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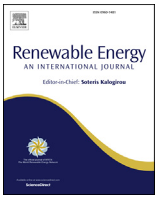

Review

Solid Oxide Fuel Cells fuelled with biogas: Potential and constraints

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Anaerobic Digestion (AD) is used worldwide for treating organic waste and wastewater. Biogas produced can be converted using conventional energy conversion devices to provide energy efficient, integrated waste solutions. Typically, the electrical conversion-efficiency of these devices is 30–40% and is lowered due to biogas utilization instead of high pure refined natural gas. The Solid Oxide Fuel Cell (SOFC) as an alternative device offers high (50–60%) electrical efficiency with low emissions (CO2, NOx) and high temperature residual heat. The high quality residual heat from SOFCs could be used to improve biogas production through thermal pre-treatment of the substrate for anaerobic digestion. This work discusses the advantages and challenges of integrated AD-SOFC systems against the most recent scientific and practical developments in the AD and SOFC domain. First, the biogas production process and its influence on the composition and level of contaminants in biogas are explained. Subsequently, the potential of various biogas cleaning techniques is discussed in order to remove contaminants that threaten stable and long-term SOFC operation. Since SOFCs utilize H2 and/or CO as fuel, possibilities for internal and external reforming are explained in detail. Special attention is given to biogas dry reforming in which CO2 naturally present in the biogas is utilized effectively in the reforming process. A detailed discussion on the choice of SOFC materials is presented, with a focus on biogas internal reforming. Various integrated SOFC system models with multiple configurations are also reviewed indicating the overall efficiencies. Some biogas SOFC pilot-plants are described and discussed to conclude with the techno-economic aspects of biogas SOFC systems.

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Nomenclature

AGR	Anode Gas Recirculation
R	Universal gas constant
APU	Auxiliary Power Unit
RWGS	Reverse Water-Gas Shift
ATR	Autothermal reaction Reformer
SC	Steam to Carbon ratio
BoP	Balance of Plant
SOFC	Solid Oxide Fuel Cell
CFD	Computational Fluid Dynamics
T	Absolute Temperature
CHP	Combined Heat and Power
TPB	Triple Phase Boundary
CCHP	Combined cooling, heating and power
UASB	Up-flow Anaerobic Sludge Blanket
CNT	Carbon Nanotube
UBF	Up-flow blanket filter
COD	Chemical Oxygen Demand
V	Potential
CPOX	Catalytic Partial Oxidation
VS	Volatile Solid
CSTR	Continuous Stirred Tank Reactor
WAS	Waste Activated Sludge
DIR	Direct Internal Reforming
WGS	Water-Gas Shift
E	Potential
WWTP	Wastewater Treatment Plant
EIS	Electrochemical Impedance Spectroscopy
YSZ	Yttria-Stabilized Zirconia
F	Faraday's constant
GDC	Gadolinium Doped Ceria
Greek letters	
GHG	Greenhouse Gas
Λ	Excess air value
GT	Gas Turbine
η	Ohmic resistance
IC	Internal Combustion
ΔG^0	Change of standard Gibbs free energy, (kJ mol^{-1})
LHV	Lower Heating Value
MBR	Membrane Bioreactor
ΔH^0	Enthalpy change, (kJ mol^{-1})
MCFC	Molten-Carbonate Fuel Cell
U_f	Fuel utilization factor
MSR	Methane Steam Reforming
N	Number of electrons participating in the
Subscripts	
electrochemical reaction	
Act	Activation polarisation
OCV	Open Circuit Voltage
Conc	Concentration resistance
P	Partial pressure
Ohmic	Ohmic resistance
POX	Partial Oxidation
Rev	Reversible

1. Introduction

Fossil fuels are currently the major source for electrical power generation, which subsequently increases the rate of greenhouse gas (CO_2, CH_4) emission. It has been agreed at the Climate Change Conference 2015 in Paris (COP21) to reduce greenhouse gas emissions in order to limit global temperature increase to less than 2 °C compared to pre-industrial era temperature [1]. The GHG (Greenhouse Gas) effect is mostly attributed to methane and carbon dioxide emissions into the atmosphere [2]. In order to reduce the use of fossil fuels and their negative impact on the environment, renewable energy resources have been receiving much attention in recent years [3]. Sanitation systems, centralized Wastewater Treatment Plants (WWTPs) and organic waste digesters give an ample opportunity for resource recovery to produce biogas that contains mainly methane and carbon dioxide [4]. The low conversion efficiency of conventional energy conversion devices like internal combustion engines and turbines prevents biogas from reaching its full potential as over 50% of chemical energy is dissipated.

Torrijos has reported on the state of biogas production in Europe and the anticipated future market [5]. Germany and Italy are leading countries in Europe in terms of number of anaerobic digestion plants. Biogas production in France and UK is growing fast especially from landfill and sewage. In the Netherlands, the idea of the NEW (energy & raw materials) Factory has been introduced. In this concept, wastewater is considered as a resource of nutrients, energy and clean water [6]. In Prague Central WWTP the biogas production is more than 50000 m^3/day. The energy generated from biogas meets the heat requirement and more than 70% of the electricity demand of the WWTP [7]. In the Amsterdam-west WWTP, approximately 25000 m^3/day of biogas is produced, and that is used in Combined Heat and Power (CHP) units with electrical net efficiency of maximum 30%. The environmental benefit of this plant is considerable as it avoids 3200 ton CO_2-eq/year [8]. It will be possible to increase the net efficiency to 50% or more if a high efficiency energy conversion device is used instead of the CHP unit.

The application of biogas as a fuel to high efficiency energy conversion devices like fuel cells, especially Solid Oxide Fuel Cell (SOFC) has been reported for stationary applications. SOFCs are modular, silent, low-emission and vibration free devices that generate electrical power by electrochemical reactions [9]. Moreover, the high-temperature operation gives an opportunity to use the heat for co-generation or bottoming cycles and enables high exergy efficiencies [10]. However, there are still challenges with operating SOFCs that need to overcome the hurdles to emerge as a widely implemented technology.

This paper presents a literature review on the process of power generation by biogas fuelled SOFC, discusses operational issues and assesses the efficiency of integrated anaerobic digestion-SOFC systems. First, the theory and working principle of SOFC and anaerobic digestion are explained. Subsequently, biogas production from different waste sources is reviewed and the impact of pretreatment and digestion conditions on biogas production and quality are evaluated. Afterward, integrated biogas-SOFC technology is described, including fuel processing, reforming and operating challenges. Biogas-SOFC modelling studies at different levels like, cell, stack and system are reviewed and efficiency of integrated systems with different equipment is considered. Finally, performances of some biogas-SOFC pilot-plants are evaluated and techno-economic aspects of Anaerobic Digestion-SOFC integrated system (AD-SOFC) are assessed.

1.1. Working principle of Solid Oxide Fuel Cell

The Solid Oxide Fuel Cell converts the chemical energy of a fuel into the electrical energy through electrochemical reactions. The SOFC is composed of three major layers. A dense layer of ceramic called solid electrolyte is sandwiched between two electrodes (anode and cathode). The anode and cathode are made out of specific porous conducting material. Electrochemical reactions are driven by the difference in oxygen partial pressure across the electrolyte. SOFCs operate at high temperatures in the range of 500–1000 °C to enable oxygen ion transport through the solid electrolyte and they are suitable for long-term stationary applications [9]. Generally, at high temperature, oxygen at the cathode is reduced to oxygen ions and is transferred through the electrolyte. The oxygen ions react with fuel at Triple Phase Boundary (TPB) where the fuel gases H_2 and CO (gas phase), electrolyte (ionic phase) and electrode (electronic phase) meet. A thin layer helps to increase the ions flow and decreases the ohmic losses and resistance [9]. Electrochemical reaction of hydrogen at the anode (Eq. (1)) and oxygen at the cathode (Eq. (2)) sides are shown below:

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

$$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{2}$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \tag{3}$$

The ideal fuel for fuel cells is hydrogen, but because of complications in hydrogen production, storage and associated costs, alternative fuels are widely considered. Oxidation of carbon monoxide in SOFCs can also take place at the anode by free oxygen ions as shown in Eq. (4).

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{4}$$

However, the effective diffusion coefficient for the larger CO molecules is lower than for the smaller H_2 molecules. As a result, slower CO diffusion and larger concentration variation have been observed in the porous layer, which results in a slower CO electrochemical oxidation in comparison to H_2 [11,12]. It is also observed that the polarisation resistance with hydrogen is less than with carbon monoxide in nickel and ceria pattern anode SOFCs [13]. A poor performance of CO fed Ni-YSZ anode SOFC has been observed by Costa-Nunes et al. [14]. This can be improved by using the Cu–CeO_2–YSZ anode instead of conventional anode materials.

In case of having a fuel mixture of CO, H_2 and some steam or carbon dioxide, Water Gas Shift (WGS) reaction (Eq. (5)) is considered to occur simultaneously.

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{5}$$

In addition to the type of fuel gas, other conditions such as temperature, pressure and local gas concentrations affect fuel cell performance. The theoretical reversible Potential (E_{rev}) of the SOFCs can be calculated using the Nernst equation:

$$E_{rev} = \frac{RT}{nF}\ln\left(\frac{P_{O_2}cathode}{P_{O_2}anode}\right) \tag{6}$$

Where R is the universal gas constant, T is the absolute temperature (K), n is the number of electrons transferred for each mole of oxygen, for which is $n = 4$, and F is the Faraday's constant (96485 C/mol). The actual voltage of the operating cell is always lower than the theoretical Nernst value due to various losses (overpotential). These include ohmic overpotential (η_{Ohmic}), charge-transfer (activation) overpotential (η_{Act}), and diffusion (concentration) overpotential (η_{Conc}) [15]. Hence, the actual cell potential can be calculated using the following equation:

$$V = E_{rev} - \eta_{Ohmic} - \eta_{Act} - \eta_{Conc} \tag{7}$$

Methane-containing fuels such as syngas and biogas are potential fuels for SOFCs. The power generation from biogas-SOFC is considerably high, even when the methane content of biogas is below the value that normal combustion could occur [16]. Methane in biogas can be converted into hydrogen and carbon monoxide through the reforming reaction and at high concentration of hydrogen, good performance of SOFC is realized. Despite the possibility of biogas reforming, power density (power/active area of cell) achieved by biogas fuelled SOFC is lower than hydrogen fuelled ones. For instance, Girona et al. [17] investigated the performance of biogas ($CH_4/CO_2 = 1$) fed SOFC. The Open Circuit

Voltage (OCV) was 0.99 V, which was lower than for a humidified hydrogen fuelled SOFC (1.07 V). The obtained power density for hydrogen and biogas fuelled SOFC at the same current density and fuel utilization (30%) were 207 and 245 mW cm^{-2}, respectively. Hence, biogas reforming plays an important role in SOFCs performance and needs to be investigated in detail.

1.2. Working principle of anaerobic digestion

Wastewater treatment is crucial due to sanitation requirements and for preserving clean water resources. Major wastewater contaminants include phosphates, nitrogen compounds and organic matter. These contaminants should be removed before the treated water is discharged into the environment [18]. Major issues in WWTPs are associated with the production of sludge (in aerobic WWTP) and emissions of GHGs, such as methane (CH_4), carbon dioxide (CO_2) and NOx. Additionally, the aerobic wastewater treatment process requires electrical energy for aeration, which can be cost intensive. The energy required for this process maybe compensated by the chemical energy contained in the organic matter of the wastewater [19]. Conventional aerobic digestion is the most typically used nitrogen removal process at a low capital cost. However, the operation costs are high due to high oxygen demand [20].

Anaerobic Digestion (AD) of waste activated sludge may reduce the energy needs in WWTPs [21]. AD has been known for a long time ago. The earliest reporting of biogas use is for heating water in Persia (16th century). The first modern digestion plant was developed in India in 1859 [22]. The technology was further developed and is currently being used to generate electricity in the MW range in industrialized countries [22]. Based on recent studies and specified development guidelines, biogas production using anaerobic digestion has a bright future [23–26]. Lettinga has discovered that capacity of an anaerobic reactor can be enhanced by the specific design of Up-flow Anaerobic Sludge Blanket (UASB) and up to 97% of Chemical Oxygen Demand (COD) removal can be achieved [27].

AD is the most promising technology for intensive biodegradation of organic matter [18,28]. It can be applied to different treatment plant sizes. For instance, Rajendran et al. [29] assessed the feasibility of biogas production from household waste. In large-scale municipal WWTPs, after primary and secondary treatment of the sewage and sludge separation, activated sludge is conveyed into the anaerobic bioreactor to reduce sludge volume, stabilize the sludge and produce biogas. During the anaerobic digestion process, organic compounds are converted into methane by a mixed community of bacteria and archaea. First, the complex particulate organic matter is disintegrated by physico-chemical processes that enhance the accessibility by the enzymes excreted by the microbial community in the second step, the hydrolysis. The enzymatic hydrolysis process produces amino acids, sugars and fatty acids that can be taken up into the microbial cells. Depending on the waste stream composition, proteins and carbohydrates are the dominant (more than 60%) constituents of the total organic matter [30]. At that point, the involved microorganisms use these intermediates for their metabolic respiration which results in the formation of short chain fatty acids like propionic and butyric acid in the acidogenesis step. Subsequently, this leads to the production of acetic acid, carbon dioxide and hydrogen by the acetogenic bacteria in the acetogenesis step. Finally, hydrogenotrophic and aceticlastic methanogenic archaea convert these products into methane in the methanogenesis step [31,32]. The whole process is shown in Fig. 1.

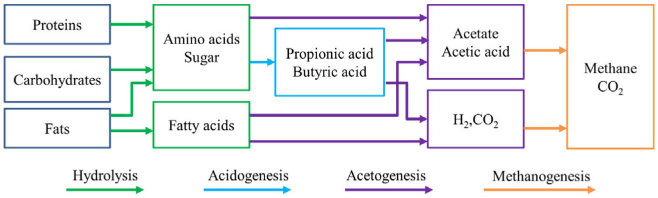

Fig. 1. The simplified process of Anaerobic Digestion [33].

The potential of methane production mainly depends on the quantity and characteristics of the organic matter in the waste stream. The degradable organic material can be estimated by the Bio Methane Potential and Chemical Oxidation Demand (COD) in the waste stream [34]. Different types of anaerobic bioreactors have been investigated including Completely Stirred Tank Reactors (CSTR), UASB, Expanded Granular Sludge Bed (EGSB), internal circulation process, etc. In Table 1, an overview of different types of anaerobic reactors at low temperature with different types of waste streams is shown.

Generally, the produced biogas consists of different gas compositions at different ranges as shown in Table 2. Typically, protein degradation results in the additional formation of NH_3 and H_2S that appear as constituents for biogas. The water vapour in the biogas follows Raoult's law and is fully dependent on the bioreactor temperature.

2. Towards integrated anaerobic digesters - Solid Oxide Fuel Cells

After contaminant removal, produced biogas from anaerobic digestion is typically used in different energy conversion devices such as gas burners, Internal Combustion (IC) engines and combined heat and power systems. Exergy analyses of these conventional combustion systems have shown that the total efficiency is generally below 50% [48], because the combustion process produces a significant exergy loss. Using electrochemical conversion devices like SOFCs could help change anaerobic digestion plants to more efficient and sustainable systems because high efficiency electrical power and high temperature heat can be generated [49].

2.1. Conventional use of biogas at WWTPs

In wastewater treatment plants, IC engines might be utilized to generate electrical power and heat from the biogas produced. In Fig. 2, a schematic block diagram is shown for the energy production process based on anaerobic digestion. The energy demand in WWTPs is mainly accounted for the thermal pre-treatment and mechanical processes. Mechanical processes demand electrical power and consist of three parts: aeration, mixing and, pumping. Innovative waste activated sludge digestion technology such as thermal/chemical process can improve the efficiency of systems because of higher sludge degradation and thus results in higher biogas yield. For pre-treatment of waste, heat is required. Based on the energy conversion device, different gas processing steps are needed. For instance, in order to burn biogas in a boiler, IC engine or gas turbine, only desulphurization is required. However, advanced biogas upgrading is needed for converting biogas into a storable fuel or for grid injection. But can partially be managed inside the digester based on the degree of reduction of the waste stream [50]. In these cases, the partial pressure of methane should be increased to reach the natural gas quality. Then it is stored in high-pressure tanks (200 bars) [51]. Also for fuel cell applications, advanced gas processing is required depending on the type of fuel cell. The energy requirement for biogas production and processing can be supplied by the energy conversion device.

At the WWTP, heat is used for several processes and the quality of heat determines how it can be used. In this article deals with low

Table 1
Anaerobic digestion of various types of waste streams under different conditions.

Anaerobic bioreactor	Waste stream	Temperature (°C)	HRT (h)	COD removal (%)/biogas production	Reference
Digester/membrane bioreactors	municipal wastewater	15–20	2.6	52–87%	[35]
UASB/side-stream membrane	municipal wastewater	Ambient (tropical climate)	5.5–10	77–81%	[36]
CSTR/side-stream membrane	municipal wastewater	25	89–120	84.5%	[37]
two-stage AD	Cheese Whey	35	10–20 days	20.8–70.9%	[38]
UASB	Industrial wastes	35	1.7–4.1	95.6%	[39]
Batch pilot-scale	Agricultural wastes	25–29	40 days	137 L biogas/day	[40]
Anaerobic Filter/UASB	dairy wastes	35–40	–	90%	[41]
batch reactors	Cattle manure (mixture)	35	23–91 days	223–368 mL biogas/gr COD	[42]
CSRT	Cattle manure	55	15	–	[43]
CSTR (Batch)	Swine,fruits	35	30 days	0.27–0.35 m^3/kg VS	[44]
UBF + MBR	Wastewater	35	24	46–99%	[45]

Table 2
General biogas composition [46,47].

Substances	Symbol	Range (%)	Average (%)
Methane	CH_4	35–75	60
Carbon dioxide	CO_2	25–50	35
Nitrogen	N_2	0.01–17	1
Hydrogen sulfide	H_2S	0.01–2	35 ppm
Ammonia	NH_3	0.01–3.5 ppm	1 ppm
Water vapour[a]	H_20	3.1	3.1

[a] (T = 25 °C, standard pressure).

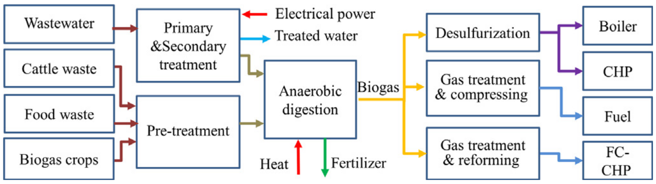

Fig. 2. Simplified schematic of energy generation from different types of organic waste and biogas crops.

(less than 60 °C) and medium (range from 60 to 180 °C) temperature. High temperature heat is also sometimes used to incinerate contaminated activated sludge, but this usually happens after transport of the sludge to a sludge incineration facility [52].

2.1.1. Low temperature heat demand in digesters

Digesters can theoretically be operated under psychrophilic (10–20 °C), mesophilic (30–37 °C) and thermophilic (50–60 °C) conditions. Too rapid changes in temperature can cause damage to the microorganisms and subsequently reduce reactor performance [53,54]. With seasonal temperature variations, the digester temperature could be reduced by reduced temperatures in the incoming substrate as well as heat losses to the environment. Accordingly, microbial biogas generation, which is temperature dependent, could vary as the season changes [55]. Keeping the temperature constant is therefore crucial for stable methane production [56]. For northern European climate, municipal sewage is usually treated aerobically, because the concentration of organic matter (COD) is too low for anaerobic treatment to generate sufficient methane to sustain the operational temperature upon combustion in a CHP. As a consequence, only more concentrated streams like manure or concentrated primary and/or secondary sewage sludge contain sufficient energy to be digested under mesophilic or thermophilic conditions [57].

2.1.2. Medium temperature heat demand in digesters

In order to accelerate the solubilization of organic matter (hydrolysis stage) and improve methane production inside the anaerobic digester, several pre-treatment techniques can be applied [58] (Fig. 2). The main improvement in performance can be achieved by increasing the surface area of the organic matter, such that enzymes excreted by the microbes can attach to the biodegradable organic matter. Many studies have been carried out to evaluate the effect of different types of pre-treatment on methane production, such as thermal, mechanical (ultrasound and high pressure) and chemical with oxidation (mainly ozonation) [30,59]. In the review article, Hendriks and Zeeman [60], revealed that thermal pre-treatment is the most commonly used technique in practice for anaerobic digestion of cellulose, hemicellulose, and lignin.

Carbohydrates, proteins, and lipids in the waste streams such as waste activated sludge, fruit and vegetable waste should be degraded, but the cell wall protects the complex polymers from the enzymatic hydrolysis. Thermal pre-treatment in the medium temperature (range from 60 °C to 180 °C) helps to destroy the cell walls and opens up the cell content for enzymatic biological degradation. Furthermore, thermal pre-treatment reduces the required retention time as hydrolysis is often the rate limiting biological step. Bougrier et al. [61] assessed thermal pre-treatment for five different types of sludge samples at different temperatures for 30 min retention time. At pre-treatment temperature below 200 °C, the COD solubilization ($COD_{soluble}/COD_{total}$) increases linearly with temperature and this increase of solubilization fraction is more considerable for temperatures higher than 130 °C. Moreover, the results showed that thermal pre-treatment between 135 °C and 190 °C does not have a substantial influence on the methane content of biogas. Perez-Elvira et al. [62] evaluated the thermal pre-treatment of mixed fresh and hydrolysed sludge at 170 °C and it has been observed that biogas production improved (with 40% higher VS removal) even at shorter retention time. To heat up the sludge generally heat exchangers or direct steam is utilized.

Alvareza and Liden [63] evaluated biogas production at three different low temperature ranges for a hydraulic residence time of 30 days. Biogas production improves by increasing digestion temperature with immediate responses. Climent et al. [64] claimed that time and temperature have the same effect on biogas production. Different kinds of treatments were studied and a 50% improvement of biogas production was observed at low temperature thermal treatment. However, they conclude that methane production does not improve by increasing the pre-treatment time more than 24 h. Qiao et al. [65] observed that thermal pre-treatment significantly increases the biogas generation for municipal sewage sludge in comparison to other waste sources and it is reported that the highest biogas production takes place on the first day of 14 days retention time. Appels et al. [66] studied the effect of low temperature thermal treatment on biogas production and compared biogas production after thermal treatment at 70 °C and 90 °C for 1 h. The results exposed that only 20 °C temperature rise can

Table 3
Influence of thermal pre-treatment on methane production for different primary sludge and waste activated sludge.

Anaerobic digestion	Retention Time (Days)	Thermal treatment	Results (increase in CH_4 production/convertibility)	Reference
CSTR	15	175 °C, 30 min	62% (COD based)	[69]
CSTR	5	175 °C, 60 min	100% (COD based)	[70]
Batch	–	70 °C, 7 days	26% (VS based)	[71]
Batch	7	121 °C, 30 min	32% (WAS based)	[72]
CSTR	20	170 °C, 60 min	61% (COD based)	[73]
Batch	10	80 °C, 30min	18.5% (SCOD based)	[74]
Batch	10	70 °C, 9 h	30% (COD based)	[75]
Batch	13	70 °C, 2 days	48% (COD based)	[76]
Batch	–	30 °C, 30 min	50.8% (COD based)	[77]
thermophilic batch	35	120 °C, 30 min	53% (COD based)	[78]
Batch	20	175 °C, 60 min	34.8% methane increase	[79]

increase biogas production considerably. Gonzalez-Fernandez et al. [67] observed double methane yield with thermal pre-treatment of sludge at 90 °C in comparison to 70 °C. Up to 48% anaerobic biodegradability has been achieved at this temperature while the rate of methane production during the first 8 days was much higher than during the rest of the 25 days experimental period. The exposure time is also a very important factor in thermal pre-treatment. Passos et al. [68] studied thermal treatment of micro-algae at lower temperatures (55 °C–95 °C) at different exposure times (5–15 h) and reported that methane production improves by 62% after increasing temperature to 95 °C compared to untreated. It states that increasing pre-treatment process from 10 to 15 h just slightly increases methane production for all temperatures studied. Some more references are shown in Table 3.

2.2. Future use in Solid Oxide Fuel Cells

Generally, SOFC efficiency is much higher than IC engines (especially for the small ones) and the presence of CO_2 is helpful for internal methane reforming [80,81]. Hence, IC engines can be potentially replaced with SOFC in WWT plants. Additionally, ammonia separation in the digester and its subsequent use as fuel in an SOFC can increase the electric power production in treatment plants. Other low-temperature fuel cells also can be applied for power production but, generated biogas must be converted to hydrogen-rich gas as a fuel and extensive gas cleaning is essential, which leads to a costly system [9]. Other types of high-temperature fuel cells like Molten-Carbonate Fuel Cell (MCFC) also can be used [82], but the electrolyte is corrosive (lifetime issues) and extra CO_2 flow is required for the cathode side, which is not always available [83,84]. SOFC seems a good candidate for biogas fuelled fuel cell for stationary integrated power plants and it is also an appropriate option for Auxiliary Power Units (APU) in vehicles [85]. Shiratori et al. [86] have fuelled an SOFC with biogas at CH_4/CO_2 ratios fluctuating between 1.4 and 1.9. An insignificant fluctuation on voltage was observed. Staniforth and Kendall [16] demonstrated that even with a high carbon dioxide fraction, biogas fed SOFC performance is comparable with hydrogen fuelled one in terms of power production. To prevent carbon deposition on the cell, providing a mixture of air and biogas is suggested. The performance of biogas fed SOFC at different operating conditions and challenges will be the focus of this paper.

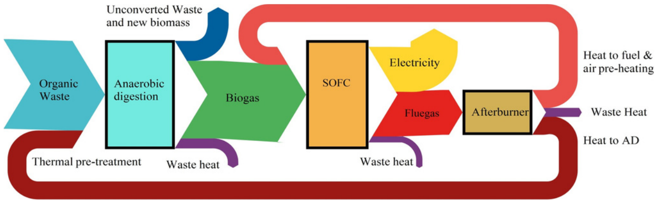

Fig. 3. A simplified energy flow diagram of AD-SOFC system.

2.2.1. An integrated AD-SOFC energy balance

Banks et al. [87] have conducted a long-term experiment on a biogas fuelled IC-CHP system (195 kW). A thermal pre-treatment system was used at 70 °C and the generated biogas was fed to an IC engine. The overall electrical conversion efficiency was 32% for CHP system and 53% of the heat was recovered, and the total recoverable energy per wet tonne of food waste was almost 405 kWh. Lübken et al. [88] developed a model to evaluate the energy balance of AD while it is self-heating at different operating conditions. The results show that the energy production during a year is much higher than the energy consumed during the entire year, however, during the winter, energy consumption (because of radiation losses) increases dramatically. Bohn et al. [89] evaluated the energy balance of AD at low temperature farm-scale system. They found that the optimum methane yield and energy production would be achieved at 30 °C (digestion temperature) and 60% net energy efficiency. Berglund and Borjesson [90] found that, in Sweden, using raw materials with high water content decreases the net power generation but, the energy demand for AD (including waste collection, transportation, electricity and heating requirements) ranges between 20% and 40% of the overall energy production. The energy balance of different biogas production methods (single and co-digestion of multiple feedstock) have been evaluated by Martina Poschl et al. [91]. It is indicated that energy input to output ratio can change from 10.5% to 64% for single feedstock digestion (mesophilic) and energy input largely depends on the type of waste materials. The Energy balance can be negative for municipal solid waste feedstock when transportation distances are more than 425 km.

Bouallagui et al. [92] evaluated the net energy production of AD at three different low temperature levels. Energy consumption at the highest temperature (thermophilic process) was about 41% higher than medium temperature (mesophilic process) AD, however increased biogas production compensates the energy consumption and net energy production is almost double at the highest temperature. Also, due to the faster kinetics at thermophilic temperature, the tank volume can be smaller. Hence, anaerobic digestion of all kind of wastes results in positive energy production and thermal pre-treatment even at low temperatures can improve biogas production and consequently energy efficiency of the system, regardless of the type of energy conversion device. Thermal pre-treatment indeed is useful in enhancing biogas production. In spite of a varying temperature range reported in the literature for thermal pre-treatment, it can be seen that heat available from SOFC or bottoming cycles could be possibly used for thermal pre-treatment offering an opportunity for efficiency improvement.

Fig. 3 depicts a simplified energy flow diagram for an AD-SOFC integrated system. It is assumed that part of the organic substrate is not converted into biogas and there is heat loss from the AD tank. The electricity generated can be used for wastewater treatment process and high temperature outlet gas is conveyed to an afterburner. Heat generated in the afterburner can be used in wastewater treatment process, more specifically for thermal pretreatment of the organic waste.

3. Biogas contaminants and fuel processing

The composition of anaerobic digester gas can vary naturally due to the digestion conditions and feed wastes. At low concentrations of methane, the IC engine efficiency declines considerably [93,94]. Bari [95] recommended to reduce the carbon dioxide content in biogas with at least 10% to improve biogas combustion in diesel engine. When using biogas containing more than 40% CO_2, the IC engine performance severely declines. Porpatham et al. [96] suggested adding 10% hydrogen to biogas to improve the performance of spark ignition engine. They concluded that this does not affect NOx production. Also, ammonia in biogas increases the NOx production in an IC engine [97]. Hence, using devices that can tolerate high CO_2 content and reduce NOx emissions would be preferable. The SOFC has these desirable features.

Biogas is therefore a promising fuel for SOFCs [98] as neither carbon dioxide nor vapour have to be removed. However, raw biogas often contains considerable quantities of undesirable trace compounds such as hydrogen sulfide (H_2S) and siloxanes that can cause SOFC degradation already at very low concentrations. Additionally, ammonia (NH_3) is also known as a contaminant in conventional CHP systems, which causes a gradual erosion and corrosion on Balance of Plant (BoP) components. Hence, biogas cleaning for such contaminants is a crucial step [99]. The amount of these contaminants varies widely depending on the biogas production unit operating conditions and raw feedstock composition [100]. In the following subsections, the effects of the most important trace contaminants on system performance are discussed.

3.1. Hydrogen sulfide

The majority of wastewaters contain sulfate, and during anaerobic treatment, sulfate is reduced to sulfide by sulfate reducing bacteria. Sulfate reducing bacteria compete for substrate with methanogenic microorganisms, which results in less methane and the presence of highly undesirable hydrogen sulfide (H_2S) [101,102]. Hydrogen sulfide is a flammable, malodorous, poisonous and colourless gas that is heavier than air. This gas is converted to environmentally hazardous compounds such as sulfur dioxide (SO_2) and sulphuric acid (H_2SO_4). H_2S is also a corrosive gas that could form concentrated sulfuric acid, depending on humidity, oxygen concentration and presence of biofilm and can thereby destroy pipe lines and other metal equipment. In general, many types of gas utilization units can tolerate H_2S levels between 100 and 3000 ppm and for expensive equipment such as CHP systems, H_2S levels below 250 ppm and water vapour removal are recommended [98]. Numerous studies have been carried out in order to investigate the H_2S removal for different applications [103–109].

The effect of H_2S on SOFC performance has been addressed in several studies. In conventional nickel-based anode SOFCs, H_2S poisons the anode by converting Ni to Ni-sulfide that forms large, dense metal sulfide particles on the anode surface. This leads to a reduction in the three phase boundaries and degradation in the electrochemical activity [110]. However, SOFC is considered the most tolerant fuel cell type to H_2S impurities [111]. According to experiments conducted by Norheim et al. [112], at a high level of H_2S impurities (>20 ppm), a reduction of SOFC performance has been observed with a Ni-YSZ anode supported cell. This reduction in the cell performance was depending up on the cell material as well as operating temperature and found to be reversible after H_2S removal from the fuel gas. Sasaki et al. [113] have analysed H_2S poisoning of SOFC with different cell materials (Yttria-Stabilized Zirconia (YSZ) and Scandia-Stabilized Zirconia (ScSZ)) with respect to impurity concentration, operational temperature, and fuel composition. The results showed that a considerable voltage drop for higher than 5 ppm H_2S poisoning occurred. Sulfur tolerance was better for the cell with ScSZ in the anodes. Appari et al. [114] concluded that poisoning at high temperature in Ni based anode material (packed bed reactor) can be easily reversed just by removal of H_2S from the feed stream. Zhang et al. [115] investigated the impact of sulfur poisoning on operational behaviour of different SOFC anode materials (Ni/YSZ and Ni/GDC (Gadolinium Doped Ceria)). Results indicated that Ni/GDC cermet (ceramic–metallic composite) anode material has a better performance during the exposure to H_2S-containing hydrogen fuels, which is likely associated with the mixed ionic and electronic conductivity of the GDC phase. Mahato et al. [15] state that better performance of Ni–GDC anodes is associated with their mixed ionic and electronic-conductivity and also with the adsorption of hydrogen on GDC. Therefore, even though the Ni surface is covered by sulfur, GDC can still prepare the required conditions for the electrochemical reactions. Da Silva and Heck [116] studied the thermodynamics of sulfur poisoning in SOFCs to identify the effect of H_2S on operating parameters such as current density. At fuel utilizations (U_f) lower than 90%, increasing current density slightly increases the interaction of sulfur with Ni. So, understanding sulfur poisoning and increasing the sulfur tolerance are important for commercialization of SOFCs.

The development of sulfur tolerant anodes, based on Ni-free electrodes such as perovskites may lead to considerable reduction in both capital and operating costs by using conventional impure fuels. Huang et al. [117] explored a mixed oxide-ion electron conductor double perovskites $Sr_2Mg_{1-x}Mn_xMoO_{6-d}$. This appeared as meeting the requirements for long-term stability with a tolerance of 50 ppm H_2S in pure hydrogen fuel at a fixed current density for 200 h. Very high power density (438 mW cm^{-2}) was also achieved for dry methane fuel (claimed as methane direct oxidation) with Sr_2MgMoO_{6-d} anode material. Similar study has been carried out by Chen et al. [118] with a $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$/GDC anode with humidified methane containing 5000 ppm H_2S considered as a fuel at constant cell voltage of 0.5 V. A relatively negligible degradation rate of (0.017%/hour) has been observed. The degradation is attributed to the coarsening of the electrode microstructure. Furthermore, it is considered as possible to oxidize H_2S as a fuel in SOFC. However realising this is considered as challenging. Aguilar et al. [119] studied SOFC performance on H_2S containing fuel for Strontium doped Lanthanum Vanadate (LSV) anode material and observed no considerable deterioration if the fuel contained less than 5% H_2S. Electrochemical oxidation of H_2S was suggested as more active compared to hydrogen fuel for this anode. Vincent et al. [120] investigated the potential of using Lanthanum Strontium Titanate (LST) anode material with conventional YSZ (mixed 50/50 mass ratio) for CH_4 fuel containing 20% H_2S. Results indicated that CH_4 and H_2S could be considered together as a fuel and a power density of 450 $mWcm^{-2}$ has been achieved. $Ce_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$ (CSCV) and NiO-YSZ anode was prepared by Danilovic et al. [121]. The cell performance was tested for methane fuel containing 5000 ppm H_2S. It is stated that the CSCV improves electro-catalytic activity towards H_2S oxidation. Ni contributed more on methane oxidation. However, Ni was not stable during the test and sulfidation of the anode was observed. While several of

Table 4
Volatile methyl siloxanes in biogas [128].

Abbreviation	Compound	Formula	Molar mass (g/mol)
D4	Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	297
D5	Decamethylcyclopentasiloxane	$C_{10}H_{30}O_5Si_5$	371

these anodes are being developed, it has to be noted that stacks and systems based on such anodes are yet to be developed.

The effect of H_2S on the internal methane reforming rate has been investigated as well. Shiratori et al. [122] studied the feasibility of biogas direct fuelled SOFCs by using a Ni–ScSZ cermet as the anode material. They observed a 9% voltage drop and 40% decline in methane conversion rate in a 1 ppm H_2S poisoning test that was conducted under operation conditions of 200 mA/cm^2 current density and a temperature of 1000 °C. Ouweltjes et al. [123] studied the influence of sulfur contaminant (2–9 ppm) on the Ni-GDC cell fed with biosyngas. Results illustrate that sulfur largely affects the internal methane reforming however, the influence was negligible for the oxidation of hydrogen and carbon monoxide. Papurello et al. [124] have used Na–X zeolites fixed bed reactor followed by a ZnO guard bed to remove H_2S from a simulated biogas contaminated with 30 ppmv H_2S, and the concentration of H_2S decreased to 0.07 ppmv for an extended test period (250 h). Further studies on H_2S tolerance with biogas in operating SOFCs are highly recommended.

3.2. Siloxane

Siloxanes are a group of silicon (Si)-bearing molecules that are used in cleaning, cosmetics, defoamer products and deodorants, and are generally found in wastewater treatment plants and landfills [125,126]. According to literature, D4 and D5 are the most abundant among the different siloxanes detected in biogas samples (Table 4). During the combustion of biogas at high temperature, silicon dioxide (SiO_2) forms. The size of SiO_2 particles ranges between 40 and 70 nm and the particles occur as fibrous dusts that are categorized as nanoparticles, and considered to be toxic to human health [125]. Ajhar et al. [127] have done a thorough study on siloxane removal from biogas. A pre-drying step is proposed before using activated carbon for the gas produced from sewage sludge. Removing Siloxanes and H_2S can be done simultaneously through activated carbon.

Schweigkofler and Niessner [129] reported that apart from activated charcoal, silica gel has shown high adsorption capacities for siloxanes. It is also advised to use a Fe-based adsorbent (meadow ore) bed. It can bring down siloxane concentration by 75%. Yu et al. [130] have evaluated different types of activated carbon for siloxane adsorption and a range of 1.7 nm–3 nm pores diameter has been suggested as the optimum pore size. Finocchio et al. [130] assessed a variety of siloxane purification solids and it was observed that activated carbon is the most efficient sorbent. Recently, Gislon et al. [131] have conducted experiments to achieve a purified biogas with less than 1 ppm siloxane. It is suggested to use activated carbon with a larger specific surface area.

In addition to siloxane removal from biogas, a few studies have also been carried out to assess the performance of SOFCs with siloxane containing fuels. Siloxane causes fatal degradation of cell performance even at ppm levels. Solid SiO_2 is formed within porous cermet anodes and near the top surface anode layer [110]. Haga et al. [132] evaluated the effect of siloxane on the performance of SOFC and they concluded that the cell voltage declines gradually at 10 ppm siloxane contaminant at different temperatures due to SiO_2 precipitated on the top surface of the anode. Sasaki et al. [110] have investigated different impurities such as chlorine, siloxane, phosphorus, and boron. A tentative concentration threshold of impurities has been defined for a humidified hydrogen fuelled SOFC, which is 2 ppm for siloxane (D5). Madi et al. [133] assessed the impact of siloxane on Ni-YSZ anode SOFCs by conducting Electrochemical Impedance Spectroscopy (EIS) tests. Adding siloxane to the fuel stream resulted in an increase in required activation energy and this is attributed to a decrease in the active triple phase boundary area. Haga et al. [134] evaluated the poisoning of Ni–ScSZ cermet anodes by various fuel impurities such as H_2S, CH_3SH, COS, Cl_2, and siloxane. Experimental studies were conducted for 10 ppm siloxane (D5) in 3%-humidified H_2 at 800, 900 and 1000 °C. The degradation was attributed to SiO_2 that was precipitated near the top surface of the porous anode and reduces TPB areas.

Arespacochaga et al. [135] suggested three steps for biogas treatment for SOFC applications. First, H_2S removal by a regenerable iron-based adsorbent unit, secondly trace components removal such as siloxanes by an activated carbon unit and the third step, to use a biogas drying unit to remove moisture.

3.3. Ammonia

Ammonia (NH_3) is the second most important contaminant present in biogas considering IC engine applications. It is corrosive and during the combustion process, slightly increases the NOx emissions [136]. Also, this water soluble gas can be a threat to aquatic plants and animals if present in high concentrations (more than 1 mg NH_3 L^{-1}) [137]. Generally, in WWTPs, ammonia and oxidized nitrogen are removed through the conventional aerobic energy-intensive activated sludge process. Moreover, ammonia has shown to be inhibiting methane production in a concentration range of 1–2 g NH3-N L^{-1} [43]. Several energy consuming physicochemical methods can be applied to remove ammonia, such as air stripping and chemical precipitation [138–141]. However, for conventional biogas energy conversion devices like IC engines, the ammonia concentration in biogas (gas phase) needs to be reduced to very low ppm level [142], which is highly energy intensive [143].

Unlike for IC engines, ammonia is considered as a fuel for SOFCs. Due to the high temperature operation, ammonia is cracked into nitrogen and hydrogen molecules. Electrical power is then subsequently produced by the electrochemical oxidation of H_2 (Eqs. (1)–(3)) [144]. Recently, the use of ammonia as a fuel for SOFC has been drawing attention as ammonia is an easily storable, efficient hydrogen carrier [145–147]. For Ammonia, endothermic cracking reaction starts at 405 °C with simultaneous evolution of nitrogen and hydrogen. Complete conversion of ammonia occurs at 590 °C following Eq. (8). No undesirable nitrogen oxides are formed on the nickel cermet anode [148].

$$NH_3 \rightleftharpoons {}^3\!/\!_2 H_2 + {}^1\!/\!_2 N_2, \quad \Delta H^0_{298} = 46.22\, {}^{kJ}\!/\!_{mol} \tag{8}$$

Results indicate that Ni-based catalyst is appropriate to promote ammonia cracking, similar to methane reforming [149]. The performance of the nickel cermet SOFC has been evaluated under various conditions at a temperature range of 700 °C–900 °C, and results showed a considerable performance in comparison to pure hydrogen fuel [150]. Note that ammonia is also considered as a biogas contaminant in IC engine applications, whereas it can be potentially used as a fuel in SOFC systems [151]. This opens up opportunities for removing ammonia directly from the digesters and to use it in SOFCs. The energy requirement for nitrification/denitrification depends on the Nitrogen concentration of the wastewater (1.224 MJ/m^3 of wastewater (roughly 24.5 MJ/kg-N) for small scale plant). This can then be significantly reduced by extracting ammonia after primary treatment of wastewater stream [152]. The removed ammonia can be used as a fuel for SOFCs. Overall energy efficiency of 81.1% and electrical efficiency of 69.3% have been reported for an ammonia fuelled SOFC-gas turbine integrated system which is equal to 15.1 MJ/kg-NH_3 overall and 12.8 MJ/kg-NH_3 electrical power based on the ammonia LHV [153]. On the other hand, it should be considered that the electrical energy demand for ammonia recovery from WWTP is roughly equal to 11.2 MJ/Kg-N [154,155]. Therefore, an energy consuming process can be converted into an energy-positive one.

4. Biogas conversion

As mentioned before, biogas is predominantly methane and direct electrochemical oxidation of methane is much slower than H_2 and CO, thus only methane reforming is considered in this article [156,157]. The reforming process can be achieved either internally using SOFCs or externally using a catalytic (pre) reformer. The three major methods for methane conversion are steam reforming, Partial Oxidation (POX), and dry reforming. Also, there are mixed methods such as Autothermal Reforming (ATR) (mixed steam reforming and methane POX).

4.1. Steam reforming

Most studies only consider steam as a reforming agent for methane reforming in SOFCs. This method also has been proposed for methane reforming of natural gas and syngas [158]. Methane is reformed by direct steam injection at high temperature through the reaction shown in Eq. (9). The Methane Steam Reforming (MSR) reaction is a highly endothermic reaction that can take place either inside or outside SOFCs. As it can be seen in steam reforming reaction, one mole of steam is required to reform one mole of methane. The carbon monoxide generated can also react with the remaining steam and produces more hydrogen through the exothermic WGS reaction (Eq. (10)). Ni present in the SOFC anode is also a good catalyst for the WGS reaction [14].

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO, \quad \Delta H^0_{298} = 206.3\ kJ/_{mol} \tag{9}$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2, \quad \Delta H^0_{298} = -41.1\ kJ/_{mol} \tag{10}$$

Steam reforming is a well-established technique, although, from a thermodynamic point of view, the chance of carbon deposition is still high at low steam to carbon ratios [159]. High temperature and a high steam/carbon ratio are favourable conditions for steam reforming [160]. This process is considerably endothermic and a heat source has to be used. Moreover, steam generation is highly energy consuming. Therefore, determining a minimum steam/carbon ratio is crucial. On the other hand, a high amount of steam is required to avoid carbon deposition. In literature, a variety of steam/carbon ratios have been proposed at different operating conditions to guarantee safe operation and improve the exergy efficiency of SOFCs. However, direct internal reforming in operating SOFCs is not well understood and much focus is now on improving catalyst materials for the same [161].

4.2. Partial oxidation (POX)

Methane conversion can also be carried out through one of the simple partial oxidation reactions which are shown in following equations. Oxygen from the air can also be used as a reforming agent [162].

$$CH_4 + {}^1\!/\!{}_2O_2 \rightleftharpoons 2H_2 + CO, \quad \Delta H^0_{298} = -44\ kJ/_{mol} \tag{11}$$

$$CH_4 + O_2 \rightleftharpoons 2H_2 + CO_2, \quad \Delta H^0_{298} = -322\ kJ/_{mol} \tag{12}$$

$$CH_4 + 2O_2 \rightleftharpoons 2H_2O + CO_2, \quad \Delta H^0_{298} = -803.03\ kJ/_{mol} \tag{13}$$

The products of Eq. (11) can be directly fed into the SOFC. This reaction is slightly exothermic and the generated heat increases the temperature of the fuel so that the required fuel pre-heating is also done through this reaction. If more oxygen is available, partial oxidation goes through Eq. (12). This reaction is much more exothermic. Required steam for steam reforming can be produced by increasing the available oxygen as in Eq. (13). This reaction is largely exothermic and sufficient heat is generated to heat the SOFC inlet fuel. These reactions can take place in a Catalytic Partial Oxidation (CPOX) unit outside of SOFC. On the other hand, in these reactions hydrogen yield is much lower in comparison to the steam reforming process. A ratio of one to one for the air to biogas ratio has been suggested to avoid carbon deposition at 800 °C in an operating SOFC, and the voltage stability was improved. However, re-oxidation of Ni metal catalyst has been observed and optimization of air dosage must be carried out [86]. Additionally, due to the presence of nitrogen in the air and fuel mixture, the partial pressure of hydrogen in the fuel is low which leads to a lower voltage in SOFC.

4.3. Dry reforming

Apart from steam, carbon dioxide also can be considered as an agent for methane reforming [162]. This type of reforming is known as dry reforming. Biogas consists of two greenhouse gases: CH_4 and CO_2. Therefore, dry reforming is the most interesting type of reforming for biogas fuel processing because one gas component (CO_2) is utilized to reform the other one (CH_4). Meanwhile, the generated gas mixture can be applied as a fuel for SOFCs. Additionally, in case of carbon deposition, the presence of CO_2 in biogas has a beneficial effect on SOFC operation, because CO_2 can fairly remove carbon deposition by gasification of carbon [163]. Nevertheless, the dry reforming reaction is highly endothermic and needs a high operating temperature (800–1000 °C) to obtain a high conversion rate of methane [164]. This reaction is shown in Eq. (14). In the case of direct internal reforming, this endothermic reaction causes a sharp temperature gradient at the entrance of the fuel channel inside SOFCs, which can result in cell cracking [165]. Moreover, hydrogen generated from the dry reforming reaction can react with the remaining CO_2 and produce CO which is also a fuel for SOFCs [166].

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO, \quad \Delta H^0_{298} = 247.3\ kJ/_{mol} \tag{14}$$

$$H_2 + CO_2 \rightleftharpoons CO + H_2O, \quad \Delta H^0_{298} = 41.1\ kJ/_{mol} \tag{15}$$

While high temperatures are required for the fast kinetics of methane reforming, Reverse Water-Gas Shift (RWGS) is slightly endothermic and high temperature is in favour of CO production. So, the partial pressure of CO is higher than the partial pressure of

H_2 in the reformed gas [167]. This leads to some problems such as carbon deposition on the anode, delamination of anode and finally deactivation of anode catalyst [168].

Generally, CH_4/CO_2 molar fraction in actual biogas is between 1.2 and 1.9 [169]. So, the CO_2 in biogas is insufficient to completely reform the methane content into hydrogen and carbon monoxide. The required CO_2 for dry reforming can be supplied from other processes for instance, from the exhaust gas of the activated sludge process [170] or by partial recirculation of the anode exhaust flow [171]. Otherwise, extra reforming agent is required which can be the steam (Eq. (9)). The required steam can be produced from different sources for instance, a steam generator or the hydrogen electrochemical reaction (Eq. (1)) on the anode side. Lanzini and Leone [172] have suggested adding 1.2 mol of CO_2 to each mole of biogas to achieve a stable voltage. An equimolar CH_4/CO_2 feed gas composition is recommended by Yentekakis et al. [173] to maximize the electrical power output of SOFC, whereas Xu et al. [174] proposed a CO_2/CH_4 ratio of 1.3 as an optimum gas composition for dry reforming. On the other hand, it has also been reported that adding CO_2 to general biogas composition increases the ohmic resistance of the cell [175].

Shiratori et al. [86] have used real and simulated biogas for SOFC, focusing on poisoning by contaminants, fluctuation in biogas composition, and carbon deposition. In spite of theoretical predictions of carbon deposition with a ternary diagram, no carbon deposition was observed for the simulated biogas. It is claimed that by drawing current, methane conversion was promoted. On the other hand, severe carbon deposition took place during the long term experiment with actual biogas. Staniforth and Ormerod [176] have studied the impact of methane partial pressures on operating SOFC performance with a low methane content (15%). Power production was high enough while carbon deposition was inevitable. They have found that at methane mole fraction of 0.45 the obtained power is the maximum corresponding to the high partial pressure of H_2 and CO through internal dry reforming. Santarelli et al. [177] have investigated internal dry reforming of biogas on a tubular (Ni-YSZ anode supported) SOFC stack with different extra moles of CO_2, corresponding to CH_4/CO_2 ratios of 0.43, 0.32, and 0.25. Performance maps of the SOFC for a wide range of current densities under different fuel flow rates have been determined. It has been reported that dry reforming is more effective for CH_4/CO_2 of 0.43. Guerra et al. [178] have assessed dry reforming on Ni/YSZ catalyst. Different parameters such as temperature, residence time and CH_4/CO_2 ratio have been studied to optimize the performance of a biogas SOFC. A range of $0.5 < CH_4/CO_2 < 0.75$ has been suggested to obtain a high methane conversion and to prevent carbon deposition. Also, it is shown that reforming reactions are fast and temperature-dependent. It is also observed that at an appropriate residence time, reaching equilibrium condition is possible even at an intermediate temperature of 800 °C. Thermodynamic equilibrium content of biogas (60% CH_4 and 40% CO_2) with air (21% O_2) were calculated and shown in Fig. 4. At 750 °C the carbon deposition disappears and at 800 °C all methane reformed to hydrogen and carbon monoxide. However, the challenges in maintaining appropriate gas composition and temperature gradients across large-area SOFC stacks make it difficult to get all hydrocarbon fuels reformed by the internal reforming [179].

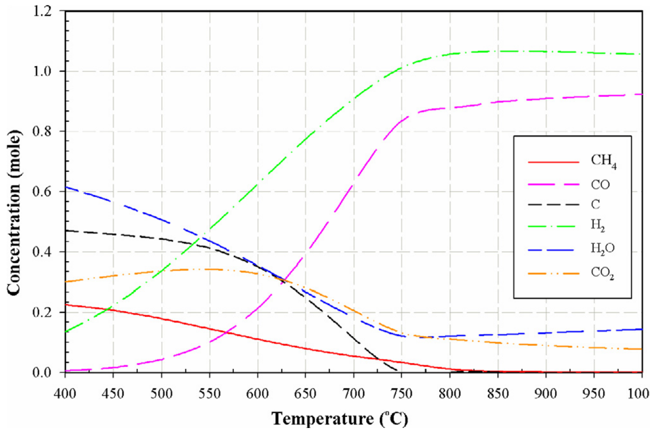

Fig. 4. Thermodynamic equilibrium concentrations (moles) in the temperature range 400–1000 °C at 1 atm for mixed biogas and air.

4.4. Combined reforming

Steam and dry methane reforming are endothermic whereas the partial oxidation is an exothermic reaction that can produce the required heat for reforming or preheating the fuel gases. Therefore, combined reforming is a good opportunity to optimize SOFC performance. The required steam for methane reforming can be produced by fuel oxidation in a Catalytic Partial Oxidation (CPOX) unit. With Autothermal Reforming (ATR), the POX and MSR take place in a reactor by feeding the hydrocarbon with both steam and air. Ahmed and Krumpelt [180] found that ATR is capable of achieving higher reforming efficiencies in comparison to steam reforming whereas the hydrogen partial pressure in steam reforming is higher. However, it is difficult to control all operational parameters such as the O/C ratio to produce a hydrogen rich fuel for SOFC.

Lanzini and Leone [172] investigated bio-methane and bio-hydrogen fuelled SOFC with different additional oxidation and reforming agents such as air, steam, and CO_2. A carbon formation boundary diagram is proposed for different reforming agents. The results showed that from a power production perspective, the best reforming agent is steam, for which the obtained overall stack electrical efficiency was 41%. Piroonlerkgul et al. [181] compared different biogas reforming agents (steam, air, and combined steam/air) for different plant configurations. The results illustrate that increasing the concentration of reforming agents decreases the electrical efficiency. However, they state that steam is the most appropriate reforming agent. Papurello et al. [124] have investigated combined reforming in external reformer at space velocities (the volumetric flow rate entering the reactor divided by the reactor volume) as high as 150000 h^{-1}. Methane conversion for dry reforming at 800 °C was reported to be about 47%. A further increase in conversion by 21% was observed with the addition of steam ($H_2O/CH_4 = 1.2$). Addition of small amounts of oxygen ($O_2/CH_4 = 0.12$) has been shown to increase the methane conversion to about 78%.

Van Herle et al. [182] illustrated the variation of electrical efficiency for an SOFC stack with different CO_2 fractions of air mixed biogas. In a developed model, when the oxygen to methane ratio and fuel utilization were kept constant ($O_2/CH_4 = 0.35$, $U_f = 0.8$), fuel gas composition with rich carbon dioxide content (60% CO_2/40% CH_4) was determined as an optimum in order to maximize the electrical power production. Takahashi et al. [165] have used air to partially oxidize methane in biogas on Ni–ScSZ and Ni–YSZ anodes. They observed that additional air can decrease the temperature gradient that is generated because of endothermic dry reforming reaction. On the other hand, the methane conversion rate decreases. Because of the short residence time, no difference was observed for these two anodes. Optimum air/biogas mixing ratio was found to be 0.7 for biogas-SOFC whereas $CH_4/CO_2 = 1.5$ for biogas at 800 °C. However, it is proposed by Takahashi that the air/biogas ratio be higher than 1 to obtain a homogeneous temperature at the fuel channel of SOFC.

Leone et al. [183] have conducted a series of experiments for biogas-SOFC single cell. A Ni-YSZ cermet (ceramic-metallic) anode supported SOFC was used with a biogas composition that possibly could lead to carbon formation. A fast voltage drop has been observed. So, a steam to carbon ratio of 0.5 has been proposed to avoid carbon formation. However, it has also been observed that adding steam to biogas results in a reduction in the current density obtained [11]. Shin-Kua Ray et al. [164] evaluated the combined steam and dry methane reforming on Ni catalyst. They observed that CO_2/H_2O ratio influences the methane reforming because Ni shows a better catalytic activity for steam in comparison with CO_2. This ratio is more effective at lower temperatures (<973 K).

As mentioned in this section, there are different methods for biogas reforming and based on the availability of reforming agents and conditions, an appropriate method should be selected. Partial oxidation of biogas is one of the simpler techniques, however, the exergy efficiency of the process is low due to the direct oxidation of methane. Furthermore, there remains a possibility of re-oxidation of anode material due to high oxygen partial pressures in the fuel gas. Biogas combined (steam/dry) reforming is a more established technology with several experimental studies carried out in the past. Dry reforming is more environmental-friendly and less expensive, however slow kinetics, high thermal stresses, risk of carbon deposition and limited experimental investigations make this method not very attractive. The optimal method for methane conversion in biogas-SOFC remains not well understood. Moreover, there are several challenges that should be handled for the continuous operation of biogas fed SOFC systems. The next section gives a comprehensive overview of these challenges.

5. Operational challenges for biogas fuelled SOFC

Using biogas fuelled SOFC as an energy conversion device offers multiple advantages, but there are many challenges that should be tackled to make sure that the fuel cell operates under safe conditions. This section elaborates on the main operating challenges encountered with biogas fuelled fuel cells with review of proposed solutions.

5.1. Direct internal reforming

Steam and dry methane reforming reactions (Eq. (9) and (15)) are considerably endothermic and a heat source is needed to run the external reformer reactions. On the other hand, electrochemical reactions (Eq. (1) or (4)) which take place in SOFCs is significantly exothermic and hence controlling the temperature is a challenge. In the case of Direct Internal Reforming (DIR), these reactions take place simultaneously in SOFC. Therefore, DIR reduces the electrical power required for cooling down the SOFC stacks compared to hydrogen fuelled ones [86]. Applying DIR makes the system compact and cost-effective. A possible drawback of DIR is the additional thermal stresses in cells because of the sharp temperature drop due to the endothermic reforming process at the entrance of the fuel channel in SOFC stacks.

The complex interaction between reforming, POX, WGS and electrochemical reactions determine the local heat production in SOFCs. Therefore, it is crucial to know the reforming reaction kinetics for operating SOFCs. Methane steam reforming kinetics for catalytic external reforming have been extensively investigated and some experimental studies on the kinetics of internal methane steam reforming especially, in Ni based anode materials have been reported [184]. Only a few studies have tried to illustrate the dry reforming reaction mechanism and associated kinetics [177,185].

Gokon et al. [186] studied the dry reforming kinetics for a low temperature SOFC (600 °C −700 °C). The catalytically activated metallic foam absorber such as Ru/Al_2O_3 catalyst on a Ni−Cr−Al alloy foam has been used for different CH_4/CO_2 ratios. Langmuir−Hinshelwood has been found as the best kinetic model to predict the methane reforming reaction rate. The power law rate equation has also been used to evaluate the reforming kinetics for different temperatures and partial pressure of fuel components. The results have indicated that Ni/La-Co(3%wt)/Al_2O_3 catalyst has the highest activity in reforming and highest activation energy (99.4 kJ/mol). Laosiripojana and Assabumrungratb [167] have reported that for a ceria (CeO_2) catalyst material (with highly mobile oxygen vacancies) the dry reforming rates are almost equal to the steam reforming rate for the same methane partial pressure. Moreover, the same reaction mechanism for methane and dry reforming is proposed. Ceria (CeO_2) has a good potential for indirect internal reforming in SOFCs and the disadvantages are the low specific surface area and catalyst deactivation because of thermal sintering. Using CeO_2, which has a large surface area, improves the performance of this catalyst. Hecht et al. [187] investigated the elementary heterogeneous chemical kinetics of dry, steam and mixed reforming of a Ni-YSZ SOFC with an anode supported cell. They found that at low current density, the reaction tends toward equilibrium.

Brus et al. [188] have analysed the thermodynamics of carbon deposition in SOFCs with combined steam and dry reforming. A numerical model has been developed to study the kinetics of reforming. With a small additional amount of steam, SOFC can operate in the safe region of coking, however high CO content in the fuel decreases the overall efficiency of SOFC. Kinetics of mixed steam and CO_2 reforming of methane in a fixed-bed reactor have been assessed over Ni/La/Al_2O_3 based catalyst by Park et al. [189].

Meng [11] has developed a numerical model to test the effect of steam addition to biogas for different operating conditions. Especially the gas composition through the fuel channel has been studied as well as the impact of current density. The results show that for a mixture of biogas and steam, despite a reduction in total current density, the local current density slightly increases toward the downstream direction. This shows that using a long fuel channel has a beneficial effect on the operation of biogas SOFC. It was observed that the rate of dry reforming is higher at the inlet and decreases significantly along the fuel channel. WGSR rate was negative at the inlet for pure biogas due to a lack of water. Also, a large temperature drop is observed from inlet to outlet due to all endothermic reactions. Furthermore, some studies have been dedicated to investigate the reforming kinetics in external reformers (catalytic CO_2 reforming). These studies mostly focused on the kinetics of steam and combined methane reforming and more studies are still needed to investigate the kinetics of biogas SOFC dry reforming. Furthermore, in case of having ammonia mixed with biogas fuel, the influence of ammonia cracking on methane reforming also needs to be investigated.

5.2. SOFC materials

SOFC consist of an electrolyte, electrodes (cathode and anode), interconnect (metal or ceramic) and inactive thermal insulator. Materials should be chosen in order to reduce losses, for instance, lowering electric resistance of the electrodes, contact resistance associated with interfaces, and lowering ionic resistance of electrolytes. Moreover, high operating temperatures with SOFCs lead to several materials problems, which include interfacial diffusion between electrolyte and electrode materials, thermal instability, mechanical and thermal stresses because of the difference in the thermal expansion coefficients for different components. Decreasing the operational temperatures would bring considerable cost benefits. Zirconia doped with 8−10 mol % yttria (yttria-stabilized Zirconia (YSZ)) is still the most effective electrolyte for the high-temperature SOFC, although several others have been investigated, for instance, ceria and lanthanum materials [9]. The catalytic effect of anode materials is also important when fuel reforming is needed.

One of the advantages of SOFCs is being fuel flexible. In literature, it is found that many reported studies evaluated the influence of material for different types of fuels and for different operating temperature on biogas-fuelled SOFC catalysts. Also, surface modifications were proposed to suppress carbon deposition and sulfur poisoning [190,191]. For fuels with short carbon chain, the catalytic reactions of fuel reforming mainly take place at a very thin layer of the catalyst. Therefore, choosing an appropriate catalyst based on the gas composition is crucial [160].

The anode has a porous structure that should transfer the fuel to the TPB rapidly. SOFC's anode is usually made of a metallic nickel cermet with a supporting structure of YSZ (e.g., Ni–YSZ and Ni-GDC). Lanzini and Leone [172] have studied Ni-YSZ anode supported cell (ASC) and Ni-GDC electrolyte supported cell (ESC) SOFC at 800 °C for current densities of 0.5 A/cm^2 and 0.3 A/cm^2, respectively. Because of thicker anode, ASC (600 μm) showed a better performance in comparison with a 40 μm GDC (ESC) cell with respect to methane internal reforming.

Sumi et al. [12] compared Ni-YSZ and Ni-ScSZ (Scandia Stabilized Zirconia) for steam and dry methane reforming. The results illustrate that generally cell degradation rate is higher with Ni-YSZ for both dry and steam reforming. Contrary, Takahashi et al. [165] showed that the performance of cell with Ni-YSZ anode materials is similar to Ni–ScSZ for biogas dry reforming whereas ScSZ is a better ion conductor. In terms of methane steam reforming the Ni-YSZ cermet anode material has a better performance compared to Ni-ScSZ. However, the carbon deposition rate is significantly higher for Ni–YSZ than Ni–ScSZ [192]. The comparison of these two experimental studies shows that the selection of reforming agent can influence the behaviour of anode materials. Ke et al. [193] investigated the Ni/ScSZ anode material for methane fuelled SOFC at high temperature and low steam partial pressure (3%). They observed that steam enrichment on the Ni surface for Ni/ScSZ cermet anode is higher than YSZ, which leads to lower carbon deposition on Ni/ScSZ.

A combined catalyst layer with a conventional Ni-based anode (4-layer coated) has been suggested by Cheekatamarla et al. [194]. Internal reforming has been studied for different fuels including biogas for a tubular SOFC. Complete methane conversion has been observed at 700 °C. Extra air has been used to assist dry reforming in such a way that O_2/C ratio was 0.1. Further investigations have been carried out to seek materials that have efficient functionalities for SOFCs. For instance, the operating temperature can be reduced further to the intermediate region (600–800 °C) by employing mixed ion-electron conducting materials, especially for the cathode in order to improve the rate of oxygen reduction reaction and to lower the cathode overpotential. Some studies have been carried out by using first-principles methods based on Density Functional Theory (DFT) to investigate the electronic structure and defect chemistry of SOFC materials [15]. For instance, Ritzmann et al. [195] have studied $La_{1\text{-}x}Sr_xCo_{1\text{-}y}$ Fe_yO_3 (LSCF) cathode material in which strontium plays a crucial role in lowering the formation energy of oxygen vacancy calculated by the DFT-based method. Moreover, the results showed that the proper amount of Co (0.25 < ice<0.5) improves the electronic conductivity while the oxygen vacancy concentration remains sufficient. Elbaz et al. [196] also used the DFT method to understand the hydrogen diffusion in novel structured material for proton conducting SOFCs in order to calculate minimum energy diffusion paths and hydrogen vacancy formation energies in nickel hydroxide phases. Several mechanisms of hydrogen transport have been considered for different crystal phases and results illustrated that the activation energy becomes lower when the phase becomes richer in hydrogen.

Trimm [197] has investigated the impact of doping Ni with a small amount of metals, like Bismuth, on carbon deposition which is significantly effective to reduce carbon formation on the nickel surface. Horita et al. [198] investigated metal/oxide interfaces of anode materials, YSZ and YDC (Y_2O_3-doped CeO_2) substrates combined with different Ni and Au electrodes. Ni is more active than Au for methane decomposition and carbon deposition. However, using YDC substrate decreases carbon deposition on the Ni surface and it is associated with hydrogen ionization and transportation capability. Alipour et al. [199] have studied Ni/Al_2O_3 catalyst with the addition of alkaline salts such as MgO, CaO, and BaO. Results show that MgO is the best aid material to promote catalytic activity and suppress carbon deposition for a wide range of gas compositions. Other materials such as copper and lanthanum also have been reported as active anode metals for the direct introduction of large hydrocarbon fuels [200]. Gorte et al. [201] have reviewed different Cu-based anode materials. The results show that Cu-cermet anodes have the potential to be used for direct oxidation of carbon fuels whereas they do not have the coking issue of Ni-based anodes. However, long term cell operation with such anodes is yet to be demonstrated. More investigations have to be carried out on biogas-SOFC materials in order to improve the methane conversion, durability of fuel cell and to decrease the material costs.

5.3. Carbon deposition

For SOFC operating on biogas, one of the major challenges is to prevent carbon deposition. The gas equilibrium calculation for general biogas (60% methane, 40% CO_2) shows that carbon deposition might occur in the SOFC over a large range of SOFC operating temperatures [172]. Carbon deposition on the active area of the cell reduces the performance and durability and in the worst case, it causes a local thermal stress, which can lead to cell cracks and delamination. Ni is a good catalyst for hydrocarbon reforming

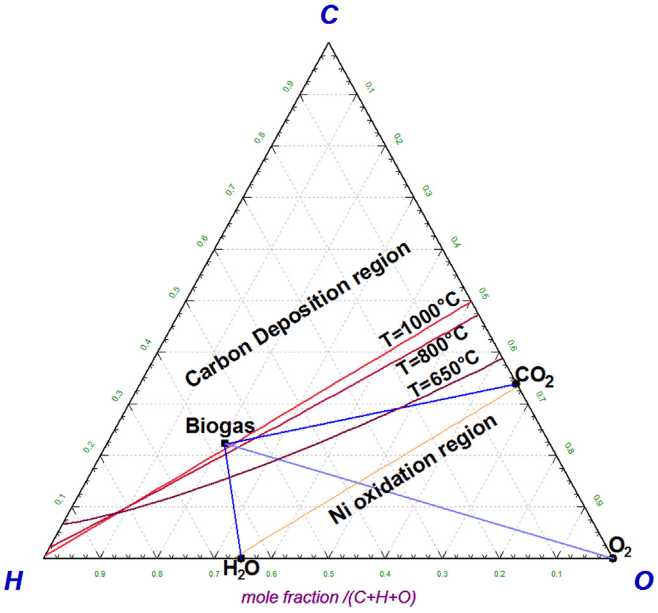

Fig. 5. Carbon deposition limits in a C-H-O ternary diagram calculated at different temperatures and under 1 atm.

reactions. In addition, it also actively promotes carbon deposition on the anode surface. The chance of getting carbon deposition depends on the fuel composition, operating conditions and anode materials used in the SOFC. The risk of carbon deposition is much higher in dry reforming on Ni-based anodes due to higher C/H ratio in comparison with steam reforming [167].

Operating parameters such as temperature, current density, and fuel utilization should be regulated in order to avoid carbon deposition. Carbon deposition mainly occurs due to: i) methane cracking at high temperature (Eq. (16)) in absence of other reforming agents such as steam and CO_2 [12], and ii) reduction of carbon monoxide or disproportionation (Eq. (17)) for high partial pressure of CO and CH_4 at low temperature.

Because the CO_2 partial pressure in biogas is not sufficient, always extra CO_2 or steam is required. Additionally, steam can remove carbon through an endothermic reaction (Eq. (18)) [202].

$$CH_4 \rightleftharpoons 2H_2 + C_s, \quad \Delta H^0_{298} = 75.6\, kJ/_{mol} \tag{16}$$

$$2CO \rightleftharpoons CO_2 + C_s, \quad \Delta H^0_{298} = -173\, kJ/_{mol} \tag{17}$$

$$H_2O + C_s \rightleftharpoons CO + H_2, \quad \Delta H^0_{298} = 131\, kJ/_{mol} \tag{18}$$

The steam required can also be produced by the electrochemical reaction of hydrogen (Eq. (3)), RWGS reaction or using an external steam generator. Choosing a proper fuel gas composition is essential. Moreover, at high current density, electrochemical reaction rate increases and, as a result, the production of steam and carbon dioxide increases, which reduces the possibility of carbon deposition [178].

In the ternary C-H-O diagram, the theoretical boundaries of carbon deposition and NiO formation can be indicated based on thermodynamic equilibrium calculations at different reaction temperatures and gas compositions. The status of biogas (60% CH_4 and 40% CO_2) is shown in ternary diagram (Fig. 5) and located at carbon deposition region at all temperatures as high as 1000 °C. Adding steam, CO_2 or oxygen can move the inlet gas composition towards the safe region.

Kuhn and Kesler [203,204] have investigated carbon deposition thresholds on Ni-based anode under different operation conditions and different gas compositions. First, based on thermodynamic equilibrium calculations, increasing fuel utilization can decrease the likelihood of carbon deposition. The presented experimental studies at 700 °C agreed with thermodynamic equilibrium calculations on nickel cermet anode. However, for lower temperatures (600 °C), a modified Gibbs free energy for carbon formation has been proposed. Moreover, the influence of Steam to Carbon ratio (SC) and Current Density (CD) on carbon deposition have been investigated. The minimum SC was found to be 1.18 at 700 °C to prevent coking.

Girona et al. [205] have determined appropriate operating conditions for biogas fed SOFC. The experimental studies were conducted at constant temperature with two gas compositions (with additional CO_2 and steam to biogas) at open circuit voltage (OCV) and operating at 120 mA/cm^2. A scenario has been proposed for carbon deposition. During the first hours, it is suggested that a film of carbon could form, which leads to degradation. It has also been observed that after a few hours, carbon precipitates germinate and nickel surface becomes active again.

Lanzini and Leone [172] have investigated carbon deposition on anode and electrolyte supported cells for pure biogas fed SOFC at high current density. With a 12-h SOFC operation, the cell voltage is shown to decrease by 7 and 14% for ASC and ESC, respectively. It is proposed that carbon deposition leads to nickel re-oxidation due to a lack of H_2 and CO on the anode side [206]. To avoid carbon formation for a CH_4-rich-biogas ($CH_4/CO_2 = 2$), the amount of required air is determined by thermodynamic calculations (0.2102 mol O_2/mole biogas) and 98.2% methane conversion has been obtained at 800 °C. Based on the equilibrium calculation, it has been suggested that operation above 740 °C is safe to prevent carbon deposition for CH_4-rich biogas (60% CH_4) composition. Nevertheless, in the absence of extra reforming agents, the chance of coking increases due to local temperature gradient and the non-homogenous gas distribution through the cells. Therefore, thermodynamic calculations cannot guarantee a safe operating condition [178].

An alternative way to avoid carbon deposition is the use of a novel anode material obtained by adding other metals to the conventional Ni based anode. Such an approach has been reported by using Cu and CeO_2 in the anode material [17]. Cerium oxide or ceria is an important material for hydrocarbons fuelled SOFCs which has highly mobile oxygen vacancies [167,193]. Pillai et al. [175] evaluated the impact of combining a porous barrier layer (partially stabilized zirconia and CeO_2) on the anode for dry reforming and partial oxidation of methane. They concluded that the barrier layer inhibits the flux of CO_2 and H_2O from the anode to the fuel channel and increases the concentration of reforming agents close to the anode material. High current density leads to the production of enough CO_2 and steam on the surface of anode to prevent carbon deposition. This barrier layer reduces the required current density. It can be observed from Fig. 5, that under higher current load the gas composition moves towards a higher partial pressure of oxygen, which is located in the non-carbon deposition region. Recently a simple innovative technique was developed to reduce the risk of carbon deposition by modification of conventional Ni-based anode material by providing an interfacial phase reaction. Qu et al. [207] proposed adding $La_{5.4}$ $WO_{12\text{-}d}$ (LW) to the conventional Ni-YSZ anode in order to chemically adsorb water in the lattice, although the specific surface area of the anode and conductivity are reduced. Absorbed water reacts with solid carbon deposited on the nickel surface (Eq. (18)) and CO_2 is released. A stability test has been conducted for Ni-YSZ-2 wt% LW anode material at 700 °C and constant current density for humidified methane (3 vol% steam) fuel. No considerable voltage drop was observed after 200 h. However, such new approaches are yet to be widely accepted.

5.4. Nickel re-oxidation

As mentioned in the previous sections, Ni based anode is one of the preferred materials for hydrocarbon fuelled SOFC due to high catalytic activity. However, there exists a risk of nickel re-oxidation. Due to the lack of fuel gas (high fuel utilization) at high temperatures, oxygen ions that pass through the electrolyte might react with nickel in the anode. Also, if air enters to the anode side because of sealing failure or control of fuel composition, nickel re-oxidation might take place (see Fig. 5). Nickel re-oxidation leads to volume expansion and consequently cell or sealing fracture. It is argued that increasing the porosity of the materials could improve the tolerance of expansion due to Ni re-oxidation [208]. Ettler et al. [209] reviewed literature about Ni reoxidation cycles and concluded that 20–25% of the Nickel reoxidation does not lead to electrolyte cracking at 800 °C and at lower temperature, the risk is lower. Pihlatie et al. [210] studied the kinetics of nickel re-oxidation on Ni-YSZ anode with intermediate and high temperature SOFCs. Different activation energies and models are proposed for the reduction and oxidation reactions at different operating temperatures. No generation of porosity was observed at low temperature [211]. Vedasri et al. [212] have studied the NiO formation during the cooling procedure of Ni/YSZ anode-supported stack from 800 °C to 600 °C. A cooling rate of 3 °C/min has been suggested to minimize the expansion due to Ni oxidation and prevent cell cracking. The mechanism of Ni re-oxidation for biogas fuelled SOFC has not been elucidated. However, results from other fuels show that increasing the operating temperature to values typical for biogas SOFCs, increases the chance of Ni re-oxidation and these aspects need to be studied more [213].

6. Technical evaluation of biogas SOFC performance

So far, the influence of different operating parameters on the solid oxide single cell has been discussed, but as a power generation unit, stacks are generally employed. Due to the cost and risk of stack damages, SOFC modelling is crucial because, to some extent, the effect of operating parameters can be evaluated. Additionally, the energy and exergy efficiency of the stack and integrated systems can be evaluated under various conditions.

6.1. Biogas-SOFC stack and system modelling

To evaluate the energy efficiency of biogas fuelled SOFC system, a comprehensive model of the SOFC stack is a useful tool. It is difficult to achieve 100% internal reforming of fuel in SOFC [179], as the fuel utilization should be maintained less than 100% in order to avoid the risk of nickel oxidation. Therefore, the anode exhaust gas always contains some fuel gases and hence the outlet gas should be combusted in a device (i.e. an afterburner). In this section, some studies on biogas-SOFC stack steady state modelling will be reviewed, which are focused on different types of reforming.

A mathematical model of methane reforming reactions (based on heterogeneous reactions) has been developed by Santarelli et al. [177]. This model can predict the gas composition profile along the fuel channel for a biogas fed tubular SOFC stack (with a Ni-YSZ anode supported cell) at different fuel utilization. The model has been experimentally validated. The results show a good performance of SOFC under direct dry reforming of biogas and high methane conversion through the fuel channel. Biogas direct steam reforming has also been investigated with SC: 0.47 at 800 °C. Results show the higher effectiveness of steam reforming in comparison with dry reforming due to the kinetically faster reaction and higher H_2 production. Lanzini et al. [214] have developed a model to evaluate the performance of a biogas fuelled tubular SOFC. The model, neglects dry reforming because of lack of dry reforming kinetic data, is experimentally validated. Maximum electrical efficiency was less than 30% due to the low conversion of methane even for low CH_4/CO_2 ratio of 0.5 at 800 °C.

A direct internal reforming model has been developed by Wongchanapai et al. [215] in order to study the combined steam, dry reforming and partial oxidation. First, fuel oxidation is considered to generate heat, steam and carbon dioxide for endothermic steam and dry methane reforming reactions. Then WGS reaction is taken into account to convert CO to hydrogen. The reaction rates of partial oxidation and steam reforming have been calculated. However, detailed kinetics of the dry reforming reaction is not explicitly included in calculations.

An energy balance model has been developed for a biogas fuelled SOFC co-generator system by Van Herle et al. [182]. The influence of various parameters such as the fuel inlet composition, stack temperature and current density, have been investigated. Air with a ratio of 1:1 is used in this study for converting methane. The obtained electrical and thermal efficiencies based on Lower Heating Values (LHVs) were 33.8 and 57.6%, respectively. The results also show that using a pressurized system decreases the electrical and thermal efficiency, despite the fact that the single cell voltage might increase by 50–100 mV in the operating system. A small SOFC stack has been modelled by Membrez and Bucheli [216]. Mixed biogas/air fuels with different excess air value (λ) were studied. Thermodynamic equilibrium has been considered to estimate the likelihood of carbon deposition at the operating temperature. Electrical and thermal efficiencies were 38.2 and 46%, respectively. The heat generated from exhaust gas, afterburner and stack have been used for pre-heating the fuel and air, and domestic hot water.

Van Herle et al. [80] have developed a model for a 100 kW biogas-SOFC system. This model was developed to investigate the performance of the complete SOFC system with steam reforming and POX. For steam reforming, the minimum required steam/carbon ratio of 0.5 had been chosen based on thermodynamic calculations and considering a safety factor. Obtained electrical efficiency was 48.7%. Generated heat in SOFC and after-burner was used for pre-heating and fuel reforming process. System electrical efficiency decreased to 43% for partial oxidation due to fuel consumption ($\lambda = 4.5$). In this case, oxygen to carbon ratio was 0.3 and thermal efficiency of the system was above 46%, which was 6% higher than steam-reformed biogas system. Piroonlerkgul et al. [181] have developed a model to thermodynamically analyse the performance of SOFC with combined biogas reforming. The model was validated by conducting experiments with various inlet gas (CH_4–CO–H_2 mixtures). The required steam and air for biogas reforming have been calculated at different temperatures. They concluded that the smaller content of CO_2 in the biogas is an advantage that reduces the energy losses from the system exhaust gas. Most modelling studies have hitherto investigated the sensitivity of steam and oxygen to the methane reforming reaction, however, the influence of CO_2 partial pressures has never been reported. This is highly encouraged as a future research activity.

6.2. Integrated system modelling

SOFCs have some additional advantages in comparison with other types of fuel cells. Operating temperature of SOFC is high and this allows using the residual heat in co-generation cycles. Higher system efficiency can be achieved by CHP generation. In a CHP system, the exhaust gas from fuel cell, which contains unconverted methane and hydrogen, can be transferred to downstream devices, such as after-burner, gas and steam turbine in order to generate heat or mechanical power. The generated heat/power can be used for different purposes. For instance, raising the temperature of anaerobic digestion increases methane production in an anaerobic bio-reactor [217,218]. The overall thermal and electrical efficiency of SOFC integrated system (with gas or steam turbine) can reach up to 90% at proper conditions and optimum system configuration [219].

System design can be evaluated by calculating the system efficiency and this can be further improved by integration. However, the integration depends on the application requirements and limitations [220]. Zhang et al. [221] reviewed different SOFC integration strategies (with different types of fuels) that include applying various designs of the Gas Turbine (GT) with pressurized, non-pressurized SOFC, indirect thermal coupling and fuel coupling. Moreover, three different configurations of SOFC with gas–cooled nuclear reactor cycle, gasification cycle and humidified air turbine cycle were reviewed.

Piroonlerkgul et al. [181] investigated the performance of different configurations of biogas fed SOFC. In addition to dry reforming with CO_2 present in the biogas, different reforming agents, including steam, air and mixed reforming were used. Thermodynamic equilibrium has been assumed to calculate the gas compositions. Use of afterburner, steam turbine and Anode Gas Recirculation (AGR) has been made for enhancing the efficiency with the different configurations. The overall electrical efficiency is around 55% (LHV based) for combined steam/dry reforming. The results of the second configuration (air-fed biogas-SOFC system) showed that both power density and overall efficiency decline with increasing the air content. Generally, the electrical efficiency of the integrated system decreases with increasing amount of reforming agents. However, these results illustrate that high electrical efficiency (59%) can be achieved with a new approach while residual heat from afterburner is used for fuel processing (reformer and steam generator). Wongchanapai et al. [215] have used a model to study a combined SOFC with a Micro Gas Turbine (MGT) fed by biogas. The influences of SOFC and MGT operating parameters have been studied. The results show that the SOFC efficiency is higher when steam is used as a reforming agent instead of partial oxidation. High fuel utilization improves the SOFC generated electrical power, but extra fuel is needed to produce the required heat. Total system efficiency of 69.7% has been achieved for a high fuel utilization ($U_f = 0.90$). The decline in electrical power production of SOFC has been observed for high amounts of air (as a methane conversion agent). It has been compensated by MGT and it has been shown that the air/steam ratio has a minor effect on electrical power production.

Farhad et al. [171] have developed three different configurations for biogas-SOFC with different fuel processing. In the first model, anode gas recirculation is considered. All fuel streams are assumed to be in thermodynamic equilibrium at the operating temperature. According to the modelling calculations, the minimum AGR flow to prevent carbon deposition is a function of fuel utilization. For instance, it is equal to 63% of SOFC inlet flow at 80% fuel utilization. The maximum electrical efficiency (42.4%) is achieved with anode exhaust recirculation system. However, the maximum CHP efficiency (80%) is obtained in the system that works under partial oxidation of biogas, however, the maximum exergy destruction took place with this system and the largest share was by the air heater.

Tjaden et al. [222] investigated the performance of a small-scale (25 kW_{elec}) biogas fed SOFC, focusing on developing appropriate gas cleaning and reforming units. Autothermal reforming has been proposed according to biogas composition. Additional steam and oxygen required are determined in order to achieve a zero heat duty for an external reformer (the required heat has been supplied by methane partial oxidation). Operating voltage and U_f sensitivity analysis have been carried out to evaluate the influence of SOFC operating conditions on system efficiency. The results show that applying direct internal reforming considerably increases the total efficiency and slightly the electrical efficiency. The maximum electrical efficiency achieved under steam reforming and at the optimum condition was 50.65%. However, the system costs under partial oxidation reforming were expected to be the lowest due to the lowest required cell active area for the same power production.

A cycle-tempo model has been also developed within our research team by Patel et al. [223] to evaluate a fuel cell gas turbine system with different fuels including methane. It is proposed that by using only 20% of steam along with methane can avoid carbon deposition due to the use of AGR. Further, it concluded that there is always enough steam from the electrochemical reaction of fuels in the proposed system to prevent carbon deposition. The reported energy and exergy efficiencies of methane-SOFC system are 78.3% and 75.5%, respectively.

6.3. *CFD modelling*

Computational Fluid Dynamic (CFD) models are helpful tools to predict temperature, pressure and species distribution in biogas fed SOFCs. In CFD models the transport equations (mass, energy, species, and momentum) are coupled to the electrochemistry equations. The CFD model can estimate the extent of electrochemical reaction through the fuel channel and accordingly, local temperature, gas composition, and current density can be calculated. Considerable research work have been carried out on internal steam methane reforming simulation compared to methane dry reforming [224–227].

A quasi-two-dimensional numerical simulation has been developed by Nishino et al. [228] to study a tubular biogas fed SOFC. The feed tube was considered as a reformer for biogas. Fuel gas has been varied with different methane partial pressures while SC ratio is changed in a range between 2 and 4. Methane dry reforming is only implicitly included in this model because it does not need to be explicitly specified since both steam and dry methane reforming reactions are considered to be mechanistically equivalent. When methane content in biogas is higher than 40%, methane is completely reformed for all the steam to carbon ratios due to enough catalyst material in the feed tube (1 gr/cm^3). The results of this study are helpful for thermal management of indirect biogas reforming. The cell voltage reduces with a decrease in the methane partial pressure in biogas under a current density of 400 mA/cm^2, which is attributed to the decrease in the electromotive force.

A three-dimensional CFD simulation has been developed for a Ni-YSZ anode planar SOFC fuelled by biogas/steam mixtures. This study investigated the location of increased thermal stresses and the likelihood of solid carbon deposition [229]. Results demonstrate that equimolar CH_4/CO_2 biogas improves the cell performance and carbon deposition possibility is higher for methane-rich mixtures. Nevertheless, major coking has not been observed under closed circuit operation because of the electro-oxidation reactions of carbon. The coking possibility is greater in the anode/gas phase interface. The maximum power production has been achieved for equimolar CH_4/CO_2 biogas with just 10% steam and increasing the steam concentration leads to power losses.

Elizalde-Blancas et al. [230] have developed a numerical model to assess the influence of actual biogas composition on the performance of an anode supported button cell. The inlet gas composition has been determined based on the equilibrium composition of biogas at 800 °C. Simultaneous oxidation of hydrogen and carbon monoxide has been considered in this study. Internal reforming has been modelled using two reactions, MSR and WGSR. In contrast, Ogura and Wakamatsu [231] only considered methane dry reforming and reverse WGSR to calculated temperature and concentration of gas species distributions along the fuel channel. A paper-structured catalyst is used to overcome the problem of local cooling due to the direct biogas reforming. The results of three-dimensional temperature profiles have been validated by experimental measurements for both cases of homogeneous and functionally-graded paper structure catalysts. This model has been extended for a three-cell-stack. Distribution of temperature is more homogeneous for this stack, which improves the durability.

7. Implementation of biogas SOFCs

7.1. *Latest developments in pilot and demo-scale implementation of biogas-SOFCs*

Fuel cell technology is moving from research and prototype demonstration to the industrial demonstration. The technology is being developed for a broad range of power generation applications [232]. Several demonstrations for hydrogen and natural gas fuelled SOFC have been carried out [233–238], however only a few have been dedicated to biogas-SOFCs.

In the Biocell project (for pilot plants in Barcelona), biogas from a WWTP has been used in two types of fuel cell [239]. The first one is PEMFC that requires external cleaning and reforming. Biogas has also been injected directly into an SOFC after cleaning process. The cleaning system consists of four steps. Biotricking filter with the live bacteria has been used for desulfurization. Supplementary purification was carried out by iron oxide, activated carbon and dryer to completely remove H_2S and halogenated compounds. Siloxanes have been reduced to 0.1 mgSi/Nm^3 (less than 0.1 ppm) as well. This pilot plant is designed for 2.8 kW_{elec}. Electrical and thermal efficiencies for the SOFC pilot plant were 24.2 and 39.4%, respectively, which are much higher than that for PEMFC pilot plant [240].

A part of SOFCOM demonstration project (DEMO 1 Torino, Italy) is dedicated to investigate the high efficiency combined cooling, heating and power (CCHP) based biogas fuelled SOFC [241]. Moreover, the influence of the fuel contaminants and biogas fuel processing on the SOFC is studied. For minimizing emissions, the possibility of CO_2 separation from the anode exhaust gases is examined [242]. Achievements of this project will be used in the DEMOSOFC project that is known as the first European industrial biogas-SOFC [243]. Three SOFC modules will be utilized to generate a total of 175 kW of electrical power and 90 kW of thermal energy. An electrical efficiency of 53% is expected. The project is planned to run until the end of 2020.

The objective of the BioZEG pilot plant is to develop a zero emission hydrogen station based on local renewable sources [244]. An upgrading gas system produces biomethane from biogas (municipal waste landfill). Through a sorption enhanced reforming process (steam reforming) hydrogen is produced and CO_2 capture is carried out by a solid CaO-based sorbent. Hydrogen is sent to a 20 kW_{elec} SOFC stack. The generated heat in the SOFC is used for the CO_2 absorbent regenerating. Bloom Energy is an SOFC manufacturer who develops SOFC units that can deliver a power of 210 kW with natural gas or biogas [245]. The net electrical efficiency is claimed to be in a range of 52–60%. The system is called as "carbon neutral" on direct-biogas.

Besides biogas, ammonium and phosphate are also the products of WWTPs that should be recovered in order to prevent their returning to the surface water. As mentioned in section 4.3, ammonia removal can be replaced by ammonia recovery and subsequently ammonia can be used in an SOFC. This concept changes an electricity-consuming process step to an energy -producing process step. Moreover, ammonia recovery from AD may increase methane production by alleviating the inhibition by dissolved NH3. Hemmes et al. [246] proposed an innovative technique to integrate the purification of wastewater with the power generation by SOFC. Ammonia and phosphate are removed in the form of struvite $MgNH_4PO_4 \cdot 6H_2O$, and subsequent decomposition of the struvite to release ammonia. The released ammonia can be fed to an SOFC. Results show that this process is more cost-effective than conventional nitrogen removal process. The first pilot plant of this concept has been initiated by DHV at Waterboard Hunze en Aa's in the Netherlands. There are on-going multiple projects and research activities at Delft University of Technology aimed at the development of integrated waste to energy SOFC systems. The objective of LOTUS project is to develop an advanced wastewater treatment technologies at a selected location in New Delhi and use produced biogas in SOFC [247]. A similar project at "TU Delft Global Initiative" focuses on biogas-SOFC energy system for rural energy supply [248]. The N2kWh project aims to develop a pilot installation using biogas and recovered nitrogen from manure and urine/reject water in an SOFC [249].

7.2. Techno-economic evaluation of the biogas-SOFC system

With the ongoing implementation of pilot and demonstration scale biogas-SOFC systems, it becomes possible to assess the economic feasibility of biogas SOFCs. There are two important challenges: 1) the economics of the gas cleaning unit, as supplying clean biogas for SOFC increases the gas cleaning cost, and 2) the cost of SOFC itself. Techno-economic characterization of the biogas-SOFC system can be helpful in order to illustrate the obstacles from an economic point of view.

Pipatmanomai et al. [250] carried out an economic evaluation of biogas to electricity system. This system primarily consists of an H_2S gas cleaning unit and a modified IC engine (1.6 kW) coupled with electric generator. In this work, H_2S removal has been focussed and a 2% KI (potassium iodide) - impregnated activated carbon adsorption is used for this purpose. It is mentioned that this method of H_2S removal increases the removal efficiency to 100%. Mainly operating cost of H_2S removal unit increases the payback period from 4 (without H_2S removal) to almost 8 years. Electricity price and governmental subsidy play important roles in the payback period, as without subsidy the payback period can go up to 11 years.

Papadias et al. [251] carried out an investigation on an integrated system. Adding AD-SOFC system to an existing waste water treatment (WWT) plant could yield positive values of internal rate of return on investment (IRR) at average electricity prices. This could compete with other options for using biogas to generate electricity. There is an uncertainty in the SOFC-CHP equipment capital costs, but the normalized cost is in the range of $3600-4000 kW^{-1}. The economic analysis of biogas production shows that the cost of electricity is about 10.5 c$/kWh (for a conventional plant generating 300 kW_e). The cost of gas clean-up represents roughly 20% of the cost of electricity. The H_2S (iron oxide bed) and siloxanes (carbon bed) removal processes contribute most to the cost.

Trendewicz and Braun [49] carried out a techno-economic investigation on an integrated SOFC-CHP plant with WWTP in 2013. The results show that the electricity price is competitive with other grid price roughly 5–8 c$/kW h. The estimated costs for the whole system could be between 3590 and 5780 $/kW for large and small scale plant respectively. In order to analyse the performance of the Biogas-SOFC plant, an Aspen Plus model has been developed with a gas cleaning unit.

Further investigations are highly encouraged to assess the economic feasibility of biogas-SOFC system, especially techno-economic evaluation of AD-SOFC integrated system with thermal pre-treatment. Moreover, it is recommended to assess the concept of producing ammonia as a fuel from the techno-economic point of view in WWTPs. Ammonia separation increases the operating and capital cost of WWTP while on the other hand, there is an advantage of using ammonia as a fuel in SOFCs.

8. Final remarks

This article presents a comprehensive review on potential and challenges in applying biogas, originating from organic waste (water) streams, as a fuel for SOFCs. Although biogas production using AD has been extensively investigated and is applied commercially on a global scale, biogas itself is utilized only for relatively inefficient heat and electricity production in gas engines and CHP units or upgraded for gas grid injection, after which a large part is burned for low temperature heat generation. With the ongoing developments in the field of SOFCs it would be about time for the wastewater treatment community to start considering thermodynamically superior alternatives like the SOFC. In the first part of this paper, literature has been reviewed that demonstrate that thermal pre-treatment of organic waste could already result in increased methane yield with temperatures below 100 °C. As the temperature of the SOFC off-gas is significantly higher, an approach for thermodynamic integration of anaerobic digestion and SOFC is presented using a Sankey-diagram which shows the energy flows in such an integrated concept. Biogas quality often however inhibits its direct employment in SOFCs. Fortunately, there is increasing awareness that the way the digester is operated influences the biogas quality. Combining the use of advanced digester designs producing cleaner gas streams and appropriate gas cleaning methods might lead to the use of biogas in more high-end applications. It is therefore proposed to direct future anaerobic digestion research into this direction.

SOFC systems bring a good opportunity for future applications because of high efficiencies, fuel flexibility, and environmental friendliness aspects compared to the conventional IC engine based CHP approach. Biogas as a renewable fuel is well-matched with SOFC systems despite the fluctuation of methane partial pressure in biogas. The high quality residual heat from the SOFC can improve the biogas production by thermal pre-treatment of sludge. This increases the overall system efficiency. Due to the possibility of biogas production in small scales and modularity of SOFC stacks, there is no size limitation for these integrated systems unlike for the traditional biogas applications. This advantage can increase the implementation in rural off-grid situations. Latest developments show that the biogas-SOFC is reaching a mature technology status, but several challenges should still be solved before the commencement of commercializing full-scale biogas-SOFC systems.

One of the most essential challenges is the durability of operation with respect to contaminants in biogas. Several experiments have been conducted to understand the tolerance of contaminants on SOFCs. Some contradictory results have been reported which show the necessity of further investigations. Moreover, biogas reforming is influenced by contaminants and this also depends on the type of reforming agents. Internal dry reforming is the most interesting reforming reaction for biogas-SOFC operation, due to the existence of CO_2 (reforming agent) and CH_4 (fuel) in biogas. But, methane dry reforming is not understood as much as steam reforming. For instance, only a very few studies have focused on the kinetics of internal dry reforming. Also, there is no comprehensive investigation on the effect of contaminants like H_2S on dry reforming reaction. On the other hand, it has been proven that depending on cell materials, the performance can be fully recovered after removing contaminants when the initial contaminant concentration was low. Moreover, the progress on developing sulfur tolerant anodes with perovskite-based anodes can contribute to the development of the biogas-SOFC system by eliminating the necessity of developing GCU or significantly simplifying its designs. This may make the systems more cost compatible. However, challenges *related to* the lower electrical conductivity and catalytic activity of such anode materials need to be tackled first. Regarding the biogas-SOFC anode material, high electronic conductivity, high methane conversion and low carbon deposition and degradation are favourable. In contrary to Ni cermet anode materials, there are only a few experimental investigations carried out on ceria based anode materials containing Cu, Pt, Au and Ag anodes in biogas-SOFC, but these show promising results. Additionally, modification of conventional Ni-based anodes might decrease the risk of carbon deposition. For instance, by impregnation with Alkali-metal oxides (with high proton conductivity and superior water-storage capability) the carbon deposition might be prevented in case of direct internal methane reforming. However, complications in achieving homogenous and uniform impregnated anode materials are still challenging.

Experimental studies have shown the feasibility of using dry reforming to reform methane in biogas. However, the results have not been achieved in complete system experiments and generally steam reforming and partial oxidation have been applied in order to prevent carbon deposition. Anode gas recirculation is an alternative to avoid the use of additional reforming agents. Integrated system modelling (steady-state) investigations have been performed on biogas-SOFC with AGR but, to the best of knowledge of authors, there have been no experimental studies reported on biogas-SOFC with AGR system. There have also been some modelling studies on biogas-SOFC stacks with combined reforming/ATR, however without considering the influence of the dry methane reforming reaction. Moreover, developing biogas-SOFC dynamic models is also highly encouraged in order to predict the performance and limitations of biogas-SOFC system operating under different electrical power demands.

Nowadays, the cost of SOFC stacks seems a major barrier for further development of biogas-SOFC systems. Based on the material investigations and new manufacturing techniques, the SOFC costs are expected to come down to some extent in the near future. High efficiencies of biogas SOFC systems, make such systems capable of competing with conventional power generation devices. However, without subsidy and governmental support, it is difficult to make the biogas-SOFC system commercially viable, unless the SOFC costs come down significantly. Integration of SOFC with gas or steam turbine shows very high efficiencies and might be an interesting approach for the development of Biogas-SOFC systems. On the other hand, there is no investigation carried out specifically on the efficiency of complete AD-SOFC integrated system (considering thermal pre-treatment) regarding the optimum heat to power ratio for such a system. Additionally, investigating the use of ammonia (from WWTP) mixed with biogas for SOFC presents an interesting option to promote the self-sustainability of WWTPs. Despite all these challenges, some demo projects show the feasibility of implementing the biogas-SOFC systems.

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