Small-Scale Biohydrogen Production from Integrated Dark Anaerobic Fermentation, Microbial Electrolysis-Fuel Cells and Electrolysis of Water Powered by Renewable Sources.

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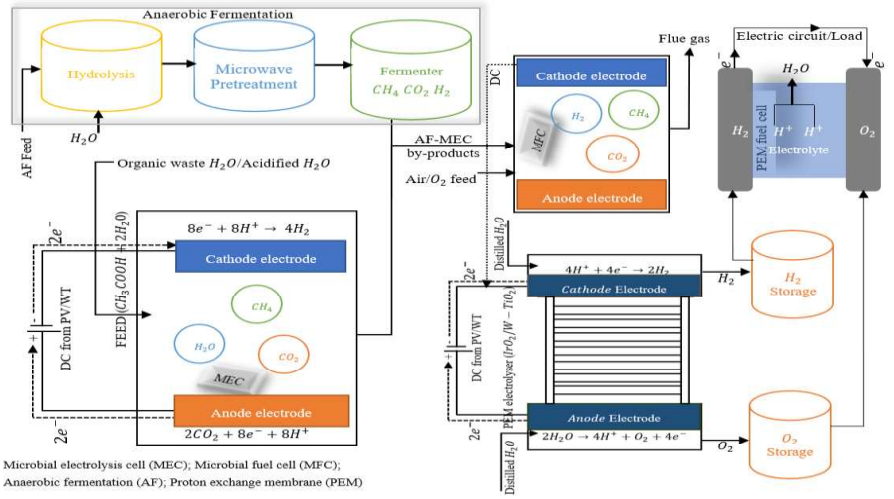
HIGHLIGHTS

- Anaerobic fermentation, microbial and H_2O electrolysis cells are presented.
- Microbial and H_2 fuel cells are introduced.
- The overall energy efficiency of the proposed system is expected to reach 68.6%.
- H_2 selling price is <$5/kg and >10% efficient than li-ion batteries.

GRAPHICAL ABSTRACT



Abstract

Small-scale biohydrogen production is a promising option to reduce GHG emissions for a sustainable economy. For this reason, an integrated AF, MEC and MFC coupled with electrolysis of H_2O and H_2 fuel cell was developed. The integrated system uses a microwave oven, solar and wind renewable energy sources for digestate pretreatment and to power electrical units. The results show that thermal pretreatment of AF digestate facilitated enzymes' activities, while the highest energy efficiency recorded in MFC was attributed to the use of AF-MEC by-products as feedstock. The MFC-generated electricity in addition to solar or wind energy systems reduced the overall cost by eliminating AF-MEC separation and purification units for biohydrogen recovery. PEMEC-powered renewable energy sources produced both H_2 and O_2. While the application of PEMFC generated electricity for the developed system in the absence of wind speed >4m/s and sunlight. Energy efficiency >68.6% and H_2 selling price <$5/kg which is cheaper than single electrolysis of H_2O unit were recorded with minimal CO_2 emission. By-product CO_2 capture is recommended for an increase in electricity production from MFC. In terms of service life and energy required for manufacturing, this developed system for energy conversation and storage outperforms li-ion batteries with >10% efficiency.

Keywords:

Solar cell and wind turbine systems

Microwave oven pretreatment

Mixed culture fermentation

Proton exchange membrane electrolyser and fuel cells

Biohydrogen production

Biohydrogen utilisation

Nomenclature

Abbreviations and Symbols

%	Percentage
°C	Degrees Celsius
e^-	Electron
H^+	Proton
OH^-	Hydroxide
pH	Power of hydrogen
AD	Anaerobic digestion
AEC	Alkaline electrolysis cell
AF	Anaerobic fermentation
CI	Conventional inert
COD	Chemical oxygen demand
CSTR	Control stirred tank reactor
DF	Dark fermentation
Eq/Eqs	Equation/Equations
FC	Fuel cell
GHG	Greenhouse gas
HX	Heat exchangers
HRT	Hydraulic retention time
kW	Kilowatt
m^2	square metre
m/s	metre per second
MEC	Microbial electrolysis cell
MFC	Microbial fuel cell
NREL	National renewable energy laboratory
NRTL	Non-random two-liquid
OLR	Organic loading rate
PEMEC	Proton exchange membrane electrolyser cell
PEMFC	Proton exchange membrane fuel cell
PSD	Particle size distribution
SAM	System advisor model
SOEC	Solid oxide electrolysis cell
TS	Total solid
VFAs	Volatile fatty acids
VS	Volatile solid
W/m^2	Watt per square metre

1.0 Introduction

Small-scale renewable methods of hydrogen (H_2) production close to the point of use remain the best alternative ways of minimising carbon dioxide (CO_2) emission and transportation issues in contrast to large-scale fossil fuel production processes. To replace the existing fossil fuel processes that are not sustainable in the long term, H_2 production and utilisation mechanisms by nature through varieties of strict aerobic and anaerobic to photosynthetic enzymes have been investigated by many researchers. While special enzymes called hydrogenases are required to initiate the mechanisms of using microbes in biohydrogen production [1]. These microbes responsible for catalytic activities to produce H_2 under ambient temperature and atmospheric pressure conditions with low overpotential contains nickel and iron [NiFe] [2]. The main types of hydrogenase protein are FeFe with an iron deposit in the active site, NiFe with a heterobimetallic active site and Fe for oxidation-reduction of feedstock. Among the listed types of hydrogenase protein, exposure to oxygen (O_2) affects NiFe the most and these catalytic mechanisms remain inapplicable in biotechnological applications [3] [4]. Another small-scale pathway to minimise the share of fossil-based methods of producing H_2 is the electrolysis of water (H_2O) due to their higher efficiency and the use of renewable energy sources. This renewable electrochemical method of producing H_2 is considered energy-intensive and requires off-grid electricity to reduce the load on the national grid transmission network. For these reasons, solar and wind powered anaerobic fermentation (AF) and microbial electrolysis cell (MEC) together with microbial fuel cell (MFC) and electrolysis of H_2O remain an attractive route to a small-scale H_2 production. The AF method of utilising microbes to initiate the catalytic activities of biodegradable feedstock requires the removal of methanogenesis reactions to produce synthetic gas. Unlike dark fermentation (DF) which produces H_2 because of the oxidation of carbohydrate-rich substrates in two chemical reactions that release the required activation energy for proton and electron neutralisation reaction, AF chemical reaction pathways involve hydrolysis, acidogenesis and acetogenesis [5]. Similar to the anaerobic digestion (AD) pathway to produce biomethane, hydrolysis is the rate-limiting step as written in Eq (1) and acidogenesis utilises hydrolysed feedstock to amino acids as represented in Eq (2). The biohydrogen production pathway which is acetogenesis as expressed in Eq (3), employs acetic acid enzymes to produce acetate by organic acid, CO_2 and H_2 [6]. Biohydrogen production from AF uses various feedstock such as organic matter and is considered a simple process. On the contrary, the main challenges of this process are low H_2 yield and higher volatile fatty acid (VFA) formation due to enzymes' inability to degrade organic matter. For instance, *Wang, et al.* [7] reported additional rancidity that slows down microbial activity in bioconversion due to excess salt and oil in feedstocks like food waste (FW). Although, *Kondusamy & Kalamdhad.* [8] study shows that the use of feedstocks such as young vegetative plants and the small size of animal soil residues in biodegradable H_2 production pathways can minimise the amount of VFA by-products. Nonetheless, a decrease of VFA amount and pH value during thermophilic pretreatment of AD feedstocks was mentioned by *Zhang,*

et al. [9]. Thus, the mixture of FW and other organic matter feedstock has been suggested for the efficiency improvement of AF in biohydrogen production [7]. For example, the co-fermentation study of biohydrogen production with a 90:10 mixture ratio of FW and Garden waste (GW) feed improves the overall efficiency by up to 82% [10]. However, the use of single GW feedstock in AF resulted in a low biohydrogen yield because of the higher content of carbohydrates like cellulose and hemicellulose [11]. Other factors affecting the effectiveness of the AF method for biohydrogen production include total solid (TS), volatile solid (VS), hydraulic retention time (HRT), organic loading rate (OLR), and temperature. As mentioned by *Hajizadeh, et al.* [12] in the OLR and HRT sensitivity analysis studies, increasing the feed rate of the AF digester above $1l/kg$ can affect biogas formation. While *Jain, et al.* [13] reported an increase in biogas production at pH values between 6.5 - 7.5 due to improved activities of microorganisms in the fermenter. The cost of separation and purification of biohydrogen can further decrease the overall efficiency of the AF process. To overcome this limitation and disadvantages by improving the efficiency of the AF, it may be necessary to combine MEC, MFC and electrolysis of H_2O as a single unit.

$$\text{Hydrolysis} + H_2O \rightarrow C_2H_4O_2 + C_2H_5NO_2 + C_2H_6O + C_3H_6NO_2S + C_3H_7NO_2 + C_3H_7NO_3 + C_3H_8O_3 + C_4H_7NO_4 + C_3H_8O_3 + C_4H_9NO_3 + C_5H_4O_2 + C_5H_9NO_2 + C_5H_9NO_4 + C_5H_{10}O_5 + C_5H_{11}NO_2 + C_6H_{13}NO_2 + C_6H_{14}N_4O_2 + C_9H_{11}NO_2 + C_{16}H_{34}O + C_{18}H_{34}O_2 + CO_2 + CH_4 + H_3N + H_2S + H_2O \quad (1)$$

$$\text{Acidogenic microbes consume amino acid and hydrolysis by} - \text{products} \rightarrow C_2H_4O + C_2H_4O_2 + CH_3NO + C_3H_6O_2 + CH_4S + C_4H_8O_2 + C_5H_7NO_2 + C_5H_{10}O_2 + C_6H_6 + C_6H_6O + C_8H_7N + H_3N + CO_2 + H_2 + H_2S + H_2O \quad (2)$$

$$\text{Acetogenic microbes consume acidogenic by} - \text{products} \rightarrow C_2H_4O_2 + C_3H_6O_2 + C_5H_7NO_2 + CO_2 + CH_4 + H_2 + H_3N \quad (3)$$

A microbial electrolysis cell (MEC) uses wastewater as feedstock with an applied voltage between 0.2V - 0.8V to promote the activities of exoelectrogens' microorganisms for biogas (H_2, CH_4 and CO_2) production. The MEC system has an efficiency between 72 - 91% and requires a membrane separator in a single chamber [14]. The high cost of single-chamber MEC was reported as one of the drawbacks and the use of mixed-culture MEC producing methane (CH_4) as one of the by-products was proposed by [15]. In addition, an integrated AD-MEC has also been suggested to enhance the biogas production rate. For example, an increase in biosyngas production by integrating MEC into AD was reported because of the transfer of exoelectrogens to the fermenter. However, combining AD and MEC to promote the biosynthetic conversion may require further research as *Lee, et al.* [16] reported a decrease in biosyngas formation after a third cycle. A microbial fuel cell (MFC) on the other hand uses a variety of wastewater feedstock and replaces metal catalysts with microorganisms such as exoelectrogens bacteria to convert stored chemical energy into bioelectric current at ambient temperature. With the application of the MFC system in wastewater treatment plants, approximately ninefold which is about 13kJ/g COD can be recovered. The recovery of this stored chemical energy in wastewater means that a minimal electrical energy input may be required for H_2O recycling [17] [18]. A PEM (proton exchange membrane) based MFC consists of one and two compartments with electron carriers such as NADPH, NADH or cytochromes. The lack of O_2 feed in a single chamber because of the exposure of the cathode chamber to the atmospheric air reduces the complicity and design cost in contrast to mixed-cultured units [19]. Up-flow MFC uses polyacrylic plastic and involves the feeding of pressurised wastewater into a stack base leaving the exit of the effluent at the top. The up-flow MFC type of electricity generation increases the overall input energy because of the involvement of a pressure changer like pumps or compressors. However, the upstream MFC may play an important role in the future, as this design has achieved a faster conversion of wastewater to electricity compared to other types of MFCs [20]. Other types of MFC are stacked and paper which exhibits higher COD removal and conversion efficiencies, chemical resistance, economic effectiveness and recyclability [21] [18]. While an efficiency between 26.8% - 91% in annular single-chamber MFC configured with meshed stainless steel and anode coated-graphite was reported by *Mardanpour, et al.* [22]. In general, the insensitivity of the operating environment, electricity production at lower operating temperatures and locations with limited electricity are the advantages of MFC [23]. Despite the merits of MFCs, limited efficiency and high cost of configuration or design limit commercialisation. As MFC is proficient in H_2O treatment plants to reduce the overall cost, integration with AF and electrolysis of H_2O systems powered by renewable sources can be beneficial. For instance, a MFC can utilise AF by-products to generate part of the required input electrolysis stack electricity and eliminate the need for AF membrane separator. Eqs $(4-6)$ represent the electrochemical reaction pathways of MEC in syngas production. While the electrochemical oxidation of acetate to release electron and cathode reduction reactions to the electron acceptor in MFC are described in Eqs (7) and (8).

$$CH_3COOH/C_2H_4O_2 + 2H_2O \rightarrow 2CO_2^- + 8H^+ + 8e^- \ (Anode) \quad E^0 = -0.28V \ vs \ SHE \ \text{(standard hydrogen electrode)} \tag{4}$$

$$2CO_2^- + 8H^+ + 8e^- \rightarrow 4H_2 \ (Cathode) \quad E^0 = -0.24V \ vs \ SHE \tag{5}$$

$$CH_3COOH/C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad E^0 = -0.52V \ \ (Overal) \tag{6}$$

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \ (Anode) \tag{7}$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- (Cathode) \tag{8}$$

Renewable energy sources such as solar and wind integrated with AF and MFC to produce H_2 for continuous power generation at low wind speed and at night can replace battery energy storage in small-scale applications with minimal carbon emission footprints. For example, a comparison of H_2 and battery grid storage shows that batteries like lithium-ion (li-ion) can reach an efficiency of 0.83 which is higher than the 0.3 efficiency of a regenerative H_2 fuel cell (RHFC). However, comparing the efficiency of the battery with RHFC as a reference to the service life and required energy for manufacturing, RHFC can reach an efficiency of 56% which is higher than 35% for li-ion batteries. Efficiency improvement of fuel cells has been suggested to compete with batteries in the energy storage market. Nevertheless, RHFC can achieve the same efficiencies as li-ion batteries by storing excess electricity during low demand [24]. Despite the high efficiency (~90%) of batteries, short life-span (about 8.5 years), degradation, leakage, disposal issues and high costs place biohydrogen production and utilisation the best alternative option for small-scale units [25] [26]. In the electrolysis of H_2O, H_2 is produced in the cathode chamber and O_2 in the anode chamber as by-products by the usage of electricity to separate H_2O. The electrolysis of H_2O for H_2 production with the absence of CO_2 by-product requires the use of DC from either renewable energy sources such as solar, wind or MFCs. The three major types of electrochemical splitting of H_2O molecule to produce H_2 are alkaline electrolysis cell (AEC), solid oxide electrolysis cell (SOEC) and proton exchange membrane electrolysis cell (PEMEC). Different operating temperatures, electrolytes and ionic agents (OH^-, H^+, O^{2-}) are used to produce H_2 from all these H_2O electrolysis technologies. For instance, AEC and PEMEC operate below 100°C temperature and use potassium hydroxide (KOH) or sodium hydroxide (NaOH) and proton-conducting polymer membrane electrolytes. While SOEC operates at intermediate temperatures ranging from 500°C - 1000°C [27]. Compared to other H_2O electrolysis types, PEMEC is advantaged for small-scale applications because of larger current density, response time, compactness and low operating temperature [28]. Not long ago, solar-assisted PEM electrolysis of H_2O to produce H_2 was developed using triple-junction solar cells and the result shows that a peak efficiency of 31% can be reached. However, due to the decrease in the rated efficiency after the 48hr test, the author recommended using high-grade materials in the stack configuration to ensure better performance. In another study, coupling solar with H_2O electrolysis for H_2 production achieved a 95% efficiency in 3hr test period with peak solar irradiance. Although, the use of wind energy to operate electrolysis of H_2O for H_2 production during periods of high wind and low demand has also been suggested as a means of energy storage [29]. At present, small-scale low-carbon biohydrogen production and utilisation can be a way forward towards solving H_2 transportation issue and prevent temperature rise above 1.5°C by 2030. Eqs (9 – 11) are chemical reactions of H_2 conducting PEMEC and Eq (12) represents H_2 fuel cell for electricity generation.

$$\text{Anode: } 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{9}$$

$$\text{Cathode: } 4H^+ + 4e^- \rightarrow 2H_2 \tag{10}$$

$$\text{Overall: } 2H_2O \rightarrow 2H_2 + O_2 \tag{11}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \tag{12}$$

This proposed study aimed to simulate and develop a solar and wind assisted AF-MEC coupled with MFC and PEM electrolysis of H_2O for small-scale applications. The proposed system is intended to use part of the generated electricity for pretreatment (microwaves oven) of AF digestate, which can promote enzymes' activities in the digester, and to use AF-MEC by-products as MFC feedstock. In addition, the produced electricity from MFC, solar and wind renewable energy sources will be used as input energy to all electrical units of the integrated system. These approaches will eliminate the need for membrane separators of both AF and MEC units which may increase the design cost, promote eco-sources of renewable energy production and utilisation in small-scale applications. The proposed work considered below points in a process simulation using Aspen Plus, SAM (system advisory model), and Matlab-Simulink software.

a) Process simulation of hydrolysis, acidogenesis, acetogenesis and electrochemical reactions to produce biogas feed to MFC.
b) Microwave oven (thermal) pretreatment of AF digestate to promote microbes' activities in the digester.

c) Electricity generation from MFC, solar and wind renewable sources with the option of battery storage for later use.

d) PEM electrolysis of H_2O for H_2 and O_2 production and PEM fuel cell for continuous electricity production.

e) Storage of produced H_2 and O_2 for later use through a fuel cell application.

Fig. 1 displays a schematic diagram of solar and wind aided AF-MEC coupled with MFC and PEM electrolysis of H_2O.

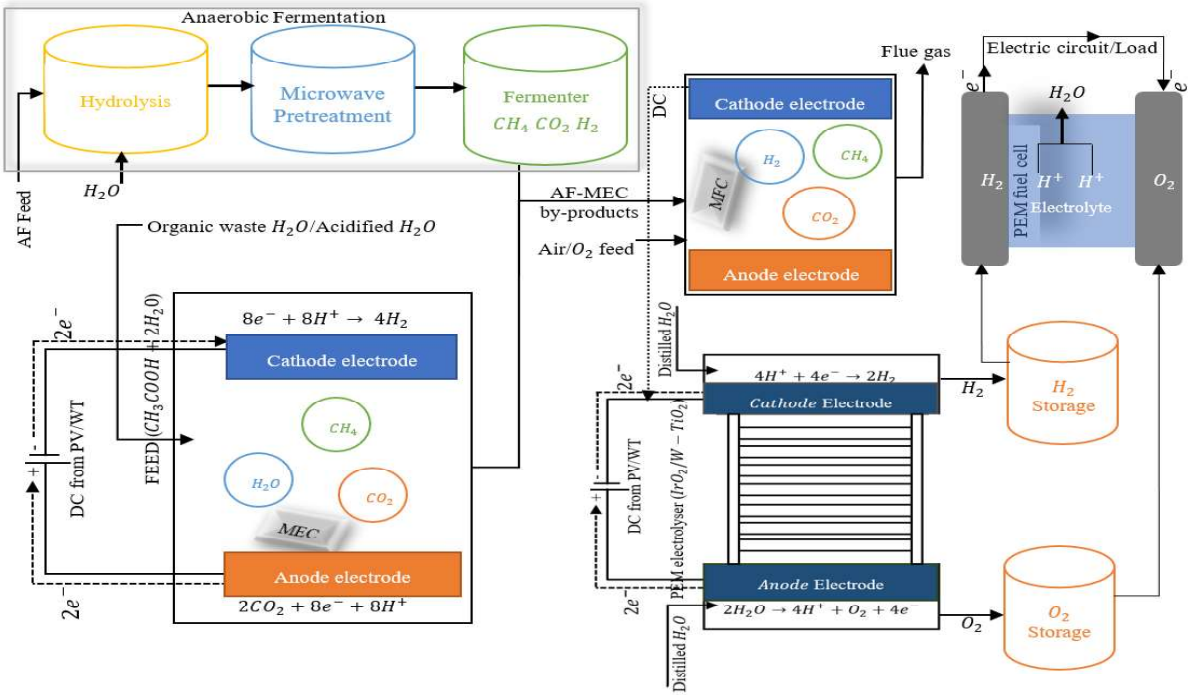


Fig 1: A schematic diagram of solar and wind assisted AF-MEC coupled with MFC and PEM electrolysis of H_2O.

2. Material and simulation method

Carbohydrates, proteins, and fats containing organic waste, wastewater and distilled H_2O are the list of the materials utilised for the production of biohydrogen in this proposed system. A total of 48 kinetic and electrochemical reactions were carried out in the AF fermenter and electrolysis stacks to model the biodegradable hydrolysis, acidogenesis and acetogenesis reactions of biogas production. Since some complex biodegradable reactions require the use of a non-conventional component type due to materials/elements missing from the Aspen Plus datasheet, a pseudo-component type was implemented. A pseudo component allows the addition of new elements based on known physical properties to improve the accuracy of the result. For Aspen Plus property set-up, mixed and conventional inert (CI) substreams, 5 mm upper and 1 mm lower normal distribution function type of logarithmic mesh particle size distribution (PSD) were registered. Peng-Robinson and non-random two-liquid (NRTL) equation of states were the property method used to correctly model the electrochemical reactions due to the presence of charged species and the model complexity.

AF-MEC (anaerobic fermentation microbial electrolysis cell) coupled with fuel cell and PEM electrolysis of H_2O. A separator and Gibbs reactor blocks were used to simulate the hydrolysis of the AF process and obtain the correct stoichiometries of the exit products. These same blocks were also used to obtain the stoichiometries of the acidogenesis reaction needed for kinetic degradation reactions in the fermenter. In the final stage of the AF degradation reaction, the by-products of acidogenesis are fed to acetogenesis microbes and produced acetic acid, H_2, and CO_2 feedstock for MFC through kinetic decomposition reactions. Gibbs reactors and separation blocks were used to obtain the correct reactant and product stoichiometries to create control stirred tank reactor (CSTR) kinetic reactions. To maintain mesophile and thermophile temperature conditions and implement pH-inhabitation, a modified Fortran code of calculator blocks from *Haider & Smith*. [30] were added. This is necessary to avoid higher VFA production and lower biogas formation. For example, in an analysis of the temperature effect of AD biomethane production, a decrease in biogas production from mesophilic to thermophilic (65°C) conditions was reported. The decrease in biogas production because of the thermophilic effect was attributed to the decrease in VFA-consuming bacteria and the increase of H_2-consuming microbes to produce biomethane. However, the increase in temperature did not affect the production rate of H_2 from 55°C to 65°C [31]. Distinct

from the AF method, the MEC used a Gibbs reactor with the electrolyte chemical ID written in Eqs (4 – 6) to convert wastewater into biogas. While MFC as mentioned in chemical reactions in Eqs (7) and (8) generated part of the required electric current for electrical units using AF-MEC by-products. This approach eliminates the need for an AF-MEC biogas membrane separation and purification unit for H_2 recovery. PEM electrolysis of H_2O in this proposed system used deionised H_2O to produce H_2 and O_2 at an applied voltage <1V at 80°C operating temperature. While PEM fuel cell takes stored H_2 and O_2 from both storage tanks to generate electricity for small-scale applications when solar and wind renewable energy systems are unavailable. Similar MFC procedures were used to implement the electrolyte chemical IDs written in Eqs (9) and (11) for PEMEC and Eq (12) for PEMFC in Aspen Plus. Renewable solar and wind energy systems. A solar panel model consists of a photovoltaic (PV) system and an inverter that converts direct current (DC) to alternating current (AC) for electrical equipment. To generate DC from PV modules needed to power electrical units, the created electron-hole relative to radiation incident by solar cells must absorb photon energy greater than the band gap energy of the semiconductor [32]. Eqs (13 – 17) written below describe the solar cell model.

$$I = I_{PV} - I_D \quad (13)$$

$$I_D = I_0\left[exp\frac{V}{AV_T} - 1\right] \quad (14)$$

$$I = I_{PV} - I_0\left[exp\frac{V}{AV_T} - 1\right] \quad (15)$$

$$I = \left[exp\left(\frac{V + I * R_s}{I_{PV}-, 0^{*V}T}\right) - 1\right] \quad (16)$$

$$P = V\left\{I_{sc} - I_0\left[exp\left(\frac{V}{AV_T}\right) - 1\right]\right\} \quad (17)$$

Where

I, I_{PV}, I_D, I_0 & I_{sc} are PV output current; generated current by incident of light; bypass diode current as dependence to junction voltage; diode reverse bias saturation current; short circuit current.

V, AV_T, R_s are voltage; ampere voltage climate temperature; series resistance.

A wind turbine with three or more blades uses the kinetic energy of the wind to produce DC, which is converted into mechanical energy and electrical energy. Eqs (18) and (19) describe the captured power by the wind turbine and the amount of the aerodynamic torque.

$$P_w = 0.5C_p\rho * A * V_w^3 \quad (18)$$

$$T_w = P_w W_w \quad (19)$$

Where

P_w, C_p, ρ, A & V_w are power derived from a wind turbine; coefficient of performance; air density; covered area by the blade rotor.

T_w & W_w are aerodynamic torque; turbine rotor speed [32] [33].

The development of solar and wind renewable energy systems was initially done in SAM-NREL (system advisory model-national renewable energy laboratory) before the modification and addition of the SAM algorithm in Matlab. Both wind and solar models were developed to generate the electrical energy needed to operate all electrical units within the integrated proposed system. To have the proposed system operating as a single unit, AspenOne was interfaced with Matlab-Simulink where the electrical power output of the developed solar or wind was connected to the electrical unit in the Simulink Environment. Table 1 lists the input parameters considered for the process modelling and simulation of both solar cells and wind turbine (WT) systems. Table 2 describes Aspen Plus blocks and material streams with descriptions.

Table 1. Design parameters for wind Turbine (WT) and solar cell (SC).

Wind turbine parameters		**Solar cell parameters**	
Parameters	**Value**	**Parameters**	**Value**
Rated power	3kW	Rated power	3kW
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 descriptions

Aspen Plus Block Name	Aspen Plus Block ID	Description
Mixer	MIX-1/MIX-2	Mixing anaerobic fermentation feed with H_2O. Merge 2 streams.
Hierarchy	HYDRO/FERM-RE/MEC	Container for directories. Act as a subsystem having a set of blocks that are grouped into a single hierarchy block. House RGibbs for electrochemical separation of wastewater into biogas with an ID name "MEC". House Fermentation reactor (Ferm-Re).
Heater/Cooler	MICRO/COOL	Thermal and phase state changer. For hydrolysis feed thermal pretreatment and product cooling.
Rigorous continuous stirred tank reactor	FERM-RE	Rate-controlled reactions based on known kinetic. For acidogenesis and acetogenesis reactions model based on obtained stoichiometries.
Rigorous reactor (RGibbs)	PEMEC/PEMFC	Set the composition of product/syngas by chemical equilibrium restriction. Gibbs free energy reactor. To produce H_2 and O_2. For H_2 and O_2 utilisation. Both blocks are housed by a subsystem block.
Duplicate	O_2/H_2 DUP	Duplicate product streams. For both H_2 and O_2 storage and utilisation in the fuel cell.
Storage	STORAGE1/STORAGE2	For syngas storage. For storing produced H_2 and O_2.
Load	LOAD	Load for produced electricity usage.

Aspen Plus stream ID	Description
FEM-FE	Anaerobic fermentation feed, mostly organic waste/biomass.
FD/any stream that starts with FD	Digestate feed before and after hydrolysis and pretreatment.
AM-ACI-A	Pretreated by-product feed to the fermenter.
AF-PRO	Anaerobic fermentation biogas feed to a fuel cell (MFC).
W-H_2O-FE	Wastewater feed to MEC.
MEC-PRO	MEC by-product (biogas).
MFC-PR and ELECTR1 and RE-PRO	MFC exit gas. Generated electricity. Recycled MFC exit gas.
H_2O/any stream that has H_2O	Water (H_2O) stream.
ELECT/ELECTRIC	Electricity generated by H_2 fuel cell.

2.1 Process simulation of integrated anaerobic fermentation (AF) and microbial electrolysis cell (MEC) coupled with microbial fuel cell (MFC) and electrolysis of water (H_2O).

Modelling of the proposed system was performed using Aspen Plus process simulation software with both NRTL and Peng-Robinson equation of state solvers. In addition, the ideal gas property and steam table free water methods have been added to the property method solver to adjust and accommodate the pressure deviation. The simulated proposed system considers the following assumptions:

- Steady-state condition for the entire process.
- AF fermenter temperature in mesophilic condition.
- The operating parameters such as pressure and temperature are atmospheric and ambient.
- The operating parameters of the fermenter, electrolysers and fuel cells are taken from the literature.
- Absence of membrane in the MEC and MFC.
- AF-MEC by-product gases would feed MFC to generate electricity.
- Absence of deactivation during multiple oxidation-reduction cycles.

The process for biogas production from AF digester to MFC starts by mixing H_2O and organic waste in a mixer with a particle size of 5 mm lower and 1 mm upper mesh particle size before the hydrolysis step. The hydrolysed feedstock from the mixer (mix-1) produces volatile and non-volatile solids and acid-like products such as acetic-acid ($C_2H_4O_2$) CO_2, xylose ($C_5H_{10}O_5$), furfural ($C_5H_4O_2$), CH_4, ammonia (NH_3), H_2S and others as described in equation 1. The rate-limiting step known as acidogenesis with acidogenic microbes degrades hydrolysis end-products to produce ethyl-cyanoacetate ($C_5H_7NO_2$), $C_2H_4O_2$, dioxolane ($C_3H_6O_2$), butene ($C_4H_8O_2$), CO_2, H_2O, NH_3 and others volatile fatty acids (VFAs) with a total of 23 chemical reactions as illustrated in equation 2. Finally, acetogenic bacteria consume the by-products of acidogenesis reactions, mainly $C_5H_7NO_2$, $C_2H_4O_2$, $C_3H_6O_2$, H_2, CH_4, CO_2, H_2S and others to release biogas and other by-products. Unlike the AD method, where methanogens consume acetogenesis end-products to increase CH_4 production, biogas from acetogenesis reactions was fed to the mixer. In addition, MEC with wastewater feed mainly of H_2O and acetic acid produces biogas like CH_4 and CO_2 and mixes with AF biosyngas in the mixer. With the aid of exoelectrogens microorganisms' activities in the MFC stack at an applied voltage between 0.2V and 0.8V, electron and flue gases were released with an option of battery storage or to power electrical units within the proposed system. To produce H_2 as one of the final by-products since H_2 produced from upstream units has been used by MFC to generate electricity, PEM electrolysis of H_2O was introduced. PEMEC with denoised H_2O feedstock produces H_2 in the cathode side and O_2 in the anode chamber via electrochemical oxidation-reduction reactions. The produced H_2 and O_2 gases when sun or wind are available to operate solar cells or wind turbine systems were stored in separate containers for later use. To include an option of using produced gases from PEMEC through fuel application, PEMFC was added to the integrated system to enable proper energy management. By using a PEM fuel cell in the proposed small-scale system, electricity can be produced when both renewable energy sources (solar and wind) are unavailable. An integrated small-scale unit for the combined H_2 production and utilisation is shown in Fig. 2.

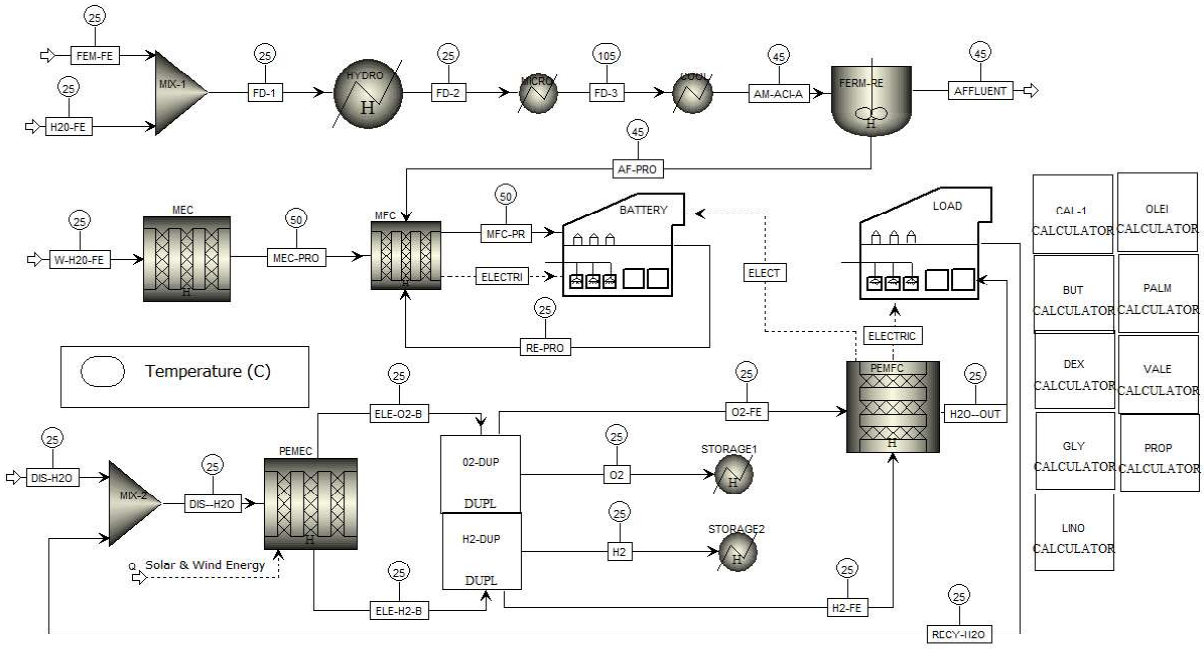


Fig 2: ASPEN Plus flow diagram for integrated AF-MEC coupled with MFC and PEMEC.

To operate the electrical units of the proposed small-scale system as more electrical current is needed despite having generated some from the MFC, the Aspen Plus simulated model was transformed into flow-driven for the Simulink interface. This is necessary for all units to work as a single system since the development of a solar and wind system to produce the necessary energy for electrical equipment such as the AF fermenter or the MEC stack is limited in Aspen Plus. The proposed system operating as a single unit is shown in Fig. 3. As shown in Fig. 3, the simulated results such as the power output of both wind turbine and solar cells systems from the Matlab environment saved as a mat file were input to the Aspen Plus file in the Simulink. In the Simulink environment, electricity from either solar arrays or wind turbine systems was connected to the electrical unit of the Aspen Plus model. A switch was applied to the system to demonstrate the flexibility of using any of the renewable electricity generation sources in addition to the electricity generated from the MFC unit. In the simulated system, it is possible to distribute the electrical current produced by any of the renewable energy sources to other electrical units.

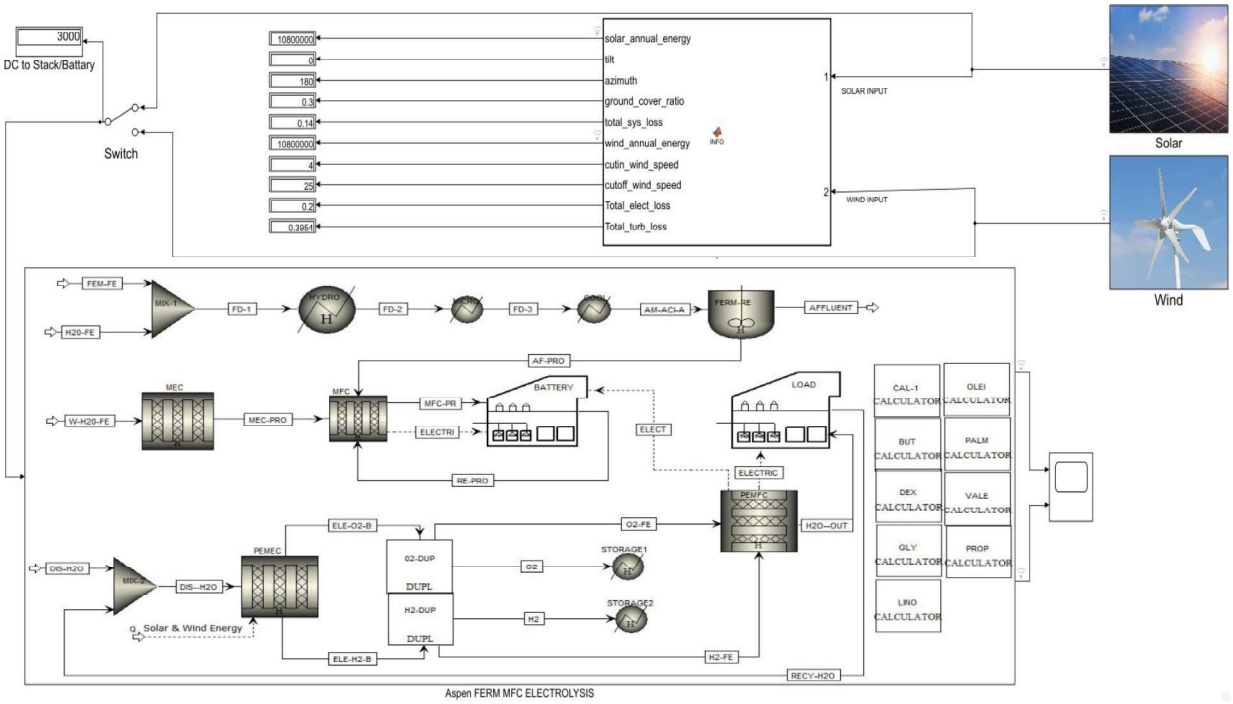


Fig 3: Solar and wind aided AF-MEC coupled with MFC and PEMEC.

3.0 Results and Discussion

3.1 Hydrogen (H_2) production from AF-MEC coupled with MFC and PEMEC

H_2 was produced from PEMEC by using electricity from solar, wind and MFC. While AF-MEC produced biogas feed for the MFC. By replacing the dark fermentation (DF) with AF and applying thermal pretreatment of the digestate, the overall conversion rate and energy efficiency of AF were improved. For instance, heat treatment of AD digestate at 180°C has been reported to increase biogas production by 20%. While heat pretreatment at a lower temperature (below 160°C) can increase the biosynthesis production rate by >5% and reduces the HRT [8]. In addition, the efficiency of AF was further improved by the introduction of MEC and MFC, which increases the total biogas production and eliminates the need to separate biohydrogen from other by-products. Using calculator blocks requiring Fortran code for correct mesophilic (35 - 40°C) and thermophilic (50 - 55°C) conditions, lower VFA and H_2S production was recorded. The same step in writing the Fortran codes was applied to control the pH value at a neutral level, HRT and OLR to boost enzymes' degradation activities in the fermenter. Unlike microbial and H_2O electrolysis cells that produced biogas as end-products, electricity, H_2O, exhaust gas and heat were by-products of microbial and H_2 fuel cell units. Compared with similar biohydrogen production such as DF or other bioelectrochemical systems, this integrated system achieved good conversion and energy efficiencies. For example, using spent DF (by-product) as MEC feedstock achieved 166% energy efficiency at 0.8V. While the use of single chamber MEC at a lower operating voltage (0.6V) attained an energy efficiency of 96%. Energy recovery between $28 - 30\%$ was recorded by using DF by-product as MFC feed in a single and double chamber compartment. In addition, the energy efficiency increased from 7.9% to 56.3% by using municipal solid waste (MSW) in AF to co-produce H_2 and CH_4 in contrast to the DF method. It was concluded that the integration of other renewable bioelectrochemical processes in DF can significantly improve the overall efficiency [34] [35] [36] [37]. Similar to these findings, the proposed small-scale H_2 production as illustrated in Table 3 achieved nearly the same result and energy efficiency of ≥68.6%. For example, AF with pretreatment substrate attained an energy efficiency ≥64% and between 58% - 64% efficiency for MEC was recorded. The energy efficiency of MFC with AF-MEC feedstock is ≥85%. The high efficiency of MFC was attributed to the use of AF and MEC by-products mainly of H_2 and CH_4 as feed material. For instance, *Nguyen, et al.* [38] reported an efficiency of 85% during an investigation of extracting energy from dual MFCs in a power management system. By using the AF method instead of DF as MEC feed to improve efficiency as suggested above, high energy efficiency was achieved. Although the PEM electrolysis cell and H_2 fuel cell reached energy efficiencies between 80% - 83% and 50% - 52% at a lower heating value (LHV) due to activation, ohmic and mass transport losses. However, the H_2 PEMFC efficiency reached 52% by taking other losses into account.

Table 3: Feed and product, power input and output results of the proposed small-scale biohydrogen production and utilisation.

Feed and product; power input and output of each key unit	AF-MEC	MFC	PEMEC	PEMFC
Digestate and H_2O feed rate	167.5kg/week	AF-MEC biogas	0.4kg/hr	PEMEC by-products
H_2/biogas by-product	3.2072kg/day		0.05kg/hr	
CO_2 by-product	21.29kg/day			
O_2 by-product			0.35kg/hr	
Electricity input	~1.7kW		1.8kW	
Electricity output		1.65kW/week		1.5kW

3.2 Analysis of operating parameters on biogas production

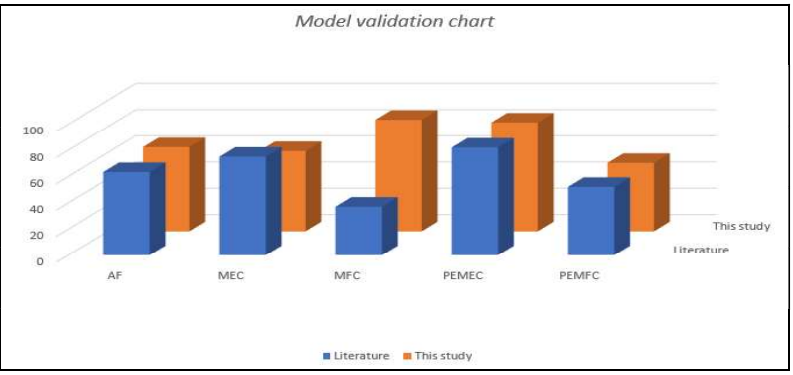
The biogas production rate of AF is highly dependent on operating parameters such as pH, temperature, organic loading rate (OLR) and hydraulic retention time (HRT). For example, a pH value between 6.5 - 7.5 was found to be more effective in biogas production due to the increased activity of fermenting microorganisms, which reduces the formation of VFA, SO_4^- and H_2S. Improved biogas conversion efficiency of AF digestate by adjusting and manipulating the pH value with NaOH was reported by *Vu, et al.* [39]. For this study, a pH value between 6.5 - 7.5 was utilised because the actual effect of pH variation cannot be properly investigated in a process simulation. In addition, increasing the feed rate was found to increase biogas formation in the AD process. For example, the sensitivity analysis of OLR studied by *Kang, et al.* [40] reported a daily increase in biosynthetic gas due to the increase in feed rate. This finding contradicts *Hajizadeh, et al.* [12] discovery which maintained that an increase in OLR decreases syngas formation. For this work, Fortran code was written to manipulate the OLR which can properly be determined in a laboratory experiment. However, the process simulation used a feed rate below $1l/kg$/day to ensure that the proposed system covers the reported strategies for enhancing biogas production. A similar procedure was carried out by writing Fortran code to manipulate the HRT of the AF fermenter to maintain 7 days incubation period capable of reaching 87% biogas production efficiency. Since the developed system is intended for small-scale use, to prevent a decrease in biogas production, an equilibrium value of OLR below $1l/kg$/day is recommended. The temperature of the fermenter was controlled to stay within 35°C - 55°C as the operating temperature greater or below this range can increase VFA formation. A temperature control algorithm in the calculation block was written to ensure that the fermenter remained within the specified range. In this proposed system, the effects of electrolysis and fuel cell operating voltage were ignored by creating stacks electrochemical and biochemical reactions using electricity as input energy. The reported energy efficiencies of all the units within the hybrid system are closely related to the efficiencies reported in the literature. By applying these parameters in this simulated system, the overall efficiency was improved and expected to reach 68.6%.

3.3 Model validation

The proposed integrated system is validated part by part with the reported efficiencies data in the literature. The AF study by *Wang, et al.* [7] with food waste (FW) and garden waste (GW) or kitchen waste (KW) as feedstock reported 61.91% efficiency in a ratio of 80:20. The efficiency was further improved by 1.38% using a 60:40 FW to GW ratio. Comparing the reported efficiency from [7] to this integrated system, a marginal difference was attained. In addition, the platinum-catalysed electrodes with Nafion solution chemical binding to improve the hydrogen evolution reaction (HER) achieved 75% efficiency [41]. The reported efficiency of MEC configured with noble metal at an applied voltage of 0.8V achieved a higher efficiency compared to the MEC unit of that proposed system [42]. The higher efficiency reported in the literature was attributed to the inclusion of precious metal in the stack configuration which facilitates higher exoelectrogens' activities and increases the unit cost. Power efficiency between 64.52% - 95% under an equal optimal circuit load of MFC was reported by by *Ieropoulos, et al.* [43]. While a study on the effect of HRT on MFC electrodes in domestic wastewater treatment also recorded a coulombic efficiency of ≤37% [44]. The MFC of the proposed system achieved a higher efficiency compared to the literature data because AF-MEC by-products were used as digestate instead of wastewater. Unlike AEC with an efficiency between $59\% - 70\%$ and SOEC which can reach 100% efficiency, *Sapountzi, et al.* [45] reported a PEMEC efficiency between $65\% - 82\%$, which is almost the same as the PEMEC unit efficiency of the simulated system. Like the MFC, the PEMFC efficiency of this integrated system achieved 52% which is almost the same as reported by *Thomas.* [46] during battery and FC comparison for low-carbon powertrains. Table 4 illustrate the model validation of literature data with the simulated integrated system.

Table 4: Model validation

Units	Literature	This study
AF	63.29% [7]	64%
MEC	75% [41] [42]	61%
MFC	37% [44]	≥85%
PEMEC	82% [45]	83%
PEMFC	52% [46]	52%



3.4 Energy and economic analyses and environmental assessment of the developed hybrid system

Various AF, DF and AD digestate pretreatment methods have been reported by many researchers to increase the conversion efficiency with a shorter HRT. For example, high-temperature thermal pretreatment of AF feedstock increased biogas production by up to 150% and decreased VFA formation because of improved degradation kinetic and digestate solubilisation [47]. While an increase of 61.54% in biogas production rate during a steam explosion and $Ca(OH)_2$ pretreatment method was reported in the literature [48]. In addition, the combination of both high temperature (250°C) and pressure (15 bar) with steam explosion and $Ca(OH)_2$ improved microbes' activities in the fermenter leading to higher biogas formation [49]. A thermal pretreatment method of boosting the digestate decomposition can significantly improve the overall efficiency in an application where waste heat recovery is applicable. However, in this work, heat treatment by solar or wind powered microwave oven was applied. Considering the low efficiency of DF (<10%) and the operational costs of other biohydrogen recovery units in both AF and MEC, the integration of MFC to achieve higher operational efficiency reduces the total cost of the proposed system. Despite the low cost of producing H_2 from fossil fuels such as hydrocarbon reforming, the low CO_2 emissions of the proposed system, which can be captured by plants and trees and its small-scale use, make it more attractive. The H_2 selling price of the proposed integrated system is projected to be <$5/kg which is cheaper than single electrolysis of H_2O. Further decrease in H_2 sale price may be expected in locations with abundant sunshine and wind speed. To keep temperature increase below 1.5°C by 2030, biohydrogen production powered by renewable sources in a small-scale application has a major role to play because of the difficulties of H_2 transportation units. In addition, mitigating the operational problems associated with biohydrogen production in developing countries is necessary to keep temperatures below 1.5°C by 2030. For example, the lack of proper technologies, operators, end-use and waste management markets in developing countries such as India has hindered the growth of the AD system [50]. For the proposed system, it is recommended to capture CO_2 by calcium oxide (CaO) to form calcium carbonate ($CaCO_3$) for geological storage in a scenario where more electricity is produced from MFC using AF-MEC by-products as feed. The advantages of this integrated system are a) higher biogas production by replacing DF with AF-MEC and application digestate pretreatment to increase the production rate., b) Efficiency improvement and cost reduction using MFC with AF-MEC by-products as feed to generate electricity for some of the electrical units., c) Application of renewable powered electrolysis of H_2O to produce H_2 as energy storage., d) Application of fuel cell system to generate electricity for small-scale applications when the sun is unavailable and wind speed is low to rotate the turbine blades.

4.0 Conclusion

An integrated biohydrogen production and utilisation powered by renewable energy sources for small-scale application was developed and simulated to promote the transition from fossil fuels to low-carbon energies. Microwave oven thermal pretreatment of AF digestate increased biogas production and lowered VFA formation. An increase in biosynthetic gas formation under controlled pH value between $6.5 - 7.5$, mesophilic and thermophilic temperature conditions, $<1 l/kg$/day feed rate and one week retention period were recorded. MFC achieved the highest energy efficiency because of the use of AF-MEC by-products as feed which promoted exoelectrogens activities in the stacks. AF-MEC separation and purification units were excluded from the simulated system by feeding biohydrogen and other syngas to the MFC, thus reducing the overall cost. Production, storage and utilisation of both H_2 and O_2 from a PEM electrolyser and fuel cells powered by solar or wind renewable energy systems can eliminate H_2

transportation issues and facilitate the energy transition. This proposed system achieved higher efficiency (>10%) in comparison with batteries for electrical energy storage by considering the service life and the energy needed for production. Energy efficiency ≥68.6% and H_2 selling price <$5/kg which is higher than the sale price of H_2 obtained from the hydrocarbon reforming method. However, the reported H_2 sale price of the proposed system is expected to be cheaper than a single-unit electrolysis system of extracting green H_2 from H_2O molecule. A small fraction of CO_2 by-product was produced from the MFC which can be captured by plants and trees. By-product CO_2 capture by adsorption process when more electricity is generated from MFC is recommended. The simulated system recommends a pilot-scale development for batteries and non-environmentally friendly energy storage substitution in small-scale applications.

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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