Biogas as alternative SOFC fuel: Research and implementation

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Abstract. With the current environment situation and the inclining demand of energy globally, SOFC fits as the perfect solution with up to 90% efficiency and ultra-low emission. Adaptation of this advanced green technology with biogas is still limited despite of the availability of the fuel. The main aim of this paper is to bring into attention the possibility of this technology implementation in agriculture-based country utilising the readily available biogas and as reliable renewable energy option. This paper briefly reports on the possible reaction in the SOFC fuelled by biogas compared to the operation with hydrogen, the material suitability and modification to tolerate biogas fuel; and finally, the demonstration of biogas fuelled SOFC with brief review on economic studies. This paper concludes that SOFC fuelled by biogas is technology and economically feasible with payback period as short as 7.7 years when paired with micro gas turbine.

1. Introduction
The high efficiency of a Solid Oxide Fuel Cell (SOFC) system in converting the electrochemical energy into electricity with significantly lower net release of pollutants [1,2] compared to other power generation process makes this technology portrayed as the future of green energy generation. However, the overall high cost of SOFC limits the implementation only to countries (or organisations) which can tolerate the long return-of-investment (ROI) period and view the benefits outweigh the high-cost factor. In Korea and Japan, the terrain with isolated islands and dense population makes the implementation of solar PV and wind power as the renewable energy resources to replace the dependency on nuclear after the Hiroshima incident to be irrelevant. In the US, along with the involvement of USA’s Department of Energy (DoE), giant leading server companies such as Microsoft, Apple and Google with needs of high level of energy security escalate the SOFC popularity. SOFC cost issues need to be tackled to implement this advanced green technology in closing the gap with the developing countries.

One of the strategies to reduce the SOFC operating cost is to use alternative fuels besides pure hydrogen as the route of producing hydrogen can be very long and costly even if the energy source originates from renewable material. This is possible as one of the significant advantage of an SOFC is it’s fuel flexibility option; various type of fuels such as ethanol, kerosene, methane and biogas can be fed instead of costly pure hydrogen [3–6]. The ability to utilise biogas as the fuel give a significant impact to the agriculture-based countries in closing the gap in adapting this new technology.

The world’s biogas production in 2012 was 56 billion m³/year with approximate energy potential of 1212 PJ [7]. Malaysia, the second largest Palm Oil exporter in the world produced 58.53 million m³ of
Palm Oil Mill Effluent (POME) based on 2014 with ability to generate 4.38 TW.h/year with gas burner with maximum efficiency of 40% [7]. With SOFC CHP efficiency up to 90% [1], greater amount of energy can be harnessed. In addition, the energy generated projection was based only on CH₄ while in SOFC, both CH₄ and CO₂ considered as fuel. Hence, it is predicted that higher amount of energy can be generated. Coupling biogas resources and SOFC technology is a smart way forward for efficient electricity generation without sacrificing the future generation.

2. SOFC Electrochemical Reaction
In hydrogen and air feed, the standard electrochemical reaction in the SOFC is summarised by Figure 1. Hydrogen and air are fed on the anode and cathode side respectively and produce water and heat as byproduct. The ion flow produces electrical potential and produce electricity in the internal circuit.

![Figure 1. Standard electrochemical reaction in an SOFC with hydrogen as fuel [8].](image)

Typical biogas composition from anaerobic digestion at a waste water treatment plant has 50-80% of CH₄, 30-50% of CO₂ with traces of H₂S, O₂, N₂, halogenated hydrocarbons, NH₃ and siloxanes [9]. The composition varied with different sources. Unlike gas burner which only accounted CH₄ as the feed, SOFC can utilise both CH₄ and CO₂. At SOFC operating temperature (700-900°C), carbon dioxide reforming reaction (Equation 1) will take place. Opposed to low temperature fuel cell, which CO poisonous to the system, CO can also powered an SOFC. With biogas, the possible reactions between methane and carbon dioxide that may take place at SOFC operating temperature are shown in Equation 1 and 2.

Carbon dioxide (dry) reforming [4,10]:

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \quad \Delta G_{f \text{700°C}} = -23.82 \text{ kJ/mol} \tag{1}
\]

Reverse water-gas shift reaction [4,10]:

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \quad \Delta G_{f \text{700°C}} = -3.24 \text{ kJ/mol} \tag{2}
\]

Unlike steam reforming, dry internal reforming usually accompanied with carbon deposition which leads to the anode deactivation. The possible reactions for carbon deposition are by methane cracking (Equation 3), the Boudouard reaction (Equation 4) and the reverse carbon gasification reaction (Equation 5).

\[
\text{CH}_4 \rightleftharpoons \text{C(s)} + 2\text{H}_2 \quad \Delta G_{f \text{700°C}} = -16.34 \text{ kJ/mol} \tag{3}
\]

\[
2\text{CO} \rightleftharpoons \text{C(s)} + \text{CO}_2 \quad \Delta G_{f \text{700°C}} = +0.76 \text{ kJ/mol} \tag{4}
\]

\[
\text{H}_2 + \text{CO} \rightleftharpoons \text{C(s)} + \text{H}_2\text{O} \quad \Delta G_{f \text{700°C}} = +4.00 \text{ kJ/mol} \tag{5}
\]

As SOFC operates at high temperature; between 700-1000°C, carbon formation via Boudouard reaction (Equation 4) and reverse carbon gasification reaction (Equation 5) are not favourable as their
Gibbs free energy value are positive above this temperature. Hence, the source of carbon deposition for an SOFC operating at this temperature range assumed to be caused by methane cracking.

![Diagram]

**Figure 2.** Reaction in an SOFC fed with dry simulated biogas with internal reforming reaction [11].

For SOFC internal reforming systems with carbon fuels, the fuel is assumed to undergo reforming reaction on the surface of coarse Ni particles in the anode substrate region while the final electrochemical reaction takes place in the anode functional layer region, which has finer Ni particles[11]. When dry simulated biogas consisting of CH$_4$ and CO$_2$ in contact with the Ni surface, a dry reforming reaction (Equation 1) is expected to occur; releasing 2 mol of H$_2$ and 2 mol of CO. The molar flow rate of biogas used was two-fold compared to hydrogen as shown by Figure 2 when same volumetric flowrate used. With double molar flow, the electrochemical performance may be doubled if 100% of the biogas fed converted to CO$_2$ and H$_2$ following Equation 1. However, the sluggish mass of CO affected the electrochemical reaction and methane cracking (Equation 3) that lead to carbon deposition may also occur at the operating temperature. In addition, the carbon deposited on the anode surface may or not be electrochemically converted to CO and CO$_2$ depends on the catalytic activity of the materials employed. Deposited carbon on the anode surface that failed to be converted to CO and CO$_2$ will lead to deactivation of anode’s reaction sites known as triple phase boundary (TPB).

### 3. Tolerating carbon and impurities

#### 3.1. Carbon tolerance anode

Due to data availability and similarity of carbon deposition problem, this section will report on anode materials with respect to hydrocarbon fuel application and not limited to biogas application only. Reported in several cases, Ni/YSZ degrades with time when the system switch from hydrogen to either simulated biogas or methane[3,4,12]. Although Ni promotes carbon deposition and a catalyst for methane cracking, Ni is also the catalyst for reforming reaction[13]. One strategy to suppress carbon deposition without sacrificing the high electronic property of Ni and its reforming ability is by reducing the affinity of nickel by replacing the support oxides or by nickel alloying[13]. The second strategy is by replacing Ni with another metal or catalyst that have similar characteristic with Ni but with low activity for carbon formation[13].

Pairing Ni with stabilised zirconia-doped-ceria (ScCeSZ) or gadolinia-doped-ceria (GDC) proven to successfully improve the tolerance of the anode tested in biogas and methane[3,14]. The type and carbon deposition behaviour on Ni/ScCeSZ was found to be different than those on Ni/YSZ cells which affected by the difference in crystalline structure [11,15]. The advantage of ceria in Ni/GDC cell has consistently shown positive remarks with methane as feed due to ceria ability to oxidise methane[13]. Ni/GDC also reported to have less tendency to form carbon which is easier to remove compared to those on Ni/YSZ cells [16]. Huang et al. [17] shows that coating Ni/ScCeSZ with GDC layer enhanced the performance in humidified methane. In work by Faro et al. [18] tested with different HC fuels pairing Ni with LSFCO/CGO perovskites managed to work well with biogas reformate, but not with methane.
Alloying Ni with small amount of precious metals (such as Au, Ru, Rh, Pt and Pd) enhances the steam reforming ability of the Ni and the electrochemical performance [19–21]. Alloying with base metals such as copper (Cu), iron (Fe), cobalt (Co), tin (Sn), and silver (Ag) has successfully proven to give quite the same effect as precious metals. Reported by Jiang et al [12], alloying Ni with 1 wt% of Sn gave the best performance in biogas compared to Ag and Cu. Enhancement with Sn alloying tested with methane and biogas also observed by Troskialina et al [4] and Nikolla et al [22]. The use of copper and cobalt as nickel-free anode approach has been extensively studied to have improvement in alternative fuels. Several example includes CuCeCo [5], Cu- Ce-ScSZ [23], and Cu-LSCM-ScSZ [24].

3.2. H$_2$S tolerance anode

Compared to low temperature fuel cell, high temperature fuel cell (SOFC, MCFC and DCFC) have higher tolerance to fuel with theoretical limit of 5ppm H$_2$S. The degradation can be attributed to adsorption of sulfur at surface active sites and to sulfidation of anode materials due to the reaction with sulfur, followed by the loss of catalytic activity, conductivity and stability at the anode[25]. Through an in-depth review by Boldrin et al [25] on-sulphur tolerance anodes, strategies to increase the tolerance includes replacement of YSZ with ceria, using all ceramic anodes, or by alloying Ni with other metals. Amongst all option, ceria-based anode especially Ni/GDC viewed as the most promising anodes with contaminated fuels as sulphur can accumulate in the surface of the GDC forming Ce$_6$S$_8$ type phases which can react with O$_2$ to produce SO$_2$[25]. The SO$_2$ can be leached out using reducing, oxidising, inert gas or steam[26,27]. All ceramic oxide option especially perovskites based anodes showed very high tolerance towards sulphur; for example Sr$_{0.6}$La$_{0.4}$TiO$_3$/YSZ (50/50 wt %) anode showed tolerance up to 5000 ppm of H$_2$S in a hydrogen fuel [28].

Example of real biogas feed with modified anode to tolerate carbon and impurities was demonstrated in a joint research of Vietnam-Japan using biogas originated from shrimp sludge. Shiratori et al. [29] shows the possibility of using biogas supplied directly to an SOFC without any H$_2$S cleaning or methane pre-reforming with Ni based paper structured catalyst (PSC) technology. 9 wt% Ni-loaded hydrotalcite ([(Mg$_6$Al$_2$(OH)$_{16}$CO$_3$)4H$_2$O-HT]-dispersed PSC(9Ni/HT-PSC) was prepared using a dual polyelectrolyte retention system and subsequent impregnation and sintering processes. From the SOFC performance, the system is tolerance up to 14 ppm of H$_2$S content.

While there are impressive works on improving anode tolerance to sulphur, the application in industrial reactors still using multiple step cleaning processes producing fuel with contaminants below 0.1 ppm of H$_2$S before feeding to an SOFC modules. Special activated carbon use for adsorbents to filter out H$_2$S and siloxane from the feeding line. Example in two pilot and industrial scale will be shown in the next section.

4. Implementation of biogas fuelled SOFC

4.1. Industry - BloomEnergy Server

The Bloom Energy (US based company) provides their clients to choose between natural gas and biogas as the feed choice in their Bloom Energy Server system. The company claimed that their 250kW server with up to 60% of electrical efficiency can deliver up to tens of megawatts with 0lbs CO$_2$/MWh released with biogas as the fuel supply. Although this is one evidence of successful application of SOFC fuelled biogas in industry, information on technical details is undisclosed. With sustainable energy generation option and high energy security guarantee, among their clients are; AT&T, Google, Walmart, Ebay and FedEx [30].

4.2. Prototype and Industrial Scale Plant

Demonstration of biogas fuelled SOFC prototype plant was carried out in BIOCELL project back in 2012 [31]. The project was successful in demonstrating the viability of the fuel cell (PEM and SOFC) to operate with biogas from waste water treatment plant but achieved quite low electrical efficiency; 24% because at high fuel loads, operation was unstable due to insufficient heat evacuation capacity [31]. Based on the layman report available on the project’s website; the team concluded that SOFC was a better choice instead of PEMFC for fuel cell system fed with biogas. However, both of the fuel
cell system evaluated to be far too expensive for the industry to adapt at that time. Further cooperation and research collaboration with the industry player, SOFC manufacturing company and the government were suggested to solve this issue.

Results by the first industrial-sized pilot-plant biogas fed SOFC was presented by DEMOSOFC project [1] funded by FCH-JU (Fuel Cell and Hydrogen Joint Undertaking) as a continuation from previous project of SOFCOM. The DEMOSOFC employed three SOFC modules (3 x 58kWe) with biogas feed of 57.9 m³/hr. Prior to feeding to SOFC modules, the biogas sourced from wastewater treatment plant (WWTP) was pre-treated for traces of H₂S and siloxane contaminants with commercial impregnated carbons adsorption, selective for sulfur and siloxanes removal [2,32]. The DEMOSOFC plant layout is presented by Figure 3.

The project reported a continuous stable operation besides planned maintenance stop. The biogas-SOFC plant produced 174 kWe which 100% self-consumed by the plant. The electrical efficiency maintained to be higher than 48-50% throughout with peak efficiency of 56% and thermal efficiency above 30%. The performance of SOFC was as specified by Convion, the supplier for SOFC modules. In addition to the performance, the output gases analysis reveals that all NOx, SOx, HCl and particulates were all below detection limit.

![DEMOSOFC plant layout](image)

**Figure 3.** DEMOSOFC plant layout [32].

Table 1 shows comparison based on DEMOSOFC and BIOCELL project only due to limited availability information on another biogas fuelled SOFC project. The power generated in DEMOSOFC reported to be stable and high efficiency achieved. Compared to the pilot plant in DEMOSOFC, it can be concluded that, the demonstration of this project is a milestone to realisation of SOFC-biogas integration. Hence, from the technical and environmental impact point of view, the technology viewed to be ready for further implementation.

Besides DEMOSOFC and BIOCELL project, the viability of biogas fuelled SOFC also demonstrated in the BIOZEG plant. The ZEG technology is a hybrid technology for co-production of hydrogen (Sorption Enhanced Reforming process or SER) and electricity (SOFC) with built in carbon capture [33]. The BIOZEG plant is a prototype plant that aims to design, build and operate a hydrogen station from local WWTP resources and to demonstrate the fuel cell technology. Unlike BIOCELL and DEMOSOFC projects, the biogas from WWTP fed to SER and the hydrogen produced fed to the
20kWe SOFC modules. In the initial test, the system reported to be operating at 66% of fuel utilisation with 1 kW of power produced.

| Table 1. Summary of SOFC-Biogas fuel demonstration. |
|----------------------------------------------------|
| Biocatana | BIOCELL [31] | DEMOSOFC [32] |
| Biogas Input (m³/hr) | 10 | 57.9 |
| Biogas source | Waste-water treatment plant | Waste-water treatment plant |
| Impurity removals | Bio trickling filter +Polishing (iron oxides, drying and activated carbon) | Activated carbon CKC for H₂S and C64 for siloxanes |
| Electrical Efficiency (%) | 24.2 | 51.0 |
| Thermal Efficiency (%) | 39.4 | 31.0 |
| CHP Total Efficiency (%) | 63.6 | 82.0 |

4.3. Economic viability
The high cost from the SOFC biogas plant originated from the SOFC modules itself and biogas cleaning up section[34]. Pipatmanomai et al [35] reported that the the payback period from the economic analysis showed that the payback period could be reduce by half without the contaminants cleaning up section. From the economic evaluation based on DEMOSOFC project, MosayebNezhad et al. [36] the payback period calculated with SOFC fuelled from biogas from WWTP will be around 11.6 years. The author [36] shows that this can be reduced by installation of micro gas turbine (MGT) that will enhance the electricity production efficiency and shorten the payback period to 7.7 years. The levelized cost of electricity (LCOE) calculated for the system with short term saving in the biogas processing unit for the plant with and without MGT were 0.134 €/kWh and 0.116 €/kWh respectively. Compare to current price of electricity of 0.16 €/kWh, the application of the plant is economically feasible [36].

5. Conclusion
With the research progress on improved materials that have higher tolerance to carbon and contaminants, it is predicted that the cost of SOFC-biogas plant can be further reduced, hence making the technology more acceptable. With evidence from the latest result from the industrial-sized SOFC-biogas plant demonstrated proves that the high efficiency of SOFC-biogas system and positive environmental impact. In the future study for biogas from agriculture wastewater, perhaps a life-cycle-analysis from the anaerobic digestion system in the agriculture waste sludge to the amount of power delivered need to be done. In the author’s opinion, in initial step in any agriculture based-country, government involvement in this technology implementation is essential as the appreciation to all these aspects usually missed out if only evaluated from the industrial site.

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