuel feedstock has been considered a more efficient method than other H_2 production processes. In addition, H_2O electrolysis is considered more eco-friendly because it can utilise electricity from renewable sources for the electrochemical disassociation of H_2O molecule into H_2 and oxygen (O_2). Unlike other types of electrolyser cells, lower carbon footprints, higher current density and purity of H_2 by-product are some of the advantages of proton exchange membrane electrolyser cell (PEMEC). However, this process cost more than any of the reforming methods (SMR, partial oxidation, autothermal and gas-heated autothermal reforming). For example, H_2 from H_2O electrolysis costs between $5.10/kg to $10.3/kg [4] [5]. Therefore, it is important to develop H_2 production systems that can reduce the amount of fossil fuel feedstock; cheaper means of producing O_2 feedstock for hydrocarbon reforming processes; the use of thermal and electrical energy from renewable sources and efficiency improvement coupled with carbon emissions reduction and capture for oil and gas exporting countries.

Hydrocarbon reforming processes of H_2 production consist of SMR, partial oxidation (POX), autothermal reforming (ATR) and gas-heated autothermal reforming (GH-ATR). SMR involves the endothermic decomposition of CH_4 and H_2O_{gas} in the reformer and exothermic reaction of syngas from the reformer with the addition of steam in the water gas shift (WGS) to produce H_2 fuel. Whereas the reaction of CH_4, O_2 and H_2O_{gas} in the reformer occurs in ATR to produce H_2 gas. Unlike ATR, GH-ATR requires a reformer to convert CH_4 and H_2O_{gas} and a combustor for partial combustion of CH_4 and O_2, followed by shift reactions (high and low temperature shifts) to produce H_2 and CO_2. Partial combustion of both CH_4 and O_2 in the combustion chamber and the use of

WGS to produce synthetic gas mainly of H_2 and CO_2 occurs in the POX method [6] [7]. Both single-reformer ATR and GH-ATR can replace the SMR process which accounts for more than 48% of total H_2 production because of reduced steam feedstock in the reformer. In addition, replacing SMR with GH-ATR can also minimise total investment costs and thermal energy demand, while using ATR instead of SMR can reduce plant size due to reduced steam flowrate [7]. On the other hand, high operating costs were reported for both ATR, POX, and GH-ATR due to the use of an air separation unit (ASU) to extract O_2 for partial combustion [8]. Burning of fossil fuels in the reformer furnace to thermally decompose substrates, which releases greenhouse gas emissions; dependency on grid electricity for electrical units and the lack of further efficiency improvements are HRPs drawbacks. However, one of our earlier studies on an integrated hydrocarbon reforming and sorption enhanced–chemical looping using a parabolic trough collection (PTC) as a solar thermal energy source mitigates some of the highlighted drawbacks. For example, using solar thermal energy to break down the raw materials (feedstock) and thermal energy recovery to operate downstream units has been found to improve overall efficiency with a minimal carbon emission footprint. Nonetheless, our earlier studies do not investigate the reduction of fossil fuel feedstock, replacement of ASU for O_2 production and off-grid electricity production for electrical units from solar and wind renewable energy. Eqs 1 – 5 describe the chemical reactions of sulphur adsorption, SMR, POX, ATR and WGS for H_2 production.

$$H_2 + S \leftrightarrow H_2S \Delta H \quad (1)$$

$$CH_4 + H_20 \leftrightarrow CO + 3H_2 \ = 206kJ/mol \quad (2)$$

$$CH_4 + 0.50_2 \leftrightarrow C0 + 2H_2 \ = -36kJ/mol \quad (3)$$

$$4CH_4 + 0_2 + 2H_20 \leftrightarrow 10H_2 \ + 4CO = -71kJ/mol \quad (4)$$

$$C0 + H_20 \leftrightarrow C0_2 + H_2 \ = -41.2kJ/mol \quad (5)$$

The electrolysis of H_2O for H_2 generation is an endothermic reaction because it involves ohmic heating (Joule heating). The method by which heat is generated due to electric current passing through semiconductors is called Joule heating. Alkaline electrolysis cells (AEC), solid oxide electrolysis cells (SOEC) and proton exchange membrane electrolysis cells (PEMEC) are the three main types of electrolysis of H_2O technology. All these H_2 production technologies use different operating temperatures, electrolytes and ionic gents (OH^-, H^+, O^{2-}). For example, AEC and PEMEC operate below 100°C and use potassium hydroxide (KOH) or sodium hydroxide (NaOH) electrolytes. Although SOEC uses an average temperature between 500 – 1000°C [9]. Low operating temperature of PEMEC and other advantages makes the electrolyser system more efficient and suitable for industrial application of green H_2 production [10]. Recent reviews of PEM electrochemical splitting of H_2O molecule to produce H_2 focus on the development of new catalysts. However, a PEMEC-assisted ATR was simulated to use O_2 by-product for partial combustion and reforming of syngas production [11]. In that study, PEMEC and pressure swing adsorption process (PSA) model were developed in Matlab, while ATR was simulated in Aspen HYSYS using Peng–Robinson equation of state solver. The simulated result shows that the levelised cost of hydrogen (LCOH) was reduced by 11.9% with the electrolysis method. However, *Kim, et al.* study does not include process simulation of other methods of hydrocarbon reforming to produce H_2, the use of renewable thermal energy and recovery of exhaust heat to produce electrolysis substrate (deionised H_2O). In addition, *Wang, et al.* investigation on energy-exergy analysis of combined LEMFC and SMR with 3:0 S/C ratio revealed that the electrolyser stages caused huge exergy destruction. The use of recovered thermal energy for steam production makes the work interesting [12]. Nonetheless, more equipment should be added to the hybrid system to improve the overall efficiency, and the studied work does not mention the source of thermal energy for the endothermic reaction of CH_4 and steam in the reformer. One of our previous works demonstrated the efficiency and environmental benefits of using solar thermal and electrical energy from the Rankine cycle in integrated pyrolysis and electrolysis of H_2O system for H_2 production. Although, hydrocarbon reforming and PEM electrolysis of H_2O were excluded from that study [13]. Eqs 6 – 8 are chemical reactions of H_2 conducting PEMEC.

$$\text{Anode: } 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad 6$$

$$\text{Cathode: } 4H^+ + 4e^- \rightarrow 2H_2 \quad 7$$

$$\text{Overall: } 2H_2O \rightarrow 2H_2 + O_2 \quad 8$$

Unlike a conventional furnace, which requires burning fossil fuels to produce thermal energy, CSP (concentrating solar power) converts solar energy into thermal energy (heat). The main types of CSP systems are parabolic dish concentrators (PDCs), parabolic trough collectors (PTC), solar energy tower (SET) and linear Fresnel collectors (LFC). Each of these systems uses thermal energy

storage (TES) to operate the Rankine cycle during the period of cloud cover. However, *Karimi, et al.* mentioned that among the four CSP systems, PDCs produce the most thermal energy and can achieve higher efficiency compared to others [14]. Installing any of these solar thermal systems in MENA (Middle East and North Africa) regions is another possible way to increase efficiency as MENA countries experience more sun during the day [15]. Despite the advantages of solar thermal energy production systems, small-scale applications and higher efficiency makes a photovoltaic (PV) system more attractive for the public. However, the low level of sunshine during the winter season in Western countries has shifted the focus to wind energy. Countries like the United Kingdom (UK) rely on offshore and onshore wind to achieve a zero-carbon emission target by 2050 [16]. Moreover, *Laha & Chakraborty*. concluded that the transition to wind energy (offshore) remains another means of decarbonisation without increasing upfront costs in areas where wind is available [17].

In summary, the review articles highlighted hybrid SMR and fuel cell for H_2 and electricity productions, combined ATR and PEMEC for ASU removal, efficiency improvements using recovered heat for generating steam reformer feedstock and use of O_2 by-product from electrolysis for partial combustion. Nonetheless, the studied works did not investigate process simulation of low-carbon hydrocarbon reforming coupled with PEMEC for efficiency improvement in most of the oil and gas exporting countries. Thus, this article focuses on integrated low-carbon hydrocarbon reforming processes coupled with PEM electrolysis of H_2O using renewable energy sources in oil and gas exporting countries. The proposed model also includes desulphurisation, the capture of CO_2 by-product, the application of the steam cycle and the assessment of environmental benefits in mitigating climate change. At present, there is currently no solar thermal, PV and wind turbine (WT) aided hydrocarbon reforming coupled with PEMEC system. Direct use of O_2 from the PEMEC stack to hydrocarbon reformers and combustors, absence of fossil fuels burning in the reformer furnace, use of recovered thermal energy to produce steam and distilled H_2O, electrical units powered by renewable energy sources and environmental assessments are advantages of this proposed model. This paper is structured as follows:

a. Hydrocarbon reforming processes combined with PEMEC to use O_2 from the PEMEC stack and efficiency improvement.
b. Heat recovery to produce steam and deionised H_2O.
c. Thermal energy from the sun for the endothermic reaction of feedstocks in the reformer.
d. PV or WT and Rankine cycle electricity for electrical equipment of the integrated system.
e. CO_2 capture with CaO adsorbent.

Fig. 1 displays a simplified diagram of solar and wind-assisted hydrocarbon reforming coupled with a PEMEC system.

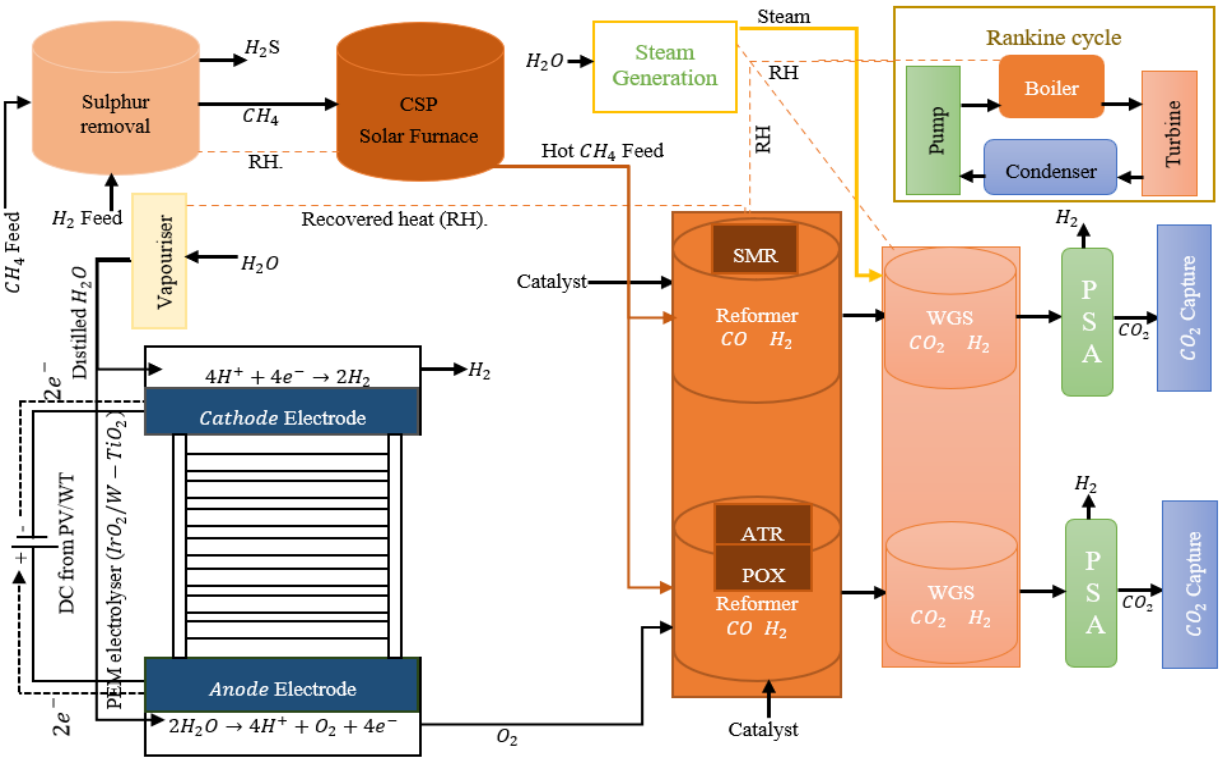


Fig 1: Schematic diagram of solar and wind aided hydrocarbon reforming coupled with a PEMEC system.

2. Material and simulation method

In this research work, CH_4 gas, air, H_2O and CaO were the selected list of feedstocks used for process simulation studies on SMR, POX, ATR, GH-ATR coupled with PEM electrolysis of H_2O for H_2 production. Aspen Plus software was used to simulate steam generation, endothermic and exothermic reactions of feedstocks for synthetic gas production and electrochemical dissociation of H_2O molecule into H_2 and O_2 gases. Mixed, Non-Random Two-Liquid (NRTL) and Peng-Robinson equation of states were substream and property methods used because of the presence of charged species during hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

Hydrocarbon reforming methods coupled with electrolysis of H_2O to produce H_2 fuel. Hydrogen sulphide (H_2S) was removed from the absorber, by reacting H_2 with sulphur present in the CH_4 feed as described in Equation 1. For instance, the sulphur content in CH_4 gas is about 5% [18]. While *Msheik, et al.* [19] affirm that a desulphurisation unit incorporated into the fossil fuel process of H_2 production is very important to reduce the early deactivation of the catalyst due to the deposition of sulphur on the active region. The SMR process involves feeding desulphurised CH_4 gas and steam from the vapouriser to a reformer to produce CO and H_2 syngas. While POX uses pure O_2 from the ASU for partial combustion of CH_4 gas in the combustor. This process is exothermic but requires thermal energy to produce synthetic gas. The ATR process is isothermal, and the reformer receives steam and O_2 from the steam generator and ASU for simultaneous reforming and oxidation reactions to produce syngas mainly of CO and H_2. This process is a combination of SMR and POX. In contrast to traditional ATR, GH-ATR allows the endothermic reaction of CH_4 gas and steam in one reformer and the exothermic reaction of CH_4 gas and O_2 in another combustor to produce CO and H_2 as by-products. A midstream unit such as WGS consisting of a high-temperature shift (HTS) and a low-temperature shift (LTS) converts CO from both reformers and combustors into CO_2 and increases the concentration of H_2 by adding steam from the vapouriser unit. Although, the upstream heat exchanger (HX) before and after the first temperature shift reactor allows proper control of CO and H_2 temperature. The downstream unit which is pressure swing adsorption (PSA) separates H_2 from CO_2 at high purity. Endothermic reforming, partial oxidation and exothermic reactions were simulated using Gibbs and stoichiometric reactors blocks. Using Gibbs and stoichiometric reactors blocks, the correct stoichiometries of reactants and products for reforming and shift reactions were obtained. The introduction of PEM electrolysis allowed recovered thermal energy from both the reformer and combustor to transform H_2O into distilled H_2O fed to the stack. Using a Gibbs reactor block with proper PEMEC chemical reaction described in equations 6 – 8 and using electricity instead of heat, a 2:1 ratio of H_2 and O_2 was obtained. PEMEC chemical reaction was set up in chemistry properties using Henry components. O_2 by-product of the PEMEC stack is fed into the combustor, eliminating the need for ASU, which is expensive to operate. Part of the thermal energy collected from the combustors and reformers was used to generate steam for the Rankine cycle.

CSP (parabolic dish concentrator (PDCs)), solar cells and wind turbine system (WT). The initial development for solar thermal, solar and wind turbine systems was done in SAM-NREL (System Advisory Model-National Renewable Energy Laboratory). The second development phase was carried out in Matlab where the SAM model algorithm was modified, added and simulated to achieve the operating requirements. Since Simulink can read a Matlab file, the simulation results of thermal and electrical energy models were saved as mat files for the Simulink model. In the Simulink environment, the thermal and electrical energy needed for the integrated system were connected, because Simulink allows interface with AspenOne. Thermal energy from the parabolic dish concentrator (PDC) and electrical energy from either a solar array or WT system were connected to the furnace block, PEMEC stack, pumps and other electrical units. Table 1 lists the main input parameters used in the modelling and simulation of PDCs, solar cells and wind turbine (WT) systems. Table 2 illustrates Aspen Plus blocks and material flows with descriptions.

Table 1. Design parameters for parabolic dish concentrators (PDCs), wind Turbine (WT) and solar cell (SC).

Parabolic dish concentrator (PDC)			
Parameters	**Value**	**Parameters**	**Value**
Heliostat, tower and receiver design parameters		**Working fluid properties**	
Design point DNI	950 W/m^2	Working fluid	CH_4
Solar multiple	2	HTF density	0.657kg/m^3
Heliostat width	2.2m	Flow rate of the working fluid	80.214kg/hr
Heliostat height	12.2m	Maximum mass flow rate of the working fluid	199.5kg/s
Heliostat mirror reflectance and soiling	0.9	**Thermal storage**	
Heliostat start up energy	0.025kW	Full load hour of storage	10 hrs
Receiver tube velocity	2.553m/s	Solar field hours of storage	3.3 hrs
Hot/loop exit HTF temperature	1050°C	**Heat transfer properties**	
Cold/loop intake HTF temperature	322°C	Tube outer diameter	40mm
Cycle thermal efficiency	0.4	Tube all thickness	1.25mm
Single heliostat reflective area	144.37 m^2		
Wind turbine parameters		**Solar cell parameters**	
Parameters	**Value**	**Parameters**	**Value**
Rated power	1.3MW	Rated power	1.3MW
Maximum cp	0.45	Array type	Roof mount
Cut-in wind speed	4m/s	Tilt	0°
Cut-off wind speed	25m/s	Azimuth	180°
Total system loss	18%	Total system loss	14%

Table 2: List of Aspen Plus unit operation model blocks and material streams description

Aspen Plus Block Name	Aspen Plus Block ID	Description
Mixer	MIX	Mix 2 streams.
Splitter	SPL/contains SPL	Split a stream into 2 or more streams.
Hierarchy	PEMEC/ASU	Container for directories. Act as a subsystem having a set of blocks that are grouped into a single hierarchy block. House RGibbs for electrochemical dissociation of H_2O into H_2 and O_2 with an ID name "PEMEC".
Heat exchanger	HX	Transfers heat from one medium to another. For waste heat recovery. For generating steam for WGS and steam turbine. To produce deionised H_2O.
Heater/Cooler	WH/HE/COOL/FURN/ DISTL	Thermal and phase state changer. For feed heating and product cooling.
Separator	PSA/H_2S-REM	Split/separate products based on specified flows/fractions. Separate H_2 gas from others.
Rigorous reactor (RGibbs)	SMR/ GH-ATR /WGS/ ATR/POX	Set the composition of product/syngas by chemical equilibrium restriction. Gibbs free energy reactor. To produce H_2 and CO. For H_2 and CO_2 production.
Turbine	STE-TURB	For electricity generation. Calculate pressure drop after work is done.
Pump	PUMB/REF-P/S-PUMP/PUMP-R	Increase feed pressure to the desired level. More effective in the liquid phase.
Aspen Plus stream ID		Description
FE		Feed.
CH_4-FE		Methane feed.

H_2-FE	Hydrogen (H_2) feed to adsorber.
H_2O/any stream that starts with H_2O	Water (H_2O) stream.
O_2/any stream that starts with O_2	Oxygen (O_2) feed to combustor and oxygen from PEMEC stack.
OTHER	Inert gas after O_2 separation.
SYN/any stream that start with SYN	Synthetic gas.
GH-ATR/ATR-FE-F/SMR-FE/POX-FE	Hot methane (CH_4) feed.
CELL-FE/any stream that start with CELL	Distilled or normal H_2O feed.
BY-H_2	Hydrogen (H_2) by-product.
BY-CO_2	Carbon dioxide (CO_2) by-product.

2.1 Process simulation of integrated hydrocarbon reforming (HR) coupled with PEMEC and steam cycle.

The production process for H_2 and other synthetic gases shown in Fig. 2 starts with the flow of pressurised CH_4 material into the adsorption column after absorbing heat from the heat exchanger 1 (HX-1). By allowing a chemical reaction between CH_4 gas H_2 in the column at an operating temperature of 350°C, hydrogen sulphide (H_2S) was formed and removed from the process. Pure CH_4 leaving the sulphur removal unit flows into the parabolic dish concentrators (PDCs) furnace to raise the temperature to 1050°C and dropped to 918°C after leaving HX-1. Since the reformer requires an operating temperature below 918°C, a feedwater heater (FWH) was introduced with a pure CH_4 exit temperature of 800°C. Since all hydrocarbon processes require desulphurised CH_4 feed to the reformer and combustor and the use of a PDCs furnace to heat the feedstock, a duplicate unit was incorporated to have all the upstream processes in a single unit. Duplicate block duplicated upstream units which consist of sulphur removal and PDCs furnace units with a reaction temperature of 800°C for pure CH_4 feed to reformers and combustors. The endothermic reaction of desulphurised CH_4 and H_2O_{gas} takes place in the SMR reformer producing CO and H_2 by-products. The syngas from the SMR reformer exhaust was used to preheat the steam for the SMR reformer and the WGS units. Unlike the SMR reformer, GH-ATR uses one reformer and one combustor. A split unit (spl-3) was added to allow the equilibrium flow of CH_4 from the duplicate unit to both the GH-ATR reformer and the combustor. Pure CH_4 gas leaving the duplicate unit was split into two for endothermic reaction with steam in the reformer and exothermic reaction or partial oxidation with O_2 from the ASU or PEMEC stack. Similar to SMR, thermal energy obtained from cooling the syngas leaving both the GH-ATR reformer and the combustor was used to transform H_2O into steam for the reformer and WGS units. The ATR process of using pure CH_4 gas from the duplicate unit allows steam reaction with O_2 or partial oxidation of O_2 in the same reformer to release CO and H_2 as by-products. In the reactor unit of POX, the exothermic reaction of pure CH_4 and O_2 produces synthetic gases mainly of CO and H_2. WGS units which consist of high and low temperature shifts have heat exchangers before and after the first shift reactions for conditioning the reactants' temperatures. The use of heat exchangers for cooling syngas between the two shift reaction units allowed more heat recovery for producing distilled H_2O for the PEMEC system. WGS reactors using CO catalyst converts the cooled product gases (CO and H_20_{gas}) into CO_2 and H_2 and H_2 gas get separated from CO_2 and other unreacted syngas in the PSA column. The operating temperature and pressure are kept at 800°C and 3 bar in all the reformers and combustors. Energy recovered from cooling syngas exiting WGS was also utilised for producing deionised H_2O. While by-product CO_2 from the PSA unit was captured by exothermic reaction with CaO to form $CaCO_3$ for geological or underground storage. Since the absence of ASU and increasing the H_2 production rate is still one of the goals of this study, the distilled H_2O generated through recovered heat was disassociated into O_2 and H_2 via electrochemical reaction in the PEMEC stack. However, ASU was included in this model because O_2 from the PEMEC stack was insufficient for the partial oxidation of CH_4 in GH-ATR, ATR and POX combustors. Pilot-scale development using a single hydrocarbon reforming method with its simulated PEMEC system does not require ASU for O_2 extraction from the air. To further maximise the overall efficiency of the hybrid system, a low steam cycle was added where part of the thermal energy recovered from the reformers and combustors was utilised. The Rankine cycle process for power generation involves the use of a pump to pressurise the H_2O feed to 41 bar before absorbing heat from a heat exchanger (HX-G). The hot pressurised steam from the HX-G drives a steam turbine to generate electricity at a discharge pressure of 2 bar. The low-temperature fluid (H_2O) that came out of the turbine after the work was done was condensed and recirculated for continuous operation.

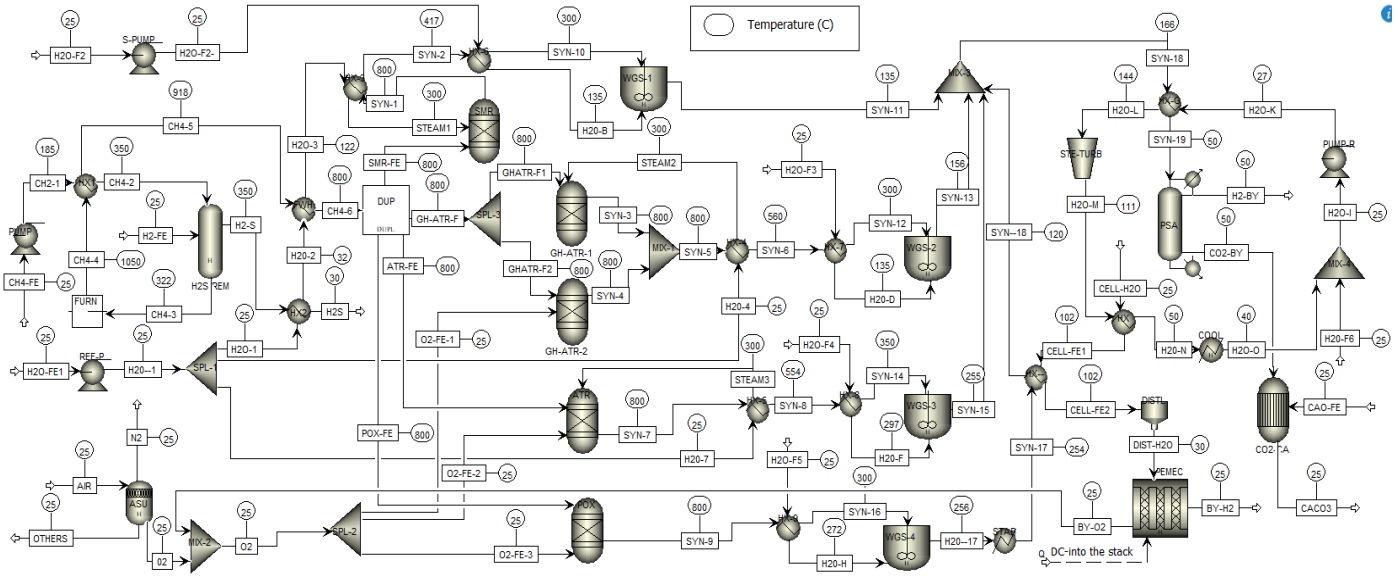


Fig 2: ASPEN Plus flow diagram for integrated hydrocarbon reforming processes coupled with PEMEC system.

Since the development of parabolic dish concentrators (PDCs), solar cells and wind turbines (WT) to generate thermal energy for reformers and combustors, and electrical power for PEMEC stack and other electric units is limited in the Aspen Plus, the integrated system as shown in Fig. 2 was transformed into flow-driven for the Simulink interface. As displayed in Fig. 3, desulphurised CH_4 feed from the sulphur removal column flows to a PDCs furnace with an exit temperature of 1050°C for endothermic and exothermic reaction in both the reformer and the combustor to produce synthetic gas mainly of CO and H_2. Unlike reformer and combustor that utilises heat for chemical reactions, solar panels (SPs) and wind turbine (WT) systems produced the electricity needed to operate the electrical equipment of the hybrid system such as the PEMEC stack. One of these renewable electricity generation sources can be connected to an integrated system, depending on the sources available at the point of use. The working fluid of the combined system is desulphurised CH_4 gas. In the Simulink environment, thermal energy from the PDCs furnace was connected to the heater, and electricity was also connected to the PEMEC stack. Further distribution of electricity to other electrical units can be done in practice because the purpose of this study is to demonstrate how this integrated system can function as a single unit for low carbon emissions in H_2 production plant.

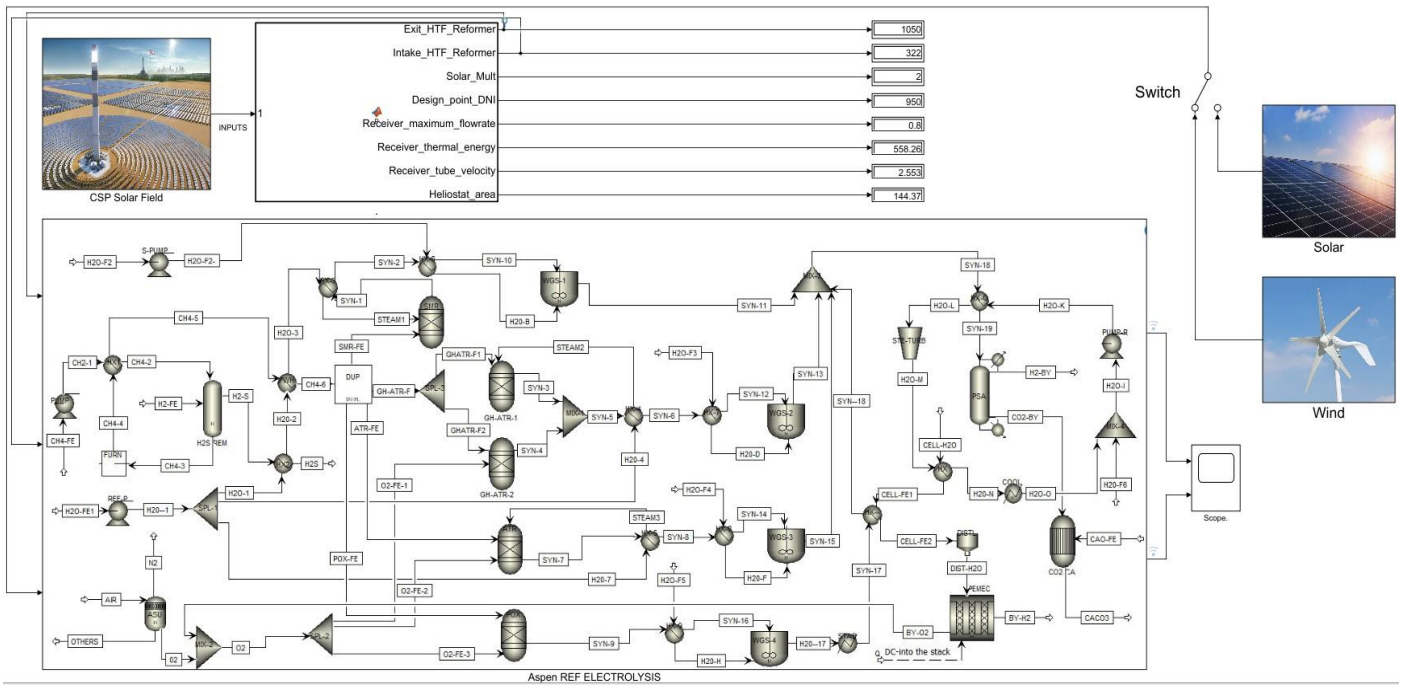


Fig 3: Integrated hydrocarbon reforming processes and PEMEC driven by PDCs, Solar cells and Wind turbine energy.

3.0 Results and Discussions

In the integrated system, low-temperature electrolysis of H_2O was adopted to produce O_2 feed for the GH-ATR, ATR and POX hydrocarbon reforming processes, as shown in Table 3. The SMR process of producing H_2 gas demonstrated the benefits of adding a PEMEC system utilising recovered heat to produce distilled H_2O feedstock to the stack. The absence of O_2 feedstock in the SMR process reduces the syngas conversion efficiency at 800°C operating temperature. However, the SMR method outperforms other hydrocarbon reforming processes by producing the highest and lowest H_2 and CO_2. In contrast to the SMR process, GH-ATR which uses a reformer and combustor achieves a lower syngas production efficiency. Nonetheless, the CO_2 by-product of GH-ATR is lower than that of POX and ATR systems. The use of O_2 feedstock and recycled heat from the combustor for preheating H_2O into steam and deionised H_2O for both WGS and PEMEC feedstocks make the process more attractive than SMR. This eliminates the need for ASU to generate O_2 feedstock in the integrated system. Among all the simulated hydrocarbon processes, ATR achieved the lowest syngas conversion efficiency, while POX generated the highest CO_2 by-product due to the absence of steam in the combustor. Each of the simulated models emits below $4kg_{CO_2}/H_2$. To ensure that the integrated system does not release carbon emissions into the environment, 1019.69kg of CaO was utilised to capture the entire CO_2 produced. With the exothermic reaction of CO_2 by-product with 1019.69kg of CaO, 1819.95kg of $CaCO_3$ was formed and ready for transportation and storage. Comparison of this proposed model with *Antzara, et al.* using lower reformer operating temperature and pressure achieved nearly the same steam to carbon (S/C) ratio (3:1) [20].

Table 3: Feed and product results of integrated hydrocarbon reforming coupled PEMEC processes of H_2 generation.

Streams		SMR		GH-ATR		ATR		POX		PEMEC	
		Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product
H_2O	$(kmol/hr)$	7.9		6.5		4.5		5		10	
	(kg/hr)	142.56		116.3		81		90.1		180.2	
CH_4	$(kmol/hr)$	5	1.05	5	0.52	5	0.25	5	8.7e-11		
	(kg/hr)	80.21	16.75	80.21	8.4	80.21	4.02	80.21	1.4e-09		
O_2	$(kmol/hr)$			2.5		2.5		5.04			5
	(kg/hr)			80		80		161.3			160
Sulphur	$(kmol/hr)$	0.25		0.25		0.25		0.25			
	(kg/hr)	8		8		8		8			
H_2	$(kmol/hr)$	0.25	15.8	0.25	15.4	0.25	14	0.25	15		10
	(kg/hr)	0.5	31.9	0.5	31.1	0.5	28.2	0.5	30.23		20.2
CO_2	$(kmol/hr)$		3.96		4.5		4.8		5		
	(kg/hr)		174.1		197.1		209		220.1		
H_2s	$(kmol/hr)$		0.25		0.25		0.25		0.25		
	(kg/hr)		8.52		8.52		8.52		8.52		
CaO	$(kmol/hr)$	3.96		4.5		4.8		5			
	(kg/hr)										

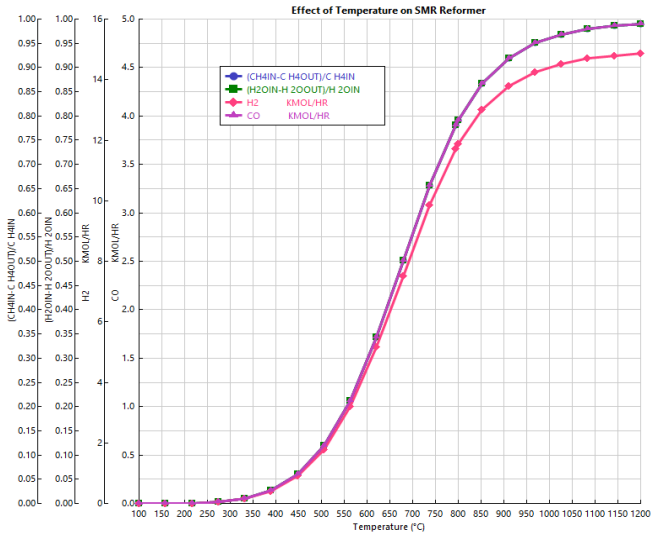
Assessment of thermal and electrical energy for the hydrocarbon reforming methods.

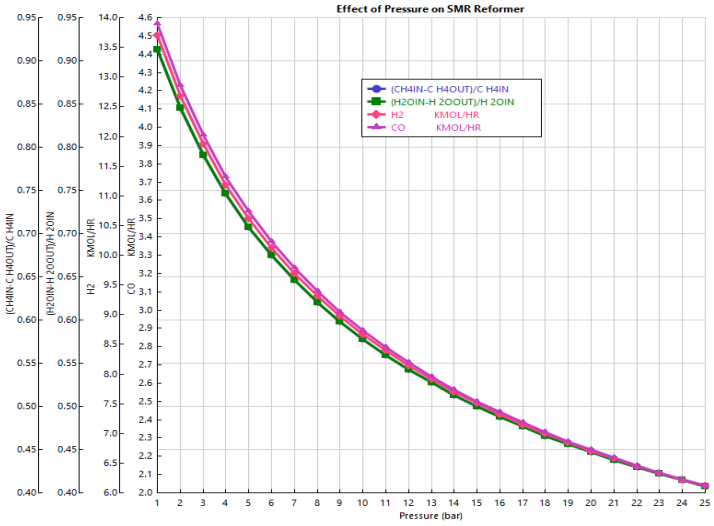
SMR: At a solar furnace operating temperature of 1050°C, the reformer requires 275.2kWh (990793.4kJ/h) under actual ideal reaction conditions (800°C and 3 bar temperature and pressure). 18.2kWh (65,847.4kJ/h) is calculated as the amount of heat (thermal energy) needed to operate the steam evaporator. The WGS exothermic reaction releases 16.9kWh (60857.6kJ/h), which is then used to produce distilled H_2O and steam for the Rankine cycle. Thus, a parabolic dish concentrator (PDCs) furnace operating at 1050°C requires a heat output of 364.4kWh (1311844.5kJ/h) to operate the system at design conditions, due to the endothermic nature of

the upstream reaction. GH-ATR: Similar to the SMR method, a reformer with a PDCs furnace operating temperature of 1050°C requires 131.2kWh (472385.97kJ/h). 39.95kWh (143858.5kJ/h) is needed to operate the steam generator. Under ideal design conditions for this system, the required heat output for a PDCs furnace operating at 1050°C is still 242.1kWh (871448.2kJ/h). ATR: Distinct from both the SMR and GH-ATR, the combustor operating at 800°C and 3 bar temperature and pressure under the same PDCs furnace temperature (1050°C) of the working fluid, releases heat. However, 30.7kWh (110451.9kJ/h) is still necessary for the operation of the steam evaporator. Therefore, the heat requirement of a PDCs furnace operating at 1050°C is 101.6kWh (365655.6kJ/h) for the proposed system to operate under the actual design operating conditions. POX: The integrated combustor of the PDCs furnace operating at 1050°C requires no heat due to the exothermic nature of the reaction. However, the steam vapouriser for WGS units requires 75.4kWh (271578.7kJ/h) to reach the designed operating temperature. Thus, for the operation of the hybrid system under the design conditions, the heat output of the solar thermal furnace can be 146.3kWh (526782.4kJ/h). PEMEC: About 0.8MWh direct current (DC) is needed to operate the cell stacks. Whereas 24.5kWh (88116.4kJ/h) of heat input is required to produce deionised H_2O feed to PEMEC stacks. Each hydrocarbon reforming method requires 9.5 kWh of electricity to operate both CH_4 and H_2O feed pumps. The electricity input to PSA is excluded because the brake power/heat duty is in negative value. Although, between 0.2 - 0.34 kWh/Nm^3 biogas electrical energy demand for PSA operation was reported by *Kohlheb, et al.* [21]. The exothermic capture of CO_2 with CaO for the entire process releases 904.5kWh (3257728.81kJ/h) under ambient and atmospheric operating conditions. Despite achieving the lowest syngas production, the ATR process remains the most affordable hydrocarbon reforming process that can be combined with PEMEC, CSP, solar cells and wind turbine systems for oil and gas exporting countries.

Sensitivity analyses on reforming and combustion temperature and pressure.

A reaction temperature and pressure between 100 - 1200°C and 1 - 25 bar were used to analyse the temperature and pressure effects on SMR syngas production. At temperature < 400°C, the syngas production rate was relatively low due to the endothermic nature of the reforming process. The rate of gas production increases as the reforming temperature increases which indicates that higher temperature favours endothermic reactions. On the other hand, an increase in pressure decreased the syngas formation rate, which also confirmed that high pressure is unfavourable for endothermic reactions. Similar observations of both temperature and pressure effects on syngas formation were reported by *Shehzad, et al.* [22]. The endothermic reaction of ATR feedstock follows the same trend as SMR. On the other hand, the increase in temperature and pressure does not affect the exothermic reaction of O_2 feedstock to both ATR and GH-ATR. However, higher and lower combustion temperatures and pressures favour the oxidation of CH_4 in the combustor, despite the exothermic nature of the reaction. Partial oxidation (POX) follows the same trend as the exothermic reaction of O_2 and CH_4 in the combustion chamber. However, the lack of increase in syngas formation from temperature rise and pressure drop, as shown in Fig. 4, was due to the use of a CSP furnace to preheat the POX feedstock (CH_4). Despite the exothermic nature of POX, GH-ATR and ATR, thermal energy is still needed to achieve partial oxidation and reforming to produce CO and H_2. The effect of pressure and temperature analyses of hydrocarbon reforming processes on feedstocks conversions in this study follows a similar trend reported by *Chehade, et al.* [23].





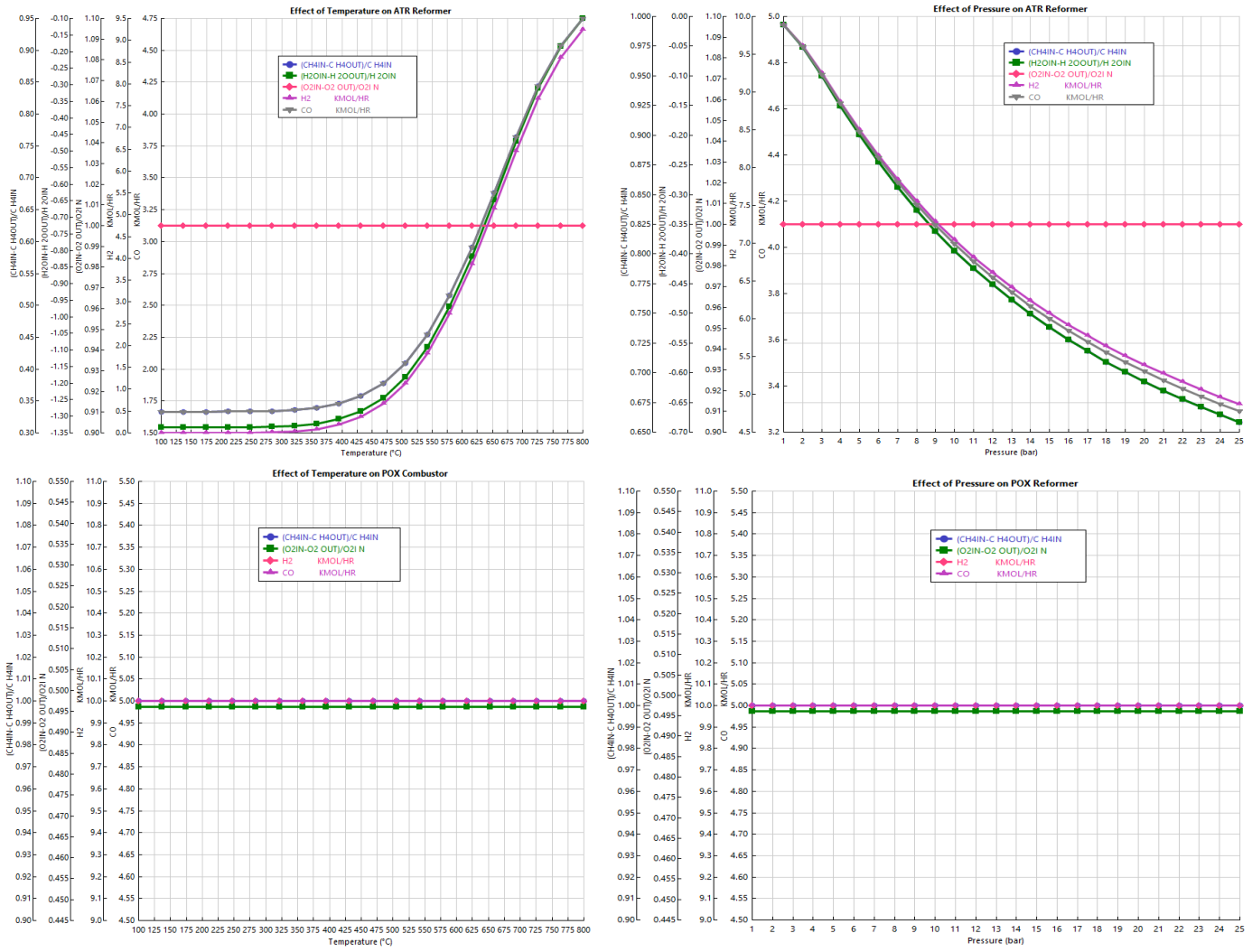


Fig 4: Temperature and pressure effect on hydrocarbon reforming processes coupled with parabolic dish concentrators (PDCs)

Environmental impact and economic analyses

This study examines the carbon emissions associated with different power plant technologies and compares them to this proposed model. For instance, 12.3kg_{CO_2}/kg_{H_2} is released in a nuclear thermochemical water-splitting plant. A coal gasification plant emits 12.2kg_{CO_2}/kg_{H_2}. While wind and solar carbon emissions range from 0.97 to 2.4kg_{CO_2}/kg_{H_2} during construction and are considered the lowest [24]. The low carbon emissions of solar and wind make both systems an alternative to fossil fuel power plants. However, the intermittency of both systems (they cannot always generate energy continuously at every moment of the day) is still a major disadvantage. The combustion of natural gas to generate energy has been adopted due to lower emissions compared to other fossil fuels. For example, between 420 – 480$gCO_{2_{eq}}/kWh$ and 570 - 750480$gCO_{2_{eq}}/kWh$ are emitted by both natural gas-fired combustion turbine (CT) and combined-cycle (CC) systems [25]. The use of H_2 fuel in power plants has drawn attention to the fact that the application of fuel cells, H_2O, electricity and heat are the only by-products. Given that a significant amount of H_2 is produced by fossil fuels methods such as conventional SMR, almost 13.7kg CO_2 (equivalent) per 1kg of H_2 by-product is released from any of these processes [26]. In addition, *Spath & Mann.* reported that the volume of natural gas needed to produce a kilogram of H_2 is about 159.6MJ [27]. While 4kg of CH_4 produces about 1kg of H_2 and 1kg of CH_4 releases 50MJ (LHV). However thermal decomposition of 4kg of CH_4 to release 1kg of H_2 requires 9.5kW (34.1MJ). Burning fossil fuel to produce 34.1MJ thermal energy releases 2.3kg of CO_2 emissions. Similar to the decomposition of CH_4 feedstock, approximately 9kg of H_2O is required to produce another kilogram of H_2 accounting for 45kW (162MJ) heat duty. A kilogram of H_2 production under thermal decomposition of H_2O method, produces about 10.7kg of CO_2 emission. Each of these estimated CO_2 emissions related to the thermal decomposition of both CH_4 and H_2O feedstocks exclude the purification and pressure changer units. As for renewable H_2 production methods such as H_2O electrolysis and biophotolysis, the high cost of H_2 selling price and low efficiency slow down the H_2 production rate. For example, between \$5.10/kg - \$10.3/kg H_2 sale price for both electrochemical H_2O separation and biophotolysis processes were

reported in the published article [4] [5]. Similar to conventional hydrocarbon reforming methods, below \$2.9/kg H_2 selling price is expected from any of the integrated systems operating with PEMEC. This is possible because more than 60% of H_2 production came from reforming methods and most of the oil and gas exporting countries are MENA (Middle East and North Africa). For example, \$0.07/kWh cost of electricity from CSP systems operating in Dubai (DEWA IV) was reported by *Lilliestam & Pitz-Paal.* [28] which is cheaper than another CSP operating in China with an electricity price of \$0.14/kWh [29]. Other researchers have mentioned that the energy costs of a CSP system are further reduced during the rainy season. For instance, during seasonal variations analysis of solar energy, it was found that the absence of dust from the solar mirrors due to continuous rain increases the absorption efficiency despite high sunshine during the summer season [30].

The role of proposed systems in reducing the carbon emission footprint of oil and gas exporting countries.

Since most of the oil and gas exporting countries have long periods of sunshine during the day, the volume of CO_2 emissions in any of these countries should be relatively low. However, carbon emissions in each of these countries have increased. For example, *Mirzaei & Bekri*. [31] reported a sixfold annual increase in CO_2 emission because of an increase in electricity demand in Iran, averaging 6.3% per year. Unlike hydrocarbon reforming methods which release or capture about 13.7kg of CO_2 per 1kg of H_2 by-product, the developed model aims to minimise the volume of CO_2 by-product by eliminating the burning of fossil fuels in a reforming furnace. The proposed scheme to reduce CO_2 emissions without compromising efficiency as shown in Fig. 5 includes:

- Electricity generation locally through solar panels and wind turbine systems, depending on the sources available.
- Feed-in-tariff (FIT) when excess electricity is generated locally.
- Grid electricity production from concentrating solar power (CSP) system during the daytime and with thermal energy storage (TES).
- The use of H_2 fuel from the proposed model to generate electricity using PEM fuel cells when solar or wind are unavailable.

The proposed idea as displayed in Fig. 5 will not only reduce carbon emission footprints but will also increase overall efficiency by reducing transmission losses. Furthermore, the application of this proposed model will reduce the volume of CO_2 by-product, CH_4 or natural gas feedstock to H_2 production plants (hydrocarbon reforming systems) and the burning of natural gas in grid power plants.

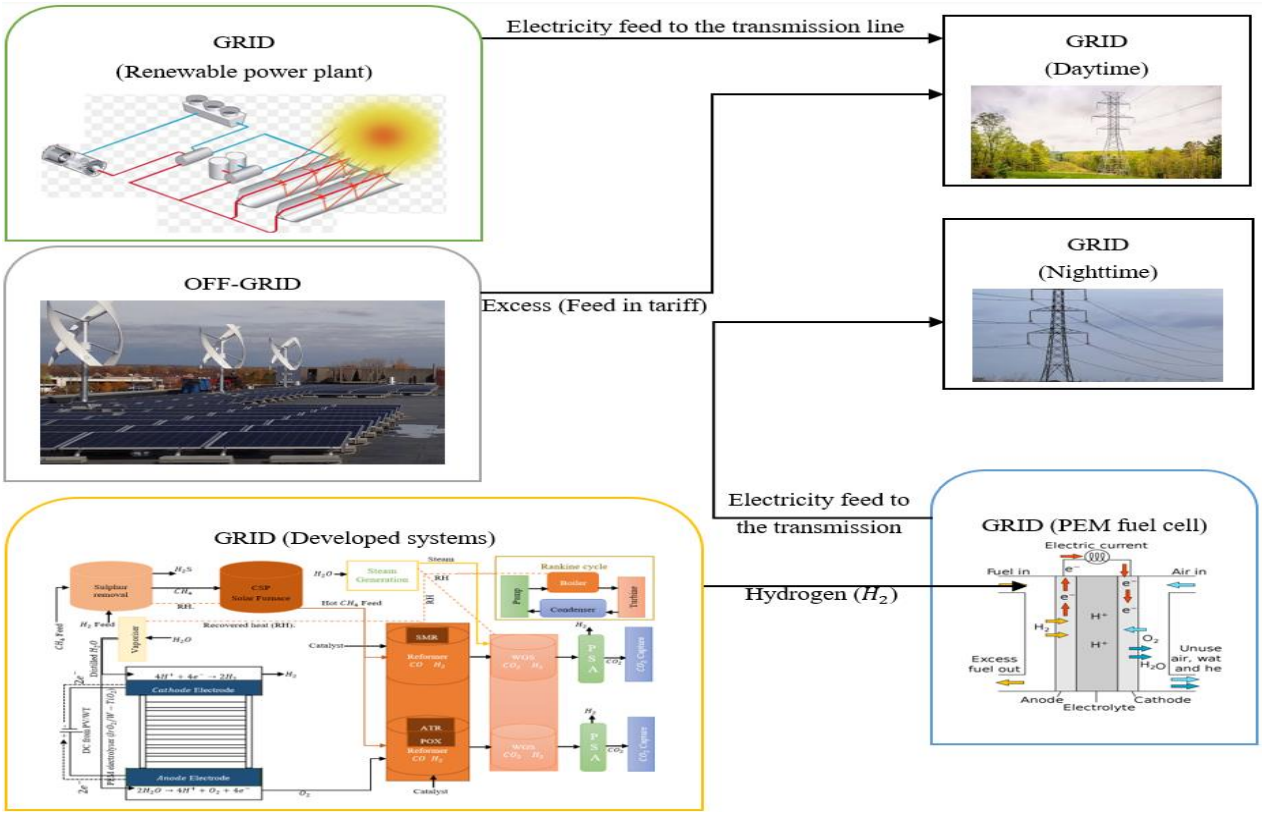


Fig 5: The role of proposed systems in reducing the carbon emission footprint of oil and gas exporting countries.

Conclusion

Integrated hydrocarbon reforming and PEMEC systems using solar and wind energy have been developed and simulated to reduce carbon emission footprints in oil and gas exporting countries. The SMR operating with PEMEC shows the highest H_2 production. However, the heat duty was the highest among the other reforming methods. The lowest heat duty and H_2 production rate was recorded in the ATR method. The introduction of PEMEC shows that the need for ASU for O_2 production is not necessary for GH-ATR, ATR and POX. The application of thermal energy recovery to operate the downstream units improves the overall efficiency with a H_2 selling price below $2.9/kg. Minimal greenhouse gas emissions were achieved using solar and wind energy sources and the exothermic capture of CO_2 by-product with CaO, which releases 3257.73MJ/h of thermal energy. The proposed system with the integration of fuel cells can replace fossil fuel combustion in a power plant when both sun and wind are unavailable. To reduce carbon emissions in oil and gas exporting countries, off-grid renewable energy generation and feed-in tariff (FIT) are recommended when both solar and wind power are available. Hydrocarbon reforming method releases between $9kg_{CO_2}/kg_{H_2}$ – $13kg_{CO_2}/kg_{H_2}$, while each of the proposed systems emits <$4kg_{CO_2}/kg_{H_2}$ which was captured. Therefore, simulated innovation models recommend pilot-scale development to achieve low greenhouse gas emissions in oil and gas exporting countries with long sunny days.

CRediT authorship contribution statement

Linus Onwuemezie: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing – Original Draft. **Hamidreza Gohari Darabkhani:** Methodology, Software, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Supervision, Project administration.
Morteza Montazeri: Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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