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Techno-economic review of biogas cleaning technologies for small scale off-grid solid oxide fuel cell applications

Henry Wasajja[a,c,*], Ralph E.F. Lindeboom[a], Jules B. van Lier[a], P.V. Aravind[b]

[a] *Water Management Department, Sanitary Engineering Section, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628CN Delft, the Netherlands*
[b] *Process and Energy Department, Faculty of 3mE, Delft University of Technology, Leeghwaterstraat 39, 2628, CB, Delft, the Netherlands*
[c] *Department of Electrical Engineering, Faculty of Engineering, Ndejje University, P.O. Box 7088, Kampala, Uganda*

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ABSTRACT

Biogas is known as a traditional energy source for off-grid population throughout the world. And currently small-scale solid oxide fuel cell (SOFC) systems are being promoted for off-grid energy supply. Also, electricity demand is increasing at a high rate due to the ever-increasing population and technological revolution. Therefore, promotion of off-grid energy supply needs to be refocused.

The small scale biogas-SOFC is an envisaged modern energy system which can meet both the thermal and electrical energy demand for off-grid population more efficiently (60% at 800 °C) than currently available technologies. However, it has been observed that cleaning of biogas could increase the system capital cost by 6–7% and > 40% of the overall annual system operating cost. Cost-effective gas cleaning is therefore important for economic feasibility of the biogas-SOFC energy system.

This review focuses on technical and economic challenges of current commercial and laboratory scale biogas cleaning technologies. Special focus is directed towards cost mitigation strategies for gas cleaning such as combined in-situ bioreactor upgrading and application of cost-effective sorbents. The results are useful to advance implementation of biogas-SOFC systems in off-grid applications in developing as well as developed world.

1. Introduction

Biogas from anaerobic digestion is considered an accessible and prominent source of energy derived from biomass. Recent research has proved that biogas usage and development can have a significant contribution to reduction of global warming potential [1]. Moreover, controlling the organic waste (water) disposal is of vital importance to avoid severe public health problems and environmental pollution problems, and at the same time producing useful fertilizers for agricultural applications [2].

Worldwide electricity generation from biogas was 331 TWh in 2010 (8% of the total electric energy generated from renewable energy sources) and it is estimated that this figure could reach 696 TWh (10% of the total electric energy generated from renewable energy sources) by 2020 and 1487 TWh by 2035 (13% of total electric energy generated from renewable energy sources) [3]. Also on a global scale, the installed bioenergy capacity of 66 GW in 2010 increased with an annual growth rate of 5% in 2012, and it is estimated that the installed capacity could

grow to 270 GW by 2030 [3]. Since fuel cells are not limited by thermodynamic Carnot efficiency [4], they are more efficient than the current widely applied combustion technologies. Hence, they may play an important future role in increasing the electricity generation capacity from biomass resources.

Currently small scale solid oxide fuel cells (SOFCs) of < 10 kW capacity are being promoted by a number of companies already [5–8]. Such systems would be suitable to meet the off-grid energy demand for both developed and developing countries by integrating them with already existing biogas systems.

Small scale biogas-SOFC energy system (Fig. 1) is seen as the next off-grid energy generation technology for both developed and developing countries due to the high efficiency of fuel cells (biogas-SOFC electrical efficiency of over 50% and 60% for SOFC-combined heat power (CHP) has been reported in literature) [9]. The working principle of SOFCs and anaerobic digestion has been recently reported [10]. SOFCs have added advantages as compared to other fuel cell types such as proton exchange membrane (PEM) to be integrated with biogas due
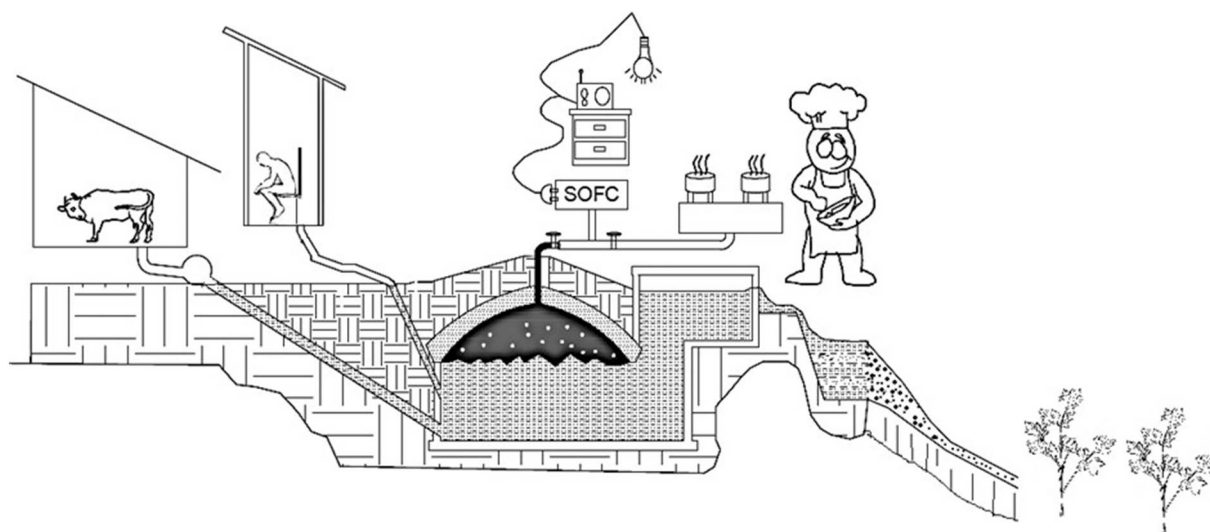

Fig. 1. Biogas-SOFC energy system.

to their relatively high tolerance to fuel impurity and flexibility [11]. Fuel cells are currently being developed to replace the conventional energy converters such as internal combustion engines because of their high efficiency. Also they have a possibility to work in reverse mode (producing H_2) which could lead to the possibilities of energy storage [12]. This can be a potential solution to major problems in the field of energy storage and grid stability. Furthermore, the heat produced from SOFC can be used to heat up the digester which could further increase biogas yield especially during winter seasons. It has been reported in literature [13] that one of the disadvantages of biogas systems is that they are not suitable for cold regions. Therefore, the use of excess heat from SOFC can level such disparities in embracing biogas technology.

However, the major challenge of using biogas as a fuel for SOFCs is that it contains various impurities such as H_2S, siloxanes and other volatile organic compounds (VOCs) which have to be removed to the required impurity level of the SOFC [4,14]. Threshold limits for SOFC

of 2 ppm(v) for H_2S and a few ppb levels for siloxanes in biogas has been recently reported which can even be lower in the presence of chlorine impurities [15]. Another challenge of SOFCs is the high initial capital and operational costs [16–18]. Therefore, the major envisaged challenge of biogas-SOFC energy systems in off-grid energy supply mix is the high initial investment and operational costs of which the gas cleaning unit, more specifically the sorbents used, are considered to have a significant cost implication to the overall economic feasibility of the system. It is also noteworthy that although price prediction was positive of reaching prices below $500 per kW by 2020, SOFC commercial production has not lived up to this expectation and goals have been re-adjusted to $1000 by 2020 [18]. Hence the economic use of biogas as a fuel for SOFC cannot be achieved without a proper and sustainable cleaning technology [19].

A proper biogas cleaning system prior to biogas-SOFC should meet both the stringent gas requirements of the SOFC system and tolerate

Table 1
Specifications of systems manufactured by Watt Imperium, Kyocera and Elcogen [5–7].[a]

Parameter	WATT Imperium	Kyocera	Elcogen
Rated output of power generation (AC)	1 kW	3 kW	1kw and 3 kW
Rated Power Generation Efficiency	N/A	52.0% (LHV, default)	N/A
Rated Overall Efficiency	N/A	90% (LHV, default)	N/A
Dimensions	571.5 W × 317.5 D × 304.8H (mm)	1150 W × 675 D × 1690H (mm)	190(W) × 315(L) × 90 (H) for 1kw and 190(W) × 230(L) × 280 (H) (mm)
Weight	20.9 kg (Dry Weight)	375 kg	17 kg for 1 kW and 33 kg for 3 kW
Gas Type	LPG (HD-5) or Natural Gas (NG)	City gas (13A)	N/A
Ambient Temperature	−10 °C to 40 °C	N/A	N/A
Nominal Voltage	12 Vdc or 24 Vdc	N/A	N/A

[a] N/A- Data not specified in the reference. Also a hot gas system is required to be added to Kyocera SOFC.

varying gas composition from anaerobic digestion. The removal of H_2S has been reviewed [20] and investigated by a number of researchers. However, limited efforts have been put to deep cleaning of the gas to the required level of SOFC more so under biogas-SOFC operating conditions where other impurities like siloxanes and VOCs are expected. Since CO_2 is not a major concern for SOFC as it can be used for dry reforming of methane, biogas upgrading is not considered in this review. This paper therefore reviews the commercialised and laboratory scale cleaning technologies for H_2S and other impurities in biogas which are considered to be detrimental to the SOFC. In addition, their possible contribution to the overall small-scale biogas-SOFC energy system levelized cost of electricity (LCOE) is discussed.

2. Recent developments in small scale SOFC Systems

Over the last few years, a number of companies (such as Watt Imperium, Kyocera and Elcogen) have started manufacturing small scale SOFC systems up to 3 kW capacity on commercial scale. Also SolidPower in conjunction with BlueGEN developed a micro SOFC-CHP system with electrical efficiency of 60% for European off grid market [8].This development indicates that at least for niche applications in the market is reaching maturity.

Watt Imperium has already commercialised a small scale SOFC fuel cell system fuelled by liquified petroleum gas (LPG) or natural gas [6]. The SOFC system is small and compact with an inbuilt battery and weighing 46 lbs. Hence it is easy to use for mobile applications and for emergency situations. Its power is approximately 1 kW with a daily maximum energy capacity of 14 kWh and fuel consumption of 34 Lb h^{-1} under continuous use. The system commercialised by this company has specifications presented in Table 1.

Kyocera also recently launched a 3 kW SOFC system for institutional co-generation [5]. It is reported that the system uses ceramic

technology with an efficiency of 52% and an overall efficiency of 90% in CHP mode. The system is designed to meet the current demand of off-grid energy supply. In addition to the capability of providing a steady 3 kW power, it can also use a demand regulated power supply. The system specifications are in Table 1. This system is an improved version of earlier SOFC of 700 W which was developed in 2012 by the same company. Such a system is a potential replacement of a small scale diesel generator of comparable size and comes with added advantages of less inconveniences in terms of emissions. Fuel cells emit water and CO_2 as the exhaust gases whereas generators with internal combustion engines are susceptible to emission of NOx gases when NH_3 is present in produced biogas [21,22]. Furthermore, recent promising innovations to capture CO_2 using microalgae can reduce emission from biogas by 1.6% [23]. The major challenge is still the high upfront cost which is expected to go down with mass production. Currently a cost of 3000–32,000 USD/kW has been reported for systems from 1 kW to 25 kW [24,25]. Cost could vary significantly depending on mass production.

Elcogen has also developed 1 kW and 3 kW stacks which are operating at relatively low temperatures of about 650 °C [7]. Such system can have an advantage of using relatively low cost materials which is critical especially when it comes to small scale power plants although their sulphur tolerance level may be low [26].

3. Biogas fuel impurities

Biogas is a CH_4 rich gas which is produced from biodegradable materials under anaerobic conditions. It is typically composed of 50–75% CH_4 and 25–50% CO_2. However, other trace materials such as water vapour, H_2S, NH_3, siloxanes and other VOCs may be present in the gas depending on the composition of the feed stock and the source [10,27,28]. Their presence beyond recommended quantities can be
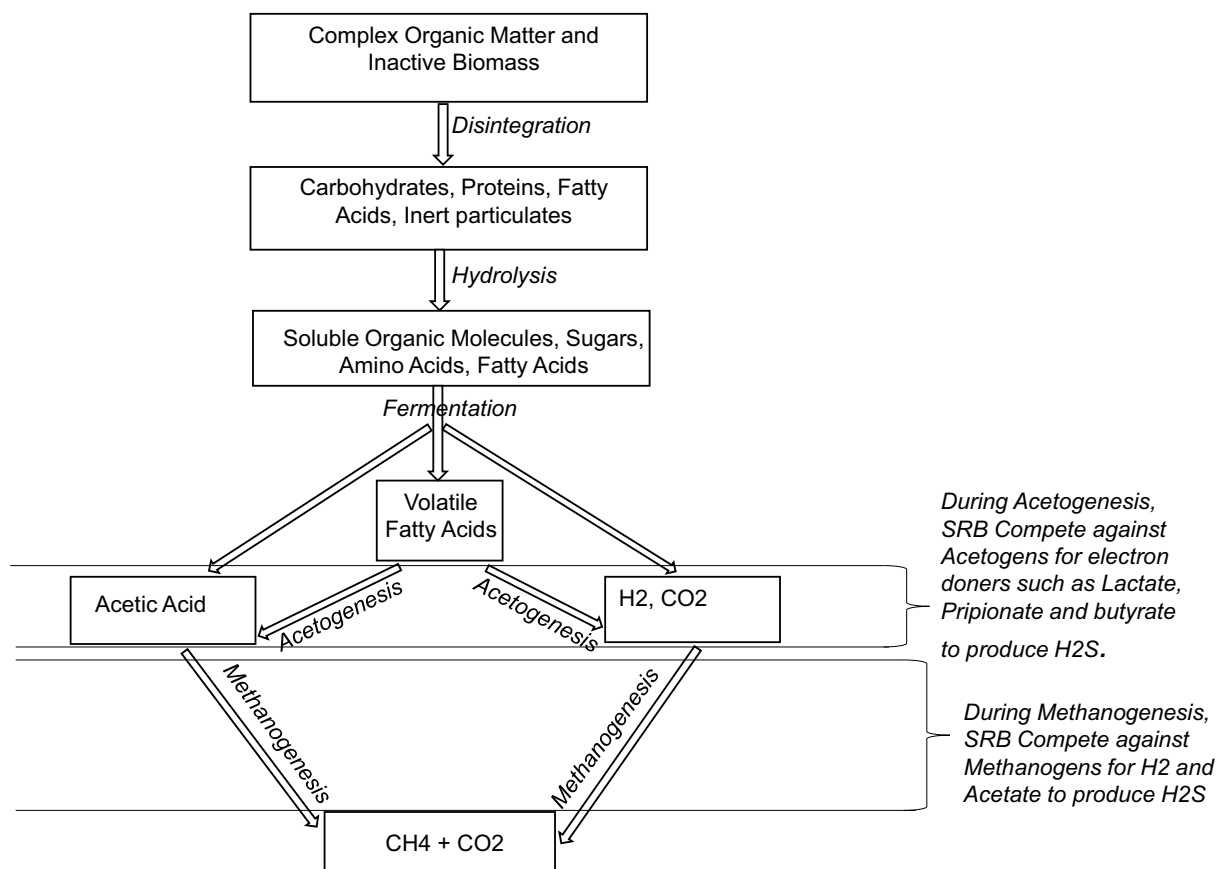
Fig. 2. H_2S production during anaerobic digestion [34].

detrimental to thermal and thermal catalytic biogas conversion devices, and also harmful to the environment in form of emissions [29–31]. In the microbial-controlled production of biogas, at least three bacterial communities are required to support the biochemical chain of hydrolysis, acidogenesis and methanogenesis. This process takes place in mesophilic (20 °C – 40 °C) or thermophilic (above 45 °C) conditions [13]. As reported earlier, apart from the typical composition of biogas, compounds such as H_2S, volatile organic sulphur compounds (VOSCs) and siloxanes, although present in small quantities, are considered to be the major biogas impurities for SOFC applications. Other less critical impurities such as halogenated hydrocarbons, alkanes, aromatics, cyclic and other VOCs are considered to be less harmful to the SOFC. However, experimental results have revealed that such compounds could influence the SOFC performance by affecting the reforming reactions and increasing the mass transport resistance [23,32]. All these compounds together are commonly referred to as impurities and their suggested lower threshold limits are shown Table 4. These different compounds generate diverse problems which include damage to other energy recovery equipment such as heat exchangers and thus reducing the economic benefits of biogas based energy systems [33]. A brief description on how each compound could theoretically affect SOFC performance depending on fuel composition and operating conditions is presented in Section 4.

3.1. H_2S in biogas

During anaerobic digestion, apart from CH_4 and CO_2, H_2S is also commonly produced generally in small quantities at ppm levels. The H_2S is produced from organically bound sulphur present in e.g. proteins, or from SO_4^{2-} (Fig. 2) by sulphate reducing bacteria (SRB), depending on the feed stock composition. Table 2 lists some typical sulphate reduction energetic reactions and methanogenic reactions. In general, it can be deduced from Table 2 that SRB have a much more wide substrate spectrum where they have kinetic and thermodynamic advantage compared to methanogens [34]. Therefore, during anaerobic digestion H_2S will always be produced by SRB if sulphate is present.

Biogas may contain H_2S concentrations of up to 5400 ppm depending on the feed stock of the digester [35]. Although the composition of biogas varies depending on the feed stock of the digesters, generally H_2S in Biogas from Land Fill Gas (LFG) is low compared to biogas from wastewater treatment plants (WWTP) [35,36].

3.2. Siloxanes in biogas

Siloxanes are chemical compounds that are found in products such as cosmetics, deodorants, water repellent wind shield coatings, detergents, soap and additives of foods [37,38]. They are semi-volatile organic compounds that are used in a number of industrial applications and consumer products and as a result they are widely spread in the environment [39].

For digesters operating at 35 °C to 38 °C temperature, siloxanes are expected to be very low since they significantly volatilise at higher temperatures during anaerobic digestion [40,41]. Siloxanes of type L2, L3 and D3 have a high vapour pressure and therefore, they tend to volatilise before anaerobic digestion and consequently, are not common in biogas [41]. D4 and D5 have a moderate vapour pressure and are the most common in biogas whereas D6 have a low vapour pressure and tend to remain in the sludge [41]. Moreover, since siloxanes containing materials such as cosmetics, deodorants and additives of foods which are relatively common in waste water, less siloxanes are expected in biogas from small scale digesters which use animal manure or food waste as feed stock.

Generally, biogas from a WWTP is expected to have high amounts of siloxanes as compared to LFG [35–37]. A maximum of 4 ppm – 9 ppm is expected for LFG, whereas for biogas from WWTP it can be as high as 41 ppm, whereas biogas from the farm digesters are expected to contain

the least amount of siloxanes [35,36,39]. As far as the authors are concerned, no information could be found on the presence of siloxanes in small scale digesters. Common types of siloxane found in biogas and their typical concentrations are shown in Table 3.

3.3. VOCs in biogas

Other impurities within biogas can exist in a complex form such as VOCs, and not all of them can be identified by gas analysis and monitoring equipment [42]. Some of these VOCs have been generally referred to as tars when coming from biomass gasification by many researchers which are often further categorised as light and heavy tars [14,44]. In biogas, VOCs are in the form of organosulphur compounds (mercaptans, sulphides, disulphides), organosilicon compounds (siloxanes, already discussed in previous section), halocarbons, aromatics, and cyclic compounds [35]. Nevertheless, aromatics in the form of benzene, toluene and halogenated hydrocarbons are more common, with toluene being the dominant compound among them [36,45]. Benzene can be as high as 21.3 ppm of land fill gas and as low as 0.85 ppm for WWTP biogas, toluene can be as high as 108 ppm for land fill gas and as low as 2.3 ppm for WWTP [35]. For halocarbons, a maximum of 13.2 ppm for land fill gas is expected and a maximum content of 1.9 ppm for WWTP biogas is expected [35]. Biogas from farm digesters contains the least amount of VOCs, followed by land fill gas and biogas from WWTPs, respectively [35,45]. Other VOCs in the form of alkanes, aromatics, poly cyclic compounds also exist in biogas in small quantities depending on the source as shown in Table 4. Similarly, trace elements of alcohols, ketones, carbon disulphide and dimethyl sulphide could exist in the gas and more details of their expected concentrations in biogas is presented in Table 4.

4. Effect of impurities on SOFC performance

4.1. The effect of H_2S on SOFC performance

The influence of H_2S on the performance of SOFC with different types of anodes is a widely researched topic. H_2S influence on the SOFC performance is a complex phenomenon and is dependent on the anode material and operating conditions such as temperature, fuel composition, operating time of the cell and H_2S concentration in the fuel [46]. The effects can mostly be classified as reversible cell degradation, irreversible cell degradations and corrosion effects. The level of poisoning effect depends largely on the type of anodes used and the concentration level of H_2S in the fuel. Aravind et al. [14] reported that the performance of SOFC can be greatly affected by H_2S even at low ppm levels. This is because H_2S is adsorbed on the active sites of the anodes and inhibits the fuel from getting adsorbed at these sites thereby affecting the fuel oxidation process. Details of how H_2S and other biogas impurities interact with Ni anodes are reviewed by Lazini et al. (2017) [47]. General effect of H_2S on the performance of SOFCs is reported in Table 4.

Table 2

Typical SRB Energetic reaction feasibility on comparison to Methanogenic reactions. Adapted from [34].

Sulphate–Reducing versus Methanogenic reactions	$\Delta G_r^{0'}$ kJ mol^{-1}
$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$	−36.4
$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	−135.5
$Acetate^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^-$	−47.6
$Acetate^- + H_2O \rightarrow CH_4 + CO_2$	−31.0
$1.33Propionate^- + SO_4^{2-} \rightarrow$	−50.3
$\quad 1.33Acetate^- + 1.33HCO_3^- + 0.75HS^- + 1.33H^+$	
$Propionate^- + 3H_2O \rightarrow Acetate^- + 3H_2 + HCO_3^- + H^+$	+76.5
$2Butyrate^- + SO_4^{2-} \rightarrow 4Acetate^- + HS^- + H^+$	−55.6
$Butyrate^- + 2H_2O \rightarrow 2Acetate^- + 2H_2 + H^+$	+48.1

Table 3
Common siloxane types [35,39,42,43].

Siloxane type	Abbreviation	Chemical formula	Molar mass (g/mol)	Expected maximum concentration in land fill biogas (ppm)	Expected maximum concentration in WWTP biogas (ppm)
Hexamethyldisiloxane	L2	$C_6H_{18}OSi_2$	162	1.89	0.03–2.26
Hexamethylcyclotrisiloxane	D3	$C_6H_{18}O_3Si_3$	222	0.25–1.89	0.05
Octamethyltrisiloxane	L3	$C_8H_{24}O_2Si_3$	236	0.41	0.25–0.47
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	297	5.68	1.00–20.14
Decamethyltetrasiloxane	L4	$C_{10}H_{30}O_3Si_4$	310	0.42	1.061
Decamethlcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	371	3.21	22.28
Dodecamethylpentasiloxane	L5	$C_{12}H_{36}O_4Si_5$	385	N/A	N/A
Dodecamethylcyclohexasiloxane	D6	$C_{12}H_{26}O_6Si_6$	445	0.08	N/A
Trimethylsilanol[a]	TMS	$C_3H_{10}OSi$	90	1.65	0.02

[a] Quantified as toluene equivalent.

It is considered that at low ppm levels of H_2S, the poisoning effect is reversible, whereas at high ppm levels, H_2S can cause irreversible poisoning effect to SOFC [48]. It has been reported that even H_2S levels of 1 ppm can have a detrimental effect on the SOFC performance although the degradation increases with increase in H_2S concentration [46,48,49]. Also, Papurello et al. [32] recently reported that even at < 1 ppm, H_2S can have an influence on the performance of SOFC as long as the cell is exposed to such an impurity for a long time. Hence the longer the cell is exposed, the higher the influence of H_2S on the SOFC performance. Its removal is of great importance to not only protect the SOFC degradation but also it can be harmful to human health if the gas is released to the environment. The removal of H_2S and other impurities from biogas prior to the reforming reactions of SOFC is therefore of paramount importance for successful system operation and reliability.

It has also been reported in literature that H_2S and other sulphur containing impurities can have an effect on the cell impedance, methane reforming, water gas shift reactions, cell voltage and polarization resistance during SOFC operation depending on the operating conditions such as temperature [26,50,51]. Matsuzaki et al. [26] studied the temperature dependent influence of H_2S on the performance of SOFC using H_2 and H_2O gas mixture, Ni-YSZ cermet electrode, complex impedance analysis and a DC polarization method. It was observed that the effect of H_2S on the performance of SOFC largely depends on the cell's operating temperature and hence, a high level of desulphurisation is required at lower operating temperatures.

Kuhn et al. [51] also reported that formation of NiS affected the SOFC performance and the magnitude of the effect seemed dependent on the nature of fuel oxidation but could not be explained for all the reactions during fuel oxidation. Therefore, the effects of H_2S on SOFC may vary according to the gas composition such as H_2O content within the fuel gas.

However, SOFC with Ni/GDC anodes are reported to have a higher sulphur tolerance levels as compared to other SOFC anodes, like Ni/YSZ [14,48]. Other materials such as $Ni_{(1-x)}Co_x$/YSZ were tested and it seems to have higher H_2S resistance in the presence of methane [52]. Other Ni free anodes have been recently reviewed by Sadabaadi et al. [10], they are reported to have a high tolerance for H_2S, although there is little development in their commercialisation probably due to higher costs as compared to Ni anodes.

As discussed before, a number of researchers have investigated in detail the effect of H_2S on the performance of SOFC using different experimental methods and setups [53–56], but further research and development is still required to completely understand the electrochemical interaction mechanism of H_2S with different SOFC materials as well as the long term effect of sulphur on the performance of SOFC. Therefore, it can be generally concluded that the influence of H_2S on the performance of SOFC depends on the various operating parameters of the SOFC, fuel composition and the materials from which the SOFC was developed. For the Biogas-SOFC energy systems, H_2S should be removed as much as possible (< 2 ppm(v) is recommended in literature [15]) to guarantee the system reliability since it can potentially affect the fuel reforming process. It is also important to note that H_2S could be harmful to human health too if the gas is to be vented in air, hence its removal from the gas is of paramount importance [57].

4.2. The effect of siloxane on SOFC performance

Siloxanes are silicon containing compounds in biogas. When siloxanes are burnt they result into formation of silica deposits. Siloxanes are considered to have a significant influence on the SOFC performance even at ppb levels [58]. Apart from SOFC, silica deposits can also result in inactivity of the system catalysts and lead to poor heat transfer, especially in heat exchangers, which could result into lower system heat efficiency [59]. Veyo [50], studied the effect of silicon impurities on the performance of a two-cell SOFC stack using simulated coal gas fuel with 13.2% H_2O, which was passed through a porous aluminosilicate insulation board composed of 74% Al_2O_3 and 26% SiO_2. It was observed that at lower H_2O content, there was accumulation of silicon on the exposed nickel, but it did not significantly affect the cell performance. However, at higher H_2O levels of approximately 50%, silicon deposition was enhanced by the H_2O content in the fuel gas and this led to an increase in the rate of cell degradation. Madi et al. [58] also investigated the effect of silicon on the performance of SOFC on Ni-YSZ anodes using both single cell testing and short stack testing ring. Posttest analysis revealed that silicon accumulated more on the anode contacts layer than in the inner anode region. Hence, it was concluded that during SOFC operation, silicon deposits would accumulate on the interconnects forming an insulating layer that would increase the ohmic resistance. Recently, the same research group [60] also reported that silicon condenses and deposits on the anodes and down to the electrolyte, even at ppb levels. At 5 ppm levels, D4 siloxanes caused a nonreversible effect to the SOFC [60]. Therefore, it has to be removed completely from the fuel for successful SOFC operation. For small scale biogas-SOFC energy systems operating in a temperature range from 35 °C to 38 °C (digester temperature), siloxanes are expected to be very low since they significantly volatilise at higher temperatures during anaerobic digestion [40,41].

4.3. The effect of VOCs and other biogas impurities on SOFC performance

The existence of other trace elements in terms of VOCs could have a strong detrimental effect to SOFC even at very low ppm levels. If they are not removed from the fuel gas, they could interfere with the methane reforming reactions and other reactions during fuel oxidation by decreasing the reactive surfaces of the catalyst [32]. VOCs can be generally categorised as siloxanes (organosilicon) organosulphur, halocarbons and hydrocarbons. Siloxanes have been already discussed in the previous sections of this paper and therefore, they will not be considered in this section.

Table 4
Summary of common impurities within biogas and their reported effects to human health and environment, process equipment and SOFC.

Component	Concentration in raw gas	Required limit for SOFC	Limit to human health and the environment	Potential effect to human health and environment	Potential effect to process equipment	Specific potential effect on the SOFC
H_2S	0–500 ppm, 100–1000 ppm, 0–10,000 ppm(v), 0–8000 mg m⁻³ [35,45,73–75]	< 1 ppm [4,14,76]	-Odor threshold < 0.014 mg m⁻³ [57] - < 1 ppm for at least few days for eye irritation, respiration irritation etc.,. [77]	-Causes bad smell [20] -Unhealthy, causes eye irritation [57,77,78] -Environmentally hazardous since it leads to formation of SO_2 and H_2SO_4 [77,79]	Highly corrosive [30,80]	Inhibits the fuel molecules from adsorption and hence affects fuel oxidation [32,46] Affects fuel reforming [81,82] Causes mass transport resistance [32], through the electrodes caused by the sulphur blocking the sites
NH_3	0–500 ppm(v/v) [28,74]		Maximum emission rate < 50 ppm(v) [65]. Conversion of NH_3 to NOx is < 10% during combustion, however this conversion depends on the % of Ammonia in fuel gas and the mode of combustion [83]	Leads to formation of NO_x emissions in engines [28,75]	Can be corrosive although less corrosive than H_2S [70,71]	Considered harmless to SOFC since it can crack to H_2 and N_2 during operation [65,66,69]
Siloxanes	0–50 ppm [35,36,39] < 1 ppm(v) [32] < 0.01–100 ppm [72] 0–5.0 mg Nm⁻³ [75] < 400 mg m⁻³	< 10 ppb [19] < 100 ppb(v) [41]		Siloxanes may not have a negative effect to the environment [84], however they may be responsible for fouling post-combustion emissions control- catalytic systems [41]	They lead to the formation of glassy micro-crystalline silica which reduces the life span of process equipment [19,41]	Silicon deposits on the interconnects of the cell, forming an insulating layer resulting in increased ohmic resistances [19,58]. Reduce the porosity and flow of the fuel towards the active sites [32]
N_2	0–5% (v) [28]			Nitrogen is considered harmless to the environment	Considered harmless [73]	Considered harmless
Water Vapour	1–5% (v/v) [28]		Water vapour is considered harmless to the environment		Considered harmless [73]	Operation of SOFC with humidified gas does not affect the cell performance [85], however the water content can be used during the reforming process of the gas
Other Trace elements within Biogas which can potentially affect the performance of SOFC						
Other Sulphur compounds such as CH_4S, CS_2, C_2H_6S	1.16 ppm–18.55 ppmᵃ [35]			Could result in various diseases if exposed for long time [86]	Could result into corrosion, although the effect is less severe than H_2S [87]	Since they contain sulphur, they could have the same corrosion effects like those of H_2S. Increases the rate of cell degradation [61]
Halocarbon such as CH_2CL_2	1.9–98.24 ppmᵃ [35]	< 0.5 ppm as ppm in Biogas [19]		If ends up in the environment, it contaminates water and can result in healthy effects [88]	It is highly corrosive in the presence of water [72] Can result into dioxins and furans which are highly toxic [72]	Could result in formation of $NiCl_2$ which has a sublimation temperature of 985 °C which is near the typical SOFC operating temperatures [61]
Alkanes Such as Ethane	184.13–222.86 ppmᵃ [35]					Could increase polarization resistance [32] Could influence reforming and fuel oxidation reactions
Benzene Toluene	0.85–21.3 ppmᵃ 2.27–108ppm					
Other aromatics such as Ethylbenzene	14.94–166.64 ppmᵃ [35]		Emission limit is < 0.0004 mg L⁻³ in water, < 0.6 mg m⁻³ in soil and < 0.2mg m⁻³ in air [89]	If present in the fuel, Could result in increased emissions on NO_x for engines [90] Could results into increased particulate emission and could cause respiratory effects [90]		Could increase polarization resistance [32]
Cyclic Such as Cyclohexane	49.42–84.9 ppmᵃ [35]				Could have a detrimental effect on process catalysts [91]	Could increase polarization resistance [32] Could influence reforming and fuel oxidation reactions

6

Table 4 (*continued*)

Component	Concentration in raw gas	Required limit for SOFC	Limit to human health and the environment	Potential effect to human health and environment	Potential effect to process equipment	Specific potential effect on the SOFC
Alcohols (Ethanol and 2-propanol)	7.02 ppm[a] [35]					Could influence reforming and fuel oxidation reactions
Esters such as ethyl acetate						Could influence reforming and fuel oxidation reactions
Ketones such as Acetone						Could influence reforming and fuel oxidation reactions
Particulate Matter	< 10 μm particle size		< 20 μg/m^{-3} for 24 h for particles < 2.5 μm [92]		Could ware down the equipment and could plug the gas system [72] Could plug the pores of adsorbents [72]	

[a] Cumulative maximum.

4.3.1. Organic sulphur compounds

Haga et al. [61] evaluated the effect of H_2S, CH_3SH, COS, Cl_2 and siloxanes using Ni-ScSZ cermet anodes by characterisation of the rate of degradation based on the measured cell voltage and anode polarization at a constant current density with humidified H_2 and CH_4 fuels. It was discovered that mercaptans such as CH_3SH compounds within the fuel gas may have a strong long-term detrimental effect to SOFC if they are not carefully removed. Their effect can be greater than that of H_2S even at very low ppm levels. Also, Madi et al. [62] observed that thiophene (C_4H_4S) at a concentration as low as 1 ppm can influence the SOFC performance. Therefore, any H_2S impurity limit to the SOFC should be considered as the limit of the total reduced sulphur compounds and a biogas-SOFC cleaning system should aim at removing all sulphur compounds and siloxanes in the fuel gas.

4.3.2. Halocarbons

The same research group [61], also observed that the existence of trace chlorine compounds, such as halocarbons, could lead to the formation of $NiCl_2$ which is very unstable (sublimates) at high SOFC operating temperatures, thereby resulting in permanent cell degradation.

4.3.3. Hydrocarbons

The effect on the performance of SOFC by hydrocarbons such as toluene, which is one of the aromatic compounds within the biogas, has been investigated by a few researchers. Papadias et al. [35] reported most of the frequently occurring trace compounds in LFG and in biogas from anaerobic digestion (AD) systems. Based on their results and if a scenario is considered that all the VOCs reported can be present at their maximum value, the expected VOCs (hydrocarbons) load within the biogas from AD is approximately 250–260 ppm. Also, analysis of total VOCs by Rasi [45] indicates that the expected maximum total VOCs variation between days is 4.1–6.6 ppm for farm biogas plants, 37.9–142.5 ppm for landfills and 10.7–220.7 ppm for WWTPs. Papurello et al. [32] recently observed that in the presence of methane, simulated VOCs (using naphthalene and toluene as VOC representatives) increased polarization resistance and have a great effect on the SOFC (Ni-YSZ anodes) performance even at low concentrations. However, Hofman et al. [63] had earlier reported that the high real VOC load of up to 3000 mg Nm^{-3} did not have a significant effect on the Ni-GDC anodes operated for 7 h duration. The same authors [64] did a similar study considering the VOC load of > 10 g Nm^{-3} and still no significant effect on the performance was observed for SOFC operated again for 7 h. Therefore, it can be concluded that for biogas–SOFC energy system, VOCs may not be a big challenge as far as poisoning of the SOFC is concerned, especially if they do not contain other elements such as sulphur and chlorine. However, their detailed analysis will predict their long term effect to the reforming process of biogas in SOFCs and their effect on sorbent performance.

4.3.4. Other biogas impurities

Other biogas impurities such as NH_3, alcohols and particulate matters could also exist in biogas in varying quantities, depending on the source. However, NH_3 is considered to be harmless as far as the SOFC is concerned. In fact, NH_3 can be an additional fuel to the fuel cell since it can be cracked and form extra fuel in form of H_2 [65–69]. Its effect could be outside the SOFC in terms of corroding the equipment like gas pipes [70,71]. To the authors knowledge, little is known about the effect of alcohols in SOFC. Particulate matter may not have an effect on the performance of SOFCs but if they are relatively large and exist in high concentration of > 16.5 ppm in the gas for 24 h, they may wear out the process equipment and plug the gas system [72].

4.4. Limit of biogas impurity levels for SOFC applications

From the available literature, the limit of impurity levels reported by different researchers widely vary, depending on the methods and

materials used during the experiment and the effective duration of the experiment. Even at low ppm levels reported in the literature, impurities could have a detrimental effect on the SOFC if exposed to such impurities for a long operation period [32]. Therefore, it can be concluded that the effect of impurities on the performance of SOFCs is a complex phenomenon, which depends on a number of parameters such as fuel compositions and system operation conditions. To the authors' knowledge, there is no confirmed impurity concentration limit for safe SOFC operation, hence removal of fuel impurities as much as possible should be aimed at, putting the overall cost implications into consideration.

5. Biogas–SOFC energy system gas cleaning unit

The envisaged renewable fuel, biogas, contains contaminants that can potentially damage even the relatively robust high temperature fuel cell anodes and other operation and process materials that precede the fuel cell stack [35]. Therefore, impurity management plays a vital role in improving the durability and performance of the biogas fuel cell system. This, however, increases the complexity of the system and also can potentially increase the operation and capital costs of the entire system [35]. Most of the biogas upgrading technologies, such as pressure swing absorption (PSA), are focused on CO_2 removal and are not discussed in detail in this review. Such technologies are most suitable for biomethane production for gas grid injection and models for biomethane prediction are being investigated [93]. CO_2 removal is not required for a biogas-SOFC system where it is assumed that CO_2 is even needed during the dry reforming process in the SOFC system [94–98]. Moreover, so far, there is no solid evidence about the impact of methane purity and efficiency of the fuel cells [99]. Therefore, upgrading technologies such as the use of amines, pressure swing adsorption, water scrubbers and organic physical scrubbers are not considered in detail in this section. Only H_2S, siloxanes and VOCs removal technologies are discussed.

A number of researchers have investigated various technologies for H_2S and VOCs removal from biogas without upgrading or CO_2 removal. Unfortunately, most of these technologies fail in the long run either due to technical or economic reasons [33]. These technologies are classified as physical, chemical and biological processes [100]. For utilisation of biogas, the contaminants which are considered detrimental are H_2S, volatile organic sulphur compounds, halides and silicon containing compounds [101]. It is important to note that their harmful effect depends on the biogas application. For biogas-SOFC application, generally < 2 ppm(v) of H_2S is required as discussed in Section 4.1 of this paper. This may not be the case for internal combustion engines which can tolerate as high as 150 ppm of H_2S [22].

5.1. Physico-chemical gas cleaning technologies

As far as removal of the impurities from biogas is concerned, cleaning agents such as sorbents and adsorbents in the cleaning unit are

the most important components, since they determine the system efficiency and long-term cost implications. Depending on the sorbent material, the most suitable reactor can always be chosen, but the reactor (cleaning system) can potentially result in increase in capital cost of about 6–7% of the entire energy system [102,103]. There are various sorbents that have been studied by different researchers as discussed in the sections below. Most of these cleaning technologies have been used and studied widely, for instance hot gas clean up using solid sorbents has many advantages in terms of process efficiency and economy as compared to cold gas clean-up such as aqueous solvents using amines [104]. There are various technologies involved in biogas cleaning and their applications depend on the goal of biogas use. As reported earlier [100], these technologies can be primarily classified into three; that is biological, physical and chemical processes. In most cases, physical and chemical processes are utilised simultaneously in a physicochemical cleaning process. These are further classified as reactive or non-reactive absorption and reactive or non-reactive adsorption techniques [20]. For the reactive or non-reactive absorption processes, they can further be classified as solid absorption and liquid absorption. The difference between adsorption and absorption techniques will be explained further in detail in Section 5.1.2.

5.1.1. Solid absorption gas cleaning processes

Generally metal oxides have been particularly investigated for their effectiveness as absorption agents for H_2S. For theses oxides, limited focus has been put on their effectiveness to absorb other sulphur related compounds such as mercaptans. The influence of their absorption capacity by the presence of other impurities has not been extensively researched.

5.1.1.1. ZnO.
Among the many metal oxides, ZnO has been widely used for > 30 years as H_2S removal agent from natural gas [105]. ZnO is a commercially available sorbent and is characterised by a high affinity to H_2S. During absorption, sulphur is chemically bonded to ZnO by heterogeneous chemisorption according to Eq. (1) [106];

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad (1)$$

Sulphur removal to < 1 ppm using ZnO for inlet gas with sulphur concentrations of over 2000 ppm(v) has been reported in literature [104,107,108]. Its use has been limited to desulphurisation of low sulphur content gas due to its difficulty to be regenerated [106]. For ZnO sorbent, a sulphur capture capacity of 34.1 g of S per 100 g of sorbent was achieved at 2 ppm(v) break through. [108]. It is important to note that the sulphur capture capacity (S_{cap}) depends on a number of parameters which include; *1*. Space velocity, *2*. Temperature, *3*. Steam concentration, *4*. CO_2 concentration and *5*. Sorbent particle size [104,108]. However, Torkkeli et al. [109] reported that water, CO and CO_2 may not have a significant effect on the performance of the sorbent at ambient temperature. The effects of these parameters on sulphur capture capacity are summarised in Table 5.

When pure metal oxides are used as H_2S sorbents, they have a number of physicochemical limitations such as sintering, mechanical

Table 5
Parameters which affect the sulphur capture capacity of ZnO based sorbents.[a]

Parameter	How it affects the S_{cap} of ZnO
H_2S concentration	The higher the H_2S concentration, the higher the S_{cap} of ZnO sorbent [105].
Space velocity	The lower the space velocity the higher the S_{cap} [104,108].
Reaction temperature	Increase in the reaction temperature increases the S_{cap} of ZnO and optimal temperature is in the range of 300 °C– 400 °C [104].
CO_2	Decreases S_{cap} if varied from 0 to 12% in the presence of steam [105].
Steam	An increase in steam, decreases the S_{cap} and can cause the release of previously captured H_2S due to the shift of the equilibrium reaction ZnO (s) + H_2S (g) ⇔ ZnS (s) + H_2O (g) towards ZnO and H_2S [104,105].
Particle size	Optimal particle size range 150-250 μm [104].
H_2 (g)	H_2 (g) accelerates the reaction of H_2S in the presence of H_2O at 500 °C [107].
CO	CO can potentially inhibit the reaction between ZnO and H_2S according to the following equation; $ZnO + CO \rightarrow Zn + CO_2$ [107,110].

[a] The behaviour of ZnO and ZnS in the presence of very low water concentration eg < 1% is still not clear [105].

Table 6
Summary of biogas cleaning technologies.

Gas cleaning technology	Advantages to small biogas-SOFC applications	Draw-backs/limitations	Contaminants the technology has been investigated to remove from biogas	Status
Liquid Absorption Gas Cleaning Processes				
Zone	- Already commercialised and it has been used for a long time [189] - It is environmentally friendly	- Efficiency of H_2S is affected by moisture with biogas [104,105] - Sensitive to operating parameters such as temperature (It should be with an optimal range which would require more energy and have poor performance at ambient temperatures) [104,108] - The effect of co-existing gases during adsorption can result in formation of sulphur compounds such as COS which can potentially affect the SOFC [105,190] - Very low S_{cap} at low temperatures [104], therefore not effective during cold start-ups.	H_2S	Commercialised
Cu-ZnO/SiO_2 or ZnO-CuO /Activated carbon	- It is effective at ambient temperature and therefore it can protect the SOFC during cold start-ups [112,115] - Can be easily regenerated at relatively low temperatures [109] - Efficiency is not affected by humidity at ambient temperature (20 °C) [109] - S_{cap} is not affected by CO_2 gas	- High energy is required during regeneration [106] - Efficiency is highly affected by the aging effect [109]	H_2S	Commercialised and laboratory scale
CuO	- Can simultaneously remove siloxanes and H_2S [33]	- Could result in formation of larger volatile sulphides from mercaptans [117]	H_2S	Laboratory scale
Activated alumina-V_2O_5/TiO-Alkalized material	- Relatively better break through time as compared to activated carbon and zeolite [118]	- The adsorption capacity is highly affected by the humidity with in biogas [118] - There could be risk of volatile sulphide formation from mercaptans in biogas [117]	H_2S	Laboratory scale
CuO-MnO			H_2S	Commercialised
Iron oxides	- Relatively cheap [121] - Some types are environmentally friendly, they can be disposed off after use without following stringent environmental procedures [160] - Can be easily regenerated [121] - Can simultaneously absorb more than one impurity [131]		H_2S	Commercialised
Liquid Absorption Gas Cleaning Processes				
Nitric and sulphuric acid	- High siloxane removal efficiency [101]	- High potential risk to healthy and environment, and this could result in high operation costs due to safety concerns [101]. - High risks of trace sulphur elements reaching the fuel cell system	H_2S	Laboratory scale
Fe-chelated solutions		- Less efficient and high risks of contaminant to strip to solvents at high gas flows [40]	H_2S	Laboratory scale
Metal sulphate solution			H_2S	Commercialised
Organic amine solvents		- High energy consumption [135] - Low adsorption/desorption rates and amine loss during regeneration [135] - Absorbs CO_2	H_2S	Commercialised
Adsorption Gas Cleaning Processes				

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Table 6 (continued)

Gas cleaning technology	Advantages to small biogas-SOFC applications	Draw-backs/limitations	Contaminants the technology has been investigated to remove from biogas	Status
Activated Carbon	- Can efficiently remove siloxanes, linear and aromatic hydro carbons from dry biogas [100] - Can tolerant moisture content of approximately up to 40% of the total gas with negligible effect on adsorption capacity [135,140,191] - Pre-humidification of activated carbon could enhance its adsorption capacity [192] - Due to its high surface area and distinctive pore volume, It has possibility of modification with different additives and this can increase its adsorption capacity [118] - Relatively less expensive as compared to zeolites and metal oxides [118,136].	- Regeneration can potentially reduce the efficiency of activated carbon [139]. - Could require regular change due to low adsorption capacity and this could potentially increase the operations cost [40,158] - Disposal may not be environmentally friendly [33] - Adsorption capacity can be potentially decreased by gas contents such as CO_2 [193] - Activated carbon impregnated by caustic could be difficult to handle and to dispose [72,152]	H_2S, mercaptans, siloxanes and Other VOCs	Commercialised
Zeolites	- They are effective at ambient temperature [158]. - Due to narrow pores, it has good selectivity to CO_2 and CH_4, hence little effect to the SOFC reforming process [159].	- Since they are selective to CO_2 and CH_4 [159], they may be also be selective to other biogas contaminants such mercaptans and halocarbons.	H_2S and VOCs	Commercialised
Silica gel	- Due to its high hydrophilicity, it can act as a dryer for downstream gas cleaning [101]. - Easy and cost effective to regenerate [101], although adsorption capacity decreases significantly when regenerated [150]. - Could be cost effective for small scale biogas applications [40].	- Adsorption capacity is reduced by H_2O content in the gas [101,150]. - Adsorption capacity is reduced by increase in temperature [150].	Siloxanes	Commercialised
Polymeric adsorbents	- Less sensitive to humidity as compared to carbons [136]. - They can easily be regenerated [136].		VOCs	Laboratory scale/ commercialised
Activated sludge	- Cheap source and readily available. - Adsorption capacity is not affected by high moisture content in the gas [166].		H_2S	Laboratory scale
Other physicochemical biogas cleaning systems				
Water scrubbing technology		- Requires high volumes of water [33]. - Absorbs CO_2 [33] which can affect fuel cell internal reforming. - Results into formation of corrosive acids [33] which can potentially increase operation cost. - Poor removal efficiency of other siloxanes compounds due to their low solubility in water [33].	H_2S	Commercialised
Cryogenic condensation		- Very low efficiency [101] - High operation costs [33]	H_2S, siloxane, and halogens	Commercialised
Membrane separation technique		- Cannot selectively remove impurities [174,175]	Siloxanes	Commercialised/research
Biological Gas Cleaning Processes				
Bio-trickling filters and activated carbon combined with biological filters	- Can simultaneously remove a number of impurities from biogas including H_2S,siloxanes and mercaptans [59,178,179]	- Slow adaptability to gas composition and slow response time during start up [118]. - Maintenance of pH would require the use of extra chemicals like NaOH and this would increase the operation costs of the system	H_2S and mercaptans	Laboratory scale
Combined effect of activated carbon and biological H_2S removal			H_2S	
In-situ biogas cleaning and upgrading technologies				
Micro-aeration/ Oxygen or air dosing		- Would require a control system such that explosion is avoided	H_2S	Commercialised
Addition of chemicals into the digester or In-situ chemical upgrading		- Would require chemicals and this can potentially increase the operational costs, especially if chemicals are not readily available.	H_2S	Commercialised

Table 6 (*continued*)

Gas cleaning technology	Advantages to small biogas-SOFC applications	Draw-backs/limitations	Contaminants the technology has been investigated to remove from biogas	Status
Solar-photo-oxidation in combination with biological treatment	Can simultaneously remove all impurities from the gas [188]	- Depends on solar light which may not be available all the time	H_2S and VOCs	Laboratory scale

disintegrations, loss of surface area and porosity, which affect their life time and performance [111]. They are therefore normally mounted on an inert material or a catalyst which increases their mechanical stability. This can increase their effectiveness for small scale biogas-SOFC applications as reported in Table 6. Hussein et al. [112], studied different mesoporous silica materials which were synthesised and used as supports for ZnO adsorbents to desulphurise biogas at ambient temperature. These materials enhanced adsorption capacities of ZnO at ambient temperature as compared to activated carbon adsorbents and commercially available titania. It is therefore recommended that such sorbents can be used as guard beds during transition operations such as cold start-ups which is very important for the biogas-SOFC energy systems. It is important to note that SiO_2 is commonly used as a support for the Zn based sorbents. However, other materials, which can potentially be used as supports are Al_2O_3 and TiO_2 [107], although SiO_2 was found to be a better support than Al_2O_3 [113]. Enhancement of mechanical strength and possibilities of regenerating ZnO based sorbents will make them cost effective and applicable in off-grid energy supply scenario. Although such materials are promising in terms of enhancement of S_{cap} of ZnO based sorbents, more studies are needed to investigate their effectiveness at different temperatures and different working conditions such as water content and other trace impurities within the biogas prior to application in small scale biogas-SOFC energy systems.

When ZnO is doped with metals such as Cu on SiO_2 support, it improves its desulphurisation capacity over a wide range of temperatures (20 °C - 400 °C) [109]. This low temperature desulphurisation capacity for such sorbents is important to protect the fuel cell during the cold gas start up [109]. It has been reported in literature that S_{cap} of ZnO can be enhanced by pre-treating it in ammonia carbonate which leads to a sorbent with a superior morphology and higher surface area that can effectively capture H_2S [105].

5.1.1.2. Cu-ZnO/SiO2. Among metals, Cu doped with ZnO/SiO_2 has the highest sulphur saturation capacity [109]. Karvan et al. [111], investigated the effect of Cu content in the support material on the sorbent capacity. Results show that the higher the Cu content, the higher will be the sorbent S_{cap} and the more stable will be the sorbent during regeneration. This could explain why some researchers have tried to dope Cu with other oxides in order to come up with better sorbents such as copper doped zinc oxide on alumina (Cu doped ZnO/Al_2O_3) [114]. Cu-ZnO/SiO_2 can be easily regenerated in air at a lower temperature range of 300 °C – 550 °C, better than the available commercial ZnO sorbents which are regenerated at a much higher temperature [106]. Its sulphur capture capacity can fully be recovered at 550 °C in 1 h with limited capacity loss for up to 10 desulphurisation-regeneration cycles [109]. For small scale applications, regeneration of sorbents has to be evaluated in advance to justify whether it is economically feasible. Advantages and draw backs of this technology are reported in Table 6.

5.1.1.3. ZnO-CuO/AC. Balsamo et al. [115] studied the effects of adding ZnO and CuO onto a commercial activated carbon under dry conditions at room temperature. Results show that such sorbents have an increased S_{cap}, especially with increasing content of Cu in the sorbent as compared to commercially available ZnO sorbents. However, as Hussein et al. [112] reported, for such sorbents to be commercialised, more research is needed in terms of their behaviour under real operating conditions like ambient temperature, fluctuation of VOCs within biogas and among others.

The use of ZnO has been recommended by a number of researchers because of its effectiveness in sulphur capture [105]. However, its limited extent of regeneration [106] implies that more frequent replacement of the sorbent is necessary to clean the gas, and hence this results in elevated operational costs of the energy system. A more economical way especially for small scale biogas energy systems is to

use a sorbent which can be easily regenerated. Also, further research and development is still required to determine the effect of siloxanes on the rate of degradation of ZnO bed [103].

5.1.1.4. CuO sorbents. Apart from ZnO, CuO sorbent has been investigated as one of the possible sorbents for H_2S capture. It is one of the most preferred re-generable H_2S sorbents among the many metal oxides [109,116]. The advantage of such sorbents to biogas desulphurisation is that they are not affected by CO_2 [116] (Table 6). However, CuO oxide based sorbents have been reported to potentially cause formation of larger volatile sulphides from mercaptans in biogas [117].

5.1.1.5. CuO-MnO. CuO mixed with MnO sorbents are also commercially available sorbents which can be used for sulphur capture from raw biogas. Weinlaender et al. [118] investigated the effectiveness of CuO-MnO materials for removal of sulphur from biogas. A major drawback observed with the CuO-MnO sorbents is that its S_{cap} is highly affected by H_2O content in the gas (Table 6). So, application of such sorbents in small scale biogas-SOFC energy systems would require pre-drying of biogas before feeding it to the CuO-MnO filtration bed. It is important to note further that It has been recently reported that sorbents which contain copper (II) oxide as the principle active phase can effectively adsorb H_2S but there is a risk of formation of volatile sulphides from mercaptans in the biogas source [117]. Other sorbents such as aluminates of Mn and Fe ($MnAl_2O_4$ and $FeAl_2O_4$) and MnO have been investigated by a number of researchers. However, most of them did not yield satisfactory results in terms of S_{cap} or required very high temperature for efficient operation and regeneration [110,119]. Eventually, they were not given focus in subsequent research and development.

5.1.1.6. V_2O_5–TiO_2. To improve the efficiency of gas cleaning and to reduce on the complexity of the cleaning unit, a three stage state-of-art biogas cleaning unit was developed by Urban et al. [33] which can simultaneously remove H_2S and siloxanes. It involves the use of a cheap catalyst material in the first stage which decompose the siloxanes in the raw gas. In the second stage, the gases HCl, HF and SO_2 are oxidized over Vanadium-Oxide based sorbent while maintaining methane quality. In the last stage, an alkalised material is used to selectively remove acidic gases during oxidation processes. Results showed that activated alumina can effectively remove volatile siloxanes which are detrimental to V_2O_5–TiO sorbent during H_2S adsorption and the fuel cell operation. Although such technologies are promising to attain a one stage solution for small scale biogas-SOFC energy system applications, more research and development is still needed in terms of catalyst selectivity, degradation rate and sensitivity to operating parameters such as humidity within the biogas. It is important to note that the price of V_2O_5 is increasing at a high rate, therefore the use of such material as the sorbent for biogas cleaning could increase the operation costs of the cleaning system [120].

5.1.1.7. Iron oxide. Iron oxide is sometimes available in the form of iron sponges which are often iron oxide impregnated wood chips (wood chips covered with iron oxide) or iron oxide pellets. The latter has a much higher density than the former but the former is economically competitive [121]. During absorption, H_2S is first chemsorbed on the surface by molecular adsorption followed by dissociative adsorption on inner surface [122]. For iron oxide based sorbents, a three dimensionally ordered macropore (3DOM) structure has been reported to increase its sulphur capture capacity [123]. 3DOM are produced by the use of colloidal crystal templating method as opposed to conventional mechanical mixing method and greatly improve the diffusion of gaseous reactant to inner part of the sorbent [123]. 3DOM iron oxide are therefore more effective sorbents as compared to conventional ones and can be regenerated at relatively low

temperature of 100 °C [123]. Early research showed that addition of supports like Al_2O_3 and SiO_2 can influence the reactivity of iron oxide with H_2S [124]. Such supports can also enhance regeneration capability [125] and sulphur capture capacity if iron oxide [126]. Also when iron oxide is added to ZnO with a support, it can result in a more efficient and mechanically stable sorbent [127]. Therefore, as it is with ZnO based sorbents, doping of iron oxide based sorbents can greatly influence their absorption capacity [128]. Further research and development is still required to understand the effect of adding a support (to iron oxide) to the sulphur capture capacity of iron oxide, especially under varying anaerobic digestion conditions. It was also reported that iron oxide sorption capacity can be influenced by the presence of different gases [129]. Therefore, further research and development is required to completely understand how varying biogas composition influences the efficiency of iron oxide sorbents.

The major advantage of iron oxide usage for gas cleaning in small scale biogas power systems is that it can easily be regenerated at low temperatures and also can be operated at ambient temperatures [121]. Hence, this results in less energy requirement and higher system economic returns. Also iron oxide has been reported to have a higher absorption capacity for H_2S at lower temperature as compared to ZnO [130]. And It can simultaneously absorb more than one impurity [131]. Other advantages and disadvantages of this technology to small scale Biogas-SOFC system are reported in Table 6.

5.1.2. Liquid absorption gas cleaning processes

Similar to solid absorption technologies, generally liquid absorption has also been investigated for their effectiveness to remove H_2S from the gas. Limited attention has been put to their effectiveness to remove other impurities like mercaptans and VOCs or how the presence of these impurities can affect their effectiveness to remove H_2S.

5.1.2.1. Chemical absorption in aqueous solution. Chemical absorption is based on high affinity of H_2S to the metallic cation. This process can further be sub-categorised into two processes of which one involves oxidation of S^{2-} to S^0 and the other involves either capture of S^{2-} by precipitating it to its salts, which have a low water solubility, or capture by aqueous alkaline, which rapidly react with diffused H_2S (biogas contaminants) [73]. This method has not gained much attention because of reactivity of CO_2 with alkaline reactants such as NaOH and CaO [73].

5.1.2.2. Sulphuric acid and nitric acid. Sulphuric acid can be used to remove siloxanes but this is effective only at high temperatures [40,101]. However, working with acids at high temperatures poses a risk in practice. Also, if sulphuric acid is used, there are chances of trace elements of sulphuric acid escaping from absorption and reaching the energy converter. Nitric acid would reduce such risks but working with acid at high temperature seems to be impractical [101]. Other advantages and disadvantages of this technology to biogas-SOFC energy system are reported in Table 6.

5.1.2.3. Fe-chelated solutions. This technique involves the use of the redox reaction [73],

$$2Fe^{3+} + H_2S \rightarrow 2Fe^{2+} + S + 2H^+ \qquad (2)$$

$$2Fe^{2+} + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^- \qquad (3)$$

Due to limited data on kinetics in the literature, and the uncertainty on whether this technique is diffusion or reaction controlled, scaling up of such a technology is not a straight forward process [73]. Also, the technology is fairly complex to be applied on a small-scale basis.

5.1.2.4. Metal sulphate solution. With this technology, a metal sulphate solution with Fe^{2+} removes H_2S gas in the gas stream by forming insoluble sulphates. The Fe^{3+} oxidizes S^{2-} to S^0 while regenerating

Fe^{2+} solution by air oxidation under ambient conditions according to the following equations [73],

$$Me^{2+} + H_2S + 2SO_4^{2-} \rightarrow MeS(s) + 2HSO_4^- \tag{4}$$

$$MeS(s) + 2Fe^{3+} \rightarrow Me^{2+} + 2Fe^{2+} + S \tag{5}$$

$$2Fe^{2+} + \frac{1}{2}O_2 + 2HSO_4^- \rightarrow 2Fe^{3+} + H_2O + 2SO_4^{2-} \tag{6}$$

$$H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O \tag{7}$$
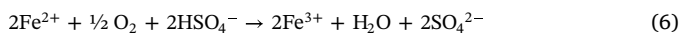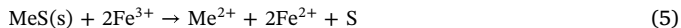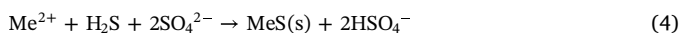
This technology is limited by diffusion kinetics at an operating temperature of above 60 °C. Due to its complexity and generation of strong acids like H$_2$SO$_4$, its application to small scale biogas system is rather difficult [73]. Furthermore, due to generation of H$_2$SO$_4$, the risk of its escape into the stream gas to the SOFC is high, this renders such a technology not favourable for biogas-SOFC energy system.

5.1.2.5. Organic solvents. Organic amine solvents are commercially used for H$_2$S removal from gas streams. The initial research of these technologies focused on simultaneously cleaning of the gas from H$_2$S and absorb CO$_2$ [132–134]. However, their major challenge was high energy consumption and low adsorption rates [135]. Therefore, application of these technologies in small scale SOFC energy systems would require high energy and chemical consumption and this would decrease the efficiency and potentially increase of both the capital and operational costs of the biogas-SOFC energy system. And since such technologies would involve biogas upgrading, they are not discussed in detail in this paper.

5.1.3. Adsorption gas cleaning processes

These technologies have been investigated for their effectiveness to adsorb H$_2$S and also other biogas impurities such as mercaptans and siloxanes. However, further research and development is still required to understand their selectivity of one impurity in the presence of the other.

Although absorption and adsorption are sometimes used interchangeably in literature, an absorber is different from an adsorber, in such a way that for an adsorber, the adsorbed material is held physically but loosely and can be easily released (desorbed) by either heat or vacuum. In contrast, an absorber reacts chemically with the material it absorbs and holds it much stronger and hence requires more energy to be desorbed [136].

5.1.3.1. Activated carbon. Carbon is produced by pyrolysis or gasification of carbon containing materials such as wood, coal, etc. to remove all the volatile materials such as gas or vapour such that only carbon is left. The remaining carbon may be activated by partially oxidizing it with steam or air at high temperatures usually between 700 °C to 1100 °C to increase its surface area available for adsorption [136,137]. The adsorption capacity depends on surface structure and surface characteristics of a given activated carbon [29]. Activated carbon can be available in three types *(i)* catalytic–impregnated (Regenerable) *(ii)* Impregnated and *(iii)* non-impregnated [73]. It has been used as an adsorbent in either granular or powdered form, the latter could have high adsorption capacity than the former [138]. Commercially available activated carbons have been proved to effectively remove H$_2$S and siloxanes from biogas to < 1 ppm [139]. Studies by Yu et al. [29] show that activated carbon can effectively remove siloxanes from biogas, although the adsorption capacity is greatly reduced by the presence of H$_2$O [140]. This has been recently re-affirmed by Calbry-muzyka et al. [117] and Papurello et al. [141]. Activated carbon is so far the most common adsorbent which is utilised for removal of halides and H$_2$S and its adsorption capacity for impurities is normally improved by impregnating it with liquid or solid chemicals [20]. The majorly used chemicals for impregnating activated carbons are KI, NaOH, KOH, NaHCO$_3$, NaCO$_3$ and KMnO$_4$ [20,118,142]. Also, it is important to note that sometimes a mixture of

these chemicals is used to impregnate activated carbon [20]. Other chemicals such as K$_2$CO$_3$ have been used to successfully impregnate activated carbon [143,144]. A major advantage of NaOH compared to KI for biogas cleaning system is that it does not requires oxygen in the gas stream during the cleaning process as shown in Eqs. (8) and (9) [118];

$$KI \qquad H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O \tag{8}$$

$$NaOH \quad H_2S + 2NaOH \rightarrow 2NaS + 2H_2O \tag{9}$$
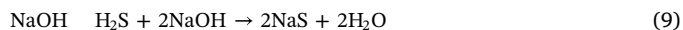
As reported earlier, impregnating activated carbon can potentially improve its affinity to sulphur containing compounds in the biogas [74,145], hence increasing its adsorption selectivity. Lazini et al. [47] reported that impregnating activated carbon can improve its sulphur capture capacity to as high as 300 g of H$_2$S per kg of adsorbent. However, for impregnated activated carbon, the adsorption capacity depends on the availability of oxygen [146]. Isik-Gulsac [147] recently investigated the effect of relative humidity, oxygen and biogas composition such as the CO$_2$ content on adsorption capacity of impregnated activated carbon. It was observed that water and oxygen can potentially enhance the adsorption capacity of impregnated activated carbon whereas CO$_2$ could have a detrimental effect to the adsorbent due to its acidic characteristics. The effect of water on the adsorption capacity of impregnated activated carbon is contrary to what has been recently reported [117] and what was reported by Yu et al. [29]. Other factors such as surface pH and diameter of micropores can as well affect the adsorption capacity of activated carbon [47].

Mescia et al. [74] also studied the effectiveness of H$_2$S removal of two activated carbons in a mixed bed on industrial scale. In this experiment, two commercially available activated carbons, namely, Norit ROZ3 and Norit RB4W, were loaded in a mixed bed (RB4W was always placed at the bottom part of the reactor) to find out whether this could enhance the S$_{cap}$. Land fill gas with approximately 200 ppm H$_2$S concentration was used as the fuel gas. Experiment results show that the S$_{cap}$ and operational cost was optimal when 70% and 30% of RB4W and ROZ3 respectively was used as adsorbent. In this experiment, the biogas was first pre-treated by a primary coalescer, which separated the first condensate, a secondary condensate separator and a dry filter which partially removed residual solids. This implies that applications of such cleaning technologies in small scale Biogas-SOFC energy systems would require a pre-treatment unit which would make the fuel cleaning process more complicated. In practice this would potentially increase both the investment and operational costs of such systems. Although the authors demonstrated that using sorbents in a mixed bed can potentially increase the cost effectiveness and efficiency of the cleaning system, they recommended that in practice, a two-stage cleaning system, which constitute first the scrubbing technique followed by the activated carbon, would be the most economic and efficient solution.

Papurello et al. [148] recently investigated a gas cleaning unit of a 500 W biogas–SOFC energy system in which 5 kg of commercially available activated carbon was used in a packed bed reactor. They monitored the cleaning of biogas from dry digestion (dry gas) for over 400 h. The results revealed that commercially available activated carbon can efficiently remove H$_2$S and other sulphur compounds such as CH$_4$S, C$_2$H$_6$S and CS$_2$, although lower removal efficiencies were reported for other impurities such as halocarbon, alkanes, aromatics and cyclic compounds. However, limited data is available about the type, source and costs of the activated carbon used, hence it is not possible to trace the economic feasibility of the activated carbon used.

The removal efficiency of siloxanes D4 from biogas by different types of activated carbon, different types of molecular sieves and silica gels was investigated by Matsui et al. [149]. It was observed that the removal efficiency depends on the adsorbent characteristics such as BET surface area, pore volume and pH. But, generally activated carbons had considerably higher tendency to adsorb siloxanes than silica gel followed by molecular sieves. This is contrary to what recently Sigot

et al. [150] reported that silica gel was more superior for removal of D4 siloxanes as compared to activated carbon and zeolites. The same group [149] also confirmed that activated carbon with good BET surface area and pore volume is capable of removing all the siloxanes from biogas and such adsorbent is currently used commercially in Japan. Cabrela-Codony et al. [151] also investigated the effectiveness of different types of activated carbons for siloxanes removal. It was observed that wood-based carbon has higher siloxane removal efficiency since it has the highest concentration of oxygen functional group when activated by H_3PO_4 which plays a key role in siloxane removal. The same group also observed that the adsorption capacity is greatly influenced by the gas composition such as CO_2 and H_2O content. Finiccho et al. [152] studied the adsorption capacity for Hexamethylcyclotrisiloxane (D3) of different activated carbons, silica gel and zeolites using synthetic biogas. It was observed that activated carbon sorbents have a higher adsorption capacity for D3 as compared to silica gel and zeolites. They also observed that pure activated carbons had a higher adsorption capacity for siloxanes as compared to alkali impregnated activated carbons. However, Nam et al. [153] recently reported that adsorption capacity of siloxanes depends on the molecular size of each siloxane type and the pore distribution of the adsorbent used, which is also re-affirmed by Yu et al. [29].

Although it is possible to regenerate any type of activated carbon, regeneration is considered not feasible for small scale applications [73]. Therefore, to pro-long the breakthrough period, activated carbon needs to be modified in terms of increasing the surface area by mechanism such as impregnation with caustic [142], if it is to be effectively used as biogas impurity adsorbent for SOFC applications. Other advantages and draw backs of activated carbon to small scale biogas-SOFC energy system are reported in Table 6. It is important to also note that apart from activated carbon, ashes and biochar are potential adsorbents for biogas contaminants [47,154].

5.1.3.2. Zeolites. Zeolites can be defined as crystalline, porous aluminosilicates in which the primary building blocks are TO_4 tetrahedrals having a Si^{4+} or Al^{3+} cation (Tetrahedral atoms) at the centre and four oxygen atoms at the corners [155]. Zeolites have uniformly sized pores through the crystal structure [156]. The various types of zeolites are determined by the ratio of silicon to aluminium in the crystal. However, the major two types are hydrophilic zeolites (naturally occurring) which have strong affinity to water and contains aluminium, and hydrophobic zeolites (de-aluminised by chemical replacement of aluminium with silicon without changing the crystal structure) which have affinity to non-polar substances such as VOCs [136]. Molecular simulations by Cosoli et al. [157] revealed that zeolites are potential adsorbers for H_2S in biogas. Also, novel molecular sieves are being developed by some research groups [158], and such adsorbers are expected to have an added advantage to absorbers like ZnO of being effective at ambient temperatures and they can be easily regenerated. Other advantages of Zeolites to small scale biogas-SOFC are reported in Table 6.

Papurello et al. [159] recently analysed the performance of commercially available Na-X pellets Zeolite (1/16 in., Carlo Erba, Italy) in a fixed bed of pyrex glass with an internal diameter of 2.5 cm and 25 cm height with 70 g of zeolite. A simulated gas containing 300 ppm of H_2S at room temperature was passed through the zeolite bed and then passed through a guard bed of ZnO sorbent at 300 °C at a flow rate of 25 Nl h^{-1}. Results show that zeolite was effective in removing H_2S to < 70 ppbv for over 250 h. They also observed that such a type of zeolite is selective for biogas composition of CH_4 and CO_2 and hence it favours the dry reforming process in SOFC systems. However, since surface water plays an important role in H_2S removal efficiency [160], in practice the use of such techniques could require to dry the biogas first, which may contain up to 5% of H_2O, before it is fed to the zeolite bed. Therefore, detailed analysis of zeolites in terms of adsorption capacity under different operation conditions such as humidity in fuel gas is still

required. For biogas–SOFC applications, a second cleaning bed would be required to clean the gas to < 2 ppm(v) H_2S concentration required by SOFC, and this could potentially increase both the capital and operation costs of the cleaning system.

5.1.3.3. Loading of activated carbon with metals and combining it with other absorbers such as zeolites. As discussed before, activated carbon has been investigated to successfully remove H_2S and most sulphur compounds such as CH_4S, C_2H_6S and CS_2 [148]. Zeolite effectively removes H_2S from the gas to an even greater extent [159]. However, sulphur compounds such as C_2H_6S (Dimethyl sulphide) was reported to be relatively difficult to be removed by activated carbon [161]. This also can be the case with several other sulphur containing compounds such as COS and halogenated compounds [162]. Modifying activated carbon by loading it with metals such as Cu, Zn and Fe can enhance its sulphur removal and selectivity capacity even for difficult compounds like dimethyl sulphides [163]. Also, combining of different activated carbons with molecular sieve bed could result into a one-step absorber which can remove all S containing compounds present in the fuel gas [162]. Activated carbon loaded with Cu mixed with zeolites loaded with Cu has been reported to effectively remove dimethyl sulphide, especially with low moisture content in the fuel gas [164].

5.1.3.4. Silica gel. Siloxanes could be completely removed by using silica gel and activated carbon at the same time. Schweigkofler [101] reported that silica gel can act as an adsorber of gas impurities especially siloxanes with relatively good efficiency. However, at high moisture content, the adsorption capacity for siloxanes decreases significantly [101]. Adsorption capacities of silica gel exceeding 100 mg of siloxanes per gram of silica gel has been reported by the same research group [101]. Since the adsorption efficiency is highly affected by H_2O content within the gas, a pre-requisite for its application as an adsorber is drying before the adsorption bed, which could be achieved by using more than one silica gel beds.

5.1.3.5. Polymeric adsorbents. Polymers are essentially long chain like structures. These adsorbents have pores built in them during manufacturing and just as carbon, they are not highly selective to which element to adsorb. However, they are considered to desorb faster than activated carbons [136]. Contrary to zeolites, polymers have a high adsorption capacity under high vapour pressure [136]. For application of such technology in small scale biogas-SOFC system, a clear understanding of their operation under varying conditions like humidity, space velocity among others is still required.

5.1.3.6. Sludge–derived adsorbents or activated sludge. The use of activated sludge as H_2S sorbent has been also investigated by a few researchers [20,165]. Xu et al. [166] investigated the removal efficiency of H_2S by sewage sludge and pig manure derived biochar. They found out that for such adsorbents, H_2O content within the gas could increase the adsorption capacity. However, limited data is available about the kinetics of such adsorbents. Breakthrough in research of such adsorbents would result in a cheap and readily available sources of adsorbent for biogas-SOFC energy system.

5.1.4. Other physicochemical biogas cleaning systems
5.1.4.1. Cryogenic condensation/adsorption cooling. This method involves condensing the gas to low temperatures typically below 5 °C which can potentially remove siloxane compounds within the biogas by 20–25% [101]. Other compounds such as H_2S and halogens can also be removed at a temperature of approximately −25 °C [167]. Although maximum contaminants removal is achieved at very low temperatures (below -70 °C), the energy consumption of such technologies would be very high, hence increasing the operational costs of the system [33,40]. For small scale biogas-SOFC energy systems, this gas cleaning technique can be used as the first pre-treatment technology operating at a

temperature just below 5 °C to reduce the moisture of the raw biogas for effective gas cleaning downstream using other methods such as silica gel and activated carbon, whose absorption capacity is greatly reduced by the humidity [101]. This could potentially reduce the energy requirement and the operational costs. Another attractive technique to reduce the energy requirement is by using adsorption cooling, utilising the already existing heat during the operation of biogas-SOFC energy system. Adsorption cooling is desirable since it requires only the heat without any mechanical energy [168].

Adsorption cooling systems have been investigated by a number of researchers. Solid desiccant cooling system can be categorised into two [169]; physical adsorption and chemical adsorption. The major difference between chemical absorption and physical absorption is that chemical adsorption is basically characterised by the strong chemical bond between the refrigerant and the absorbent and thus requires more energy to be regenerated [169]. Physical adsorption based chillers such as silica gel-H_2O adsorption chillers were investigated by Najeh et al. [170]. These cooling systems are promising for low temperature (inlet temperature lower than 90 °C) applications like solar, but for the biogas-SOFC energy system, where high temperatures are available during operation, they may not be technically attractive. Zeolite-H_2O based adsorption chillers would be more suitable for biogas-SOFC system with the driving temperature as high as 200 °C, but lower cooling temperatures are reached with such a system [169]. Therefore, in practice, they are used in air conditioning systems, where relatively high cooling temperatures are required. Other chemical based adsorption chillers which seems to be promising are $CaCl_2$-NH_3 and metal hydrides-H_2, but still their operating temperatures are low [169]. Also $CaCl_2$-NH_3 based adsorption chillers have problems of expansion, decomposition and corrosion which have hindered their application [171,172]. Liquid desiccant such as LiCl-H_2O, LiBr-H_2O and NH_4-H_2O cooling which are developed and those under research could also be having the same limitation of operating temperature as solid desiccant cooling, hence some of them may not be technically attractive as far as biogas-SOFC energy system is concerned [172]. Since ammonia–water absorption chillers require a driving temperature as high as 200 °C and cooling temperature is as low as -10 °C [172], they can presumably match with a biogas-SOFC energy system where high operating temperatures of > 700 °C are expected. However, for small scale applications of ammonia-water chillers, the power consumption of the solution pump should be considered and since ammonia is toxic, the location of the chillers should also be considered [169,172]. For a biogas-SOFC energy system, if adsorption is to be used as a cooling option, research and development is required to develop a chilling system which can efficiently utilise the available waste heat and achieve a cooling temperature much lower than 5 °C such that it can efficiently clean the gas and minimise the overall cost implication. Draw backs of this technology for small scale biogas-SOFC application are reported in Table 6.

5.1.4.2. Water scrubbing technology.

This technology is applicable for removal of H_2S from gases with high concentration of H_2S and it recovers sulphur by a (partial) oxidation process [33]. Its major drawback for biogas-SOFC energy system application is the absorption of CO_2 gas and requirement of large volume of water [33]. To reduce the water and energy requirement, counter current water scrubbers utilising waste water were studied but more research to understand their detailed kinetics is still required [173]. The application of such methods on small scale SOFC would result in less CO_2 available if dry reforming is to be used [94]. Other draw backs of this technology are summarised in Table 6. Therefore, such technology may not be suitable for SOFC application where dry reforming is envisaged. Some reports have indicated that water scrubbing can be used to selectively absorb H_2S but the cost of selective absorption is not competitive as compared to the cost of simultaneous removal of both H_2S and CO_2 [121]. Sometimes Selexol solvent is used instead of pure water but still the cost for selective absorption of H_2S is high and such a

method may not compete cost wise in small scale biogas based energy systems application [121].

5.1.4.3. Membrane separation technique.

Although this technique is primarily applied to remove CO_2 from the raw biogas, it can also be used to separate the siloxanes from biogas [19]. The removal of siloxanes by various types of membranes was extensively investigated by Ajhar et al. [174,175]. It was observed that siloxane removal by membranes could be commercially competitive but further research and development of membrane materials, which are highly selective for CO_2 and CH_4 is still required. The application of such a technique is considered not suitable for small scale biogas-SOFC energy systems application since CO_2 separation from the raw gas would affect the pre-assumed downstream dry reforming process.

5.2. Biological gas cleaning processes

These technologies can simultaneously clean the gas from H_2S and other impurities like mercaptans and siloxanes and make use of micro-organisms that oxidise the produced sulphide to elemental sulphur or the oxygenated anion (SO_3^{--}, SO_4^{--}). Weinlaender et al. [118] reported that biological methods are cost effective and environmentally friendly but their major disadvantage is poor adaptability to H_2S and other VOCs fluctuations. Therefore, in practice they are typically integrated with physicochemical solutions.

5.2.1. Bio-trickling filters

Among the biological gas cleaning units, bio-trickling technologies received attention as an alternative to chemical scrubbers of H_2S from waste water treatment plants purposely to reduce odor. Bio-trickling filters are complex combinations of different physicochemical and biological processes, under which a net polluted air stream is passed through a packed inert bed on which a mixed culture of pollutant degrading organisms is naturally immobilised [176]. As reported by Duan et al. [177], these filters have an added advantage over bio-filters since acidification can be avoided by washing away reaction products from the cleaning media. Such filters were also investigated by Cox et al. [178] on a laboratory scale. Results show that they can effectively remove H_2S and toluene in a single stage bio-trickling filter and are capable of achieving H_2S removal efficiency of > 70%. This is also reaffirmed by Montebollo et al. [179] who reported that bio-trickling filters are capable of simultaneous removal of H_2S and mercaptans. They also observed that existence of mercaptans in the gas could enhance the performance of bioreactors due to the reaction between mercaptans and sulphur which reduces sulphur accumulation in the reactor. Therefore, for biogas-SOFC application, such technologies may be suitable to reduce large impurities in biogas such as H_2S, but would require a second cleaning mechanism to bring down the H_2S concentration in fuel gas to the level acceptable for SOFC application.

Ramirez et al. [180] conducted a laboratory scale study on the effect of various operating parameters of bio-trickling filters such as sulphate concentration, pH and empty bed residence time (EBRT). They observed that the two major parameters that greatly affect the efficiency of H_2S removal by bio-trickling filters are pH, which should be in the range from 7.0 to 7.5 for optimal H_2S removal, and sulphate concentration accumulation in the recirculation media, which should be < 5 g l^{-1}. Also Chung et al. [181] reported that H_2S removal efficiency increases with increase in residence time. Contrary to gas cleaning processes which use absorbents like ZnO, for bio-trickling filters, H_2S removal efficiency is higher at lower concentrations. For other impurities like siloxanes, removal efficiency of 10–20% of D3 siloxanes for bio-trickling filters has been reported [59].

Although some researchers [118] reported that biological treatment is an economically attractive biogas cleaning technique, such systems are not as simple and effective as they appear. They would be expensive and complex to maintain for small scale biogas plants since micro-

organism activities are sensitive to parameters such as pH, micro-organism population and temperature. Maintenance of pH would require the use of extra chemicals such as NaOH, which would increase the operational costs of such plants. As reported in Table 6, slow adaptability to fluctuating gas composition would result in a detrimental effect to the SOFC system [118]. S_{cap} during the start-up is very low [182] and hence this would need a secondary gas cleaning unit if such system were to be applicable in the Biogas–SOFC energy system. Therefore, commercial stand-alone applicability of bio-trickling technologies in the nearby future especially in small scale biogas-SOFC energy system is doubtful. Further research and development is required to engineer a controllable system.

5.2.2. Combined effect of activated carbon and biological H₂S removal

In biological H_2S removal from gas streams, some researchers have investigated the combined effect of H_2S removal by both adsorption and biological means. In the bio-filtration reactor, the activated carbon acts as a support for micro-organisms in terms of shelter and protection from inhibitory compounds and a buffer for fluctuating loadings [177]. A bio-film is formed in the activated carbon bed which enhances the oxidation of H_2S adsorbed hence forming a combination of physical adsorption and bio-degradation [183]. It is also important to note that originally bio-filters were developed with soils, but soils were susceptible to clogging, hence they were eventually dropped [181].

The effectiveness of combined adsorption and biological removal of H_2S was investigated by Duan et al. [184]. In their experiment, they used four columns of diameter 4 cm and bed height 5 cm. First one with biological activated carbon (BAC) and 80% glass beads with liquid re-circulation (A). Second one with virgin activated carbon (VAC) with liquid recirculation and 80% glass beads (B). The third one was with VAC and 80% glass beads without liquid recirculation (C) and the last one was a reference column with liquid recirculation containing glass beads only (D). With inlet concentration of H_2S maintained at 45 ppm (v) at a gas flow rate of $0.944 \, l \, min^{-1}$, it was found that the BAC column (A) had a higher removal efficiency of H_2S of 30% as compared to all other columns B, C and D with removal efficiencies of 21%, 11% and 0% respectively. Therefore, this indicated that activated carbon could enhance the S_{cap} of a biological filter. They also observed that pH is a very important parameter in bio-trickling filters since the mechanism involve microbial growth, hence high acidic conditions should be avoided.

Omri et al. [185] studied the performance of a pilot scale bio-filter in terms of H_2S removal of WWTP gas. In their study, a peat packed cubic reactor was used with a top layer of soil and bottom layers of fibrous wood chips and Aleppo pine. It was observed that due to high water holding capacity of peat, it provides nutrient-rich environment that favours bacterial growth which can oxidise H_2S within the raw gas. Results show that such a system can reduce H_2S concentration of raw gas from 131 to 854 ppm down to 3–78 ppm with an average removal efficiency of 90%.

Duan et al. [177], studied the horizontal bio-trickling filter (HBF) based on activated carbon. In their experiment, a self-designed bench scale HBF system with three dark segments each with dimensions of $15 \, cm \times 15 \, cm$ width 10 cm length were used. Results show that such systems are potential H_2S cleaning units although their performance is not as good as when activated carbon is applied in a conventional bio-filter system. This is partly attributed to mass transfer inhibition to biofilm by the water layer in the HBF. Contrary to Ramirez et al. [180], they observed that pH may not have a significant effect to the performance of HBFs.

In brief, the combined biological and adsorption H_2S removal could be an attractive option in terms of enhanced S_{cap} and cost reduction, but further research and development is still required to understand the kinetics of such systems under varying operating conditions.

5.2.3. In-situ biogas cleaning and upgrading technologies

5.2.3.1. Micro-aeration or oxygen dosing.
Addition of air or oxygen to the digester is one of the simplest ways to reduce H_2S concentrations within biogas during AD. With this method, air is added directly to the digester or in the storage tank or to a gas holder which facilitates the growth of sulphide oxidizing micro-organism on the storage surface, this can potentially reduce the concentration of H_2S by up to 95% [121]. Although this method is simple and cheap, great care should be taken not to overdose the digester beyond recommended limits to avoid biogas explosion or toxicity to the anaerobic biomass [102,121].

5.2.3.2. Addition of chemicals into the digester or In-situ chemical upgrading.
This method involves adding or dosing of chemicals directly to the slurry in the digester to react with H_2S such that sulphide salts are formed which remain within the slurry. The common chemical which is normally used to dose the digester is iron chloride ($FeCl_2/FeCl_3$). This method can reduce high H_2S levels but it is less effective in maintaining low and stable H_2S levels [121]. Meanwhile other chemicals such Hematite (Fe_2O_3) can also be used as an alternative which also has an added advantage of enhancement of methanogenesis process [103]. Hence for applications of such technologies in small scale biogas-SOFC energy system, a secondary treatment unit is required. Capital investment of such a system would be favourable for small scale biogas system but operational costs of continuous chemical dosing with probably an automatic dosing system can potentially increase both the capital and operational costs.

In-situ biogas upgrade by autogenerative high pressure digestion (AHPD) has been investigated by Lindeboom et al. [186,187] and is a promising cost effective biogas upgrading system for various applications if high operational pressure (5–8 bar) can be maintained. Based on the speciation according to Henry's law, such technologies can upgrade the biogas to < 6% CO_2 content in biogas with a pressure build-up of up to 9.0 MPa. Since H_2S has a higher Henry's constant than CO_2, it is expected that H_2S will dissolve more into the liquid phase in concentration proportionally more than that of CO_2. Further research and development is required for detailed investigation to reduce the operational pressure and how it influences H_2S in biogas during AD. However, for small scale applications, the cost of such technologies could be higher than the commercially available technologies and hence may not be readily applicable in the nearby future. It is however noteworthy, that fixed dome digesters, which are currently operated in off-grid communities especially in the developing world have a similar principle of operation as the AHPD system and may therefore contribute to finding more frugal in-situ biogas upgrading solutions.

5.2.3.3. Solar-photo-oxidation in combination with biological treatment.
This technology can be used to clean the gas from H_2S and VOCs. State of the art technologies like solar advanced oxidation technologies combined with biological treatment are being investigated [188]. Results show that such technologies are promising in terms of efficiency of sulphur compounds removal from raw gas. An integrated solar advanced oxidation with a bioreactor was studied on a pilot scale in terms of removal efficiency of VOCs in the stream gas [188]. Such technologies can simultaneously remove > 65% of VOCs and H_2S from the fuel gas.

5.3. Industrial biological desulphurisation

5.3.1. Biological filters combined with water scrubbing

This is a combination of water scrubbing and biological desulphurisation which is often applied in large digesters. During desulphurisation, biogas is dosed with 4–6% of air and then it is counter flowed with raw waste water which is dispensed on the filter bed [121]. Application of industrial systems seem technically and economically doubtful in small scale rural biogas–SOFC energy applications, but are nonetheless interesting from a technical point of view.

5.3.2. THIOPAQ O&G desulphurisation technology

This technology combines the gas purification along with sulphur recovery within a single gas cleaning unit [194]. During the gas cleaning process, H_2S rich gas is passed through a scrubber (absorption section in Fig. 3, operated at atmospheric pressure and ambient temperature) in which H_2S is absorbed by NaOH to form a bisulphide rich solution. A controlled amount of air is introduced in the bio-reactor (reactor section in Fig. 3) which facilitates the growth of bacteria that oxidise bisulphide ions to elemental sulphur. This process also regenerates the NaOH solution and hence minimises the chemical consumption during the cleaning process. The sulphur rich solution is pumped to the sulphur recovery section where sulphur is captured. Since this technology is designed with a sulphur capture unit, it would require high gas flow capacities which comes with high initial investment and this may affect the economic returns for small scale applications. For SOFC applications, such a system may not clean the gas to the required impurity level of < 2 ppm(v). Hence either additional cleaning or increase on the gas contact time would be required to meet the stringent impurity requirements of SOFC. It is important to note also that auxiliary equipment in terms of pumps may lower the overall system efficiency to a great extent when it comes to small scale power plant applications. Furthermore, this technology may not simultaneously remove other impurities in biogas such as siloxanes and reaction of CO_2 with NaOH is also anticipated for biogas systems which could also reduce on the overall system gas cleaning efficiency. Therefore, for small scale biogas-SOFC energy system application, reducing the system complexity by removing the sulphur recovery section may increase the overall system efficiency and reduce on the overall operational and capital costs such that this technology could become applicable in small scale gas cleaning systems.

5.3.3. Sulphothane desulphurisation technology

This technology consists of two steps [195] (Fig. 4). During the first step, biogas is passed through a scrubber column in which H_2S is absorbed by NaOH according to Eq. (10).

$$H_2S + NaOH \rightarrow NaHS + H_2O \tag{10}$$

During the second step, NaHS is biologically oxidized to elemental sulphur and also the washing liquid is regenerated according to Eq. (11).

$$NaHS + \tfrac{1}{2}O_2 \rightarrow S + NaOH \tag{11}$$

Such a cleaning unit comes with several advantages of being environmentally safe, minimal power requirements and less maintenance due to a clogging free scrubber. As in the case before [194], since washing liquid is regenerated, less chemicals are used. However, for small scale application, such system may not be readily applicable since only standard units from 100 to 1500 $Nm^3\,h^{-1}$ of gas flow and sulphur loads of 10 to 500 kg S per day are currently available. Also, for biogas-SOFC applications, cleaning of the gas to < 2 ppm(v) of H_2S content is required, which is not the case for this system. For this system, the maximum limit of H_2S for the cleaned gas can be as high as 25 ppm, and might only be suitable in case of breakthroughs in sulphur tolerant anode materials. It is also important to note that since air is added to the system during gas cleaning process, the quality of biogas may be reduced thus affecting the overall system performance.

6. Economic review of commonly used biogas cleaning technologies

As reported in the previous sections, biogas upgrading technologies such as the use of amines, pressure swing adsorption, water scrubbers and organic physical scrubbers are not considered in detail in this review since is assumed that CO_2 will be used during the dry reforming process in the SOFC. Also, LCOE of biogas–SOFC system is beyond the scope of this study but it is important to note that the cost of biogas-SOFC cleaning unit is one of the key contributors to LCOE.

Gandiglio et al. [22] recently carried out a techno-economic analysis of small scale biogas fuelled power plants using three scenarios; *1*. Biogas-internal combustion engine (ICE) system with biogas clean-up system, *2*. Biogas-SOFC system with clean-up system and *3*. upgrading of biomethane for natural gas (NG) grid injection. Results obtained show that the biogas-SOFC system was the most cost-effective although the payback period was one and a half years higher than that of biogas-ICE system. It was followed by the biogas-ICE system and the methane upgrade system that generated the least revenues with a payback period of 15 years. This, therefore, implies that for small scale biogas energy systems, a methane upgrading system may be a big investment which
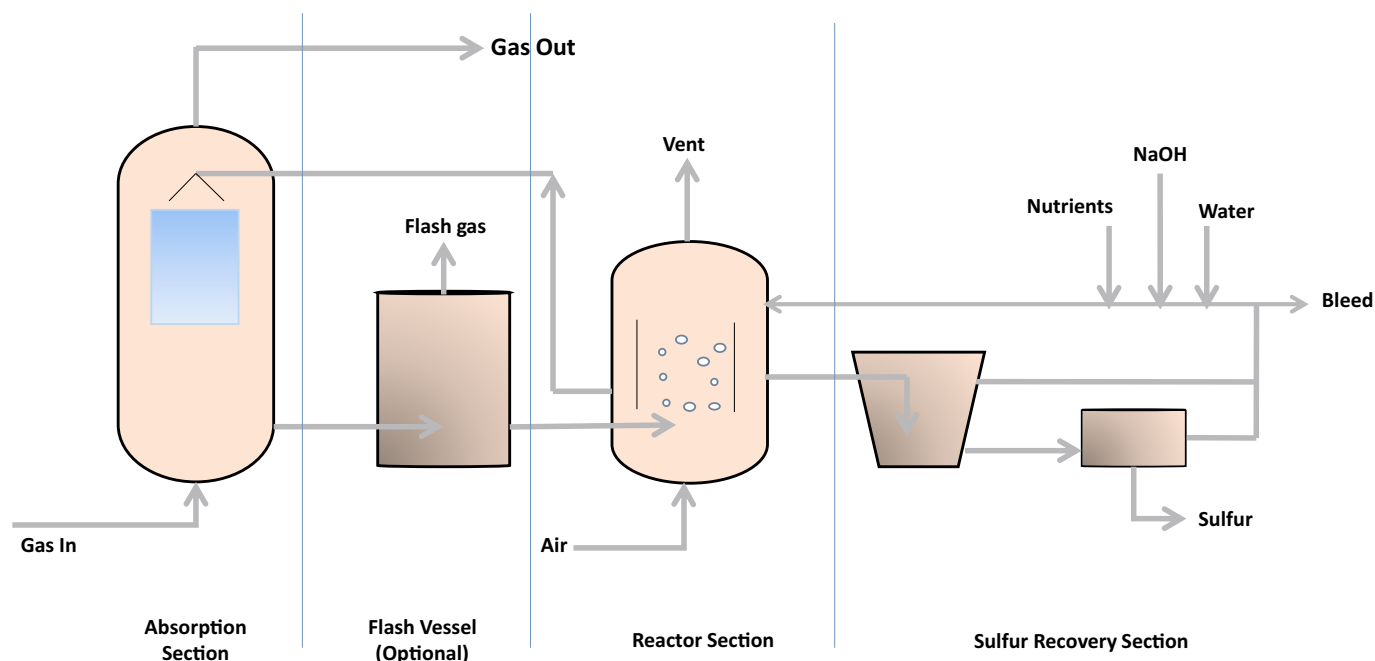

Fig. 3. Schematic flow of THIOPAQ O&G desulphurisation technology [194].
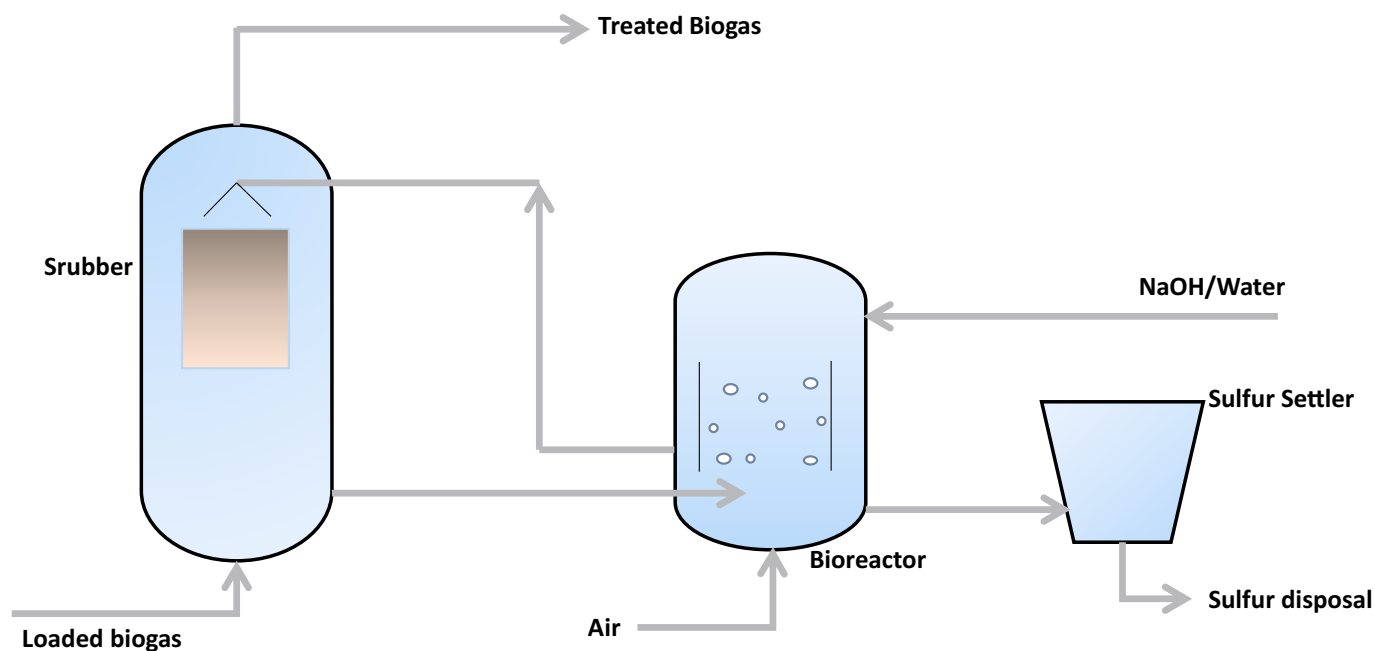
Fig. 4. Schematic flow of Sulfothane desulphurization technology [195].

could reduce the overall economic returns of the energy system. Although it has been recently reported that a mobile upgrading system could be cost effective for small scale biogas producers [196].

To get an insight on the economic status of different upgrading technologies, a few papers were surveyed which seem to follow the same approach (Fig. 5), although some of them combine gas cleaning and upgrading in one single step [197]. Bauer et al. [167] analysed the specific investment costs of different biogas upgrade technologies. In their analysis, the specific investment cost of amine scrubbers are in the range of 1400 EUR $Nm^{-3}h^{-1}$ to 3400 EUR $Nm^{-3}h^{-1}$ with an average electricity demand in the range of 0.12 kWh Nm^{-3} to 0.14 kWh Nm^{-3}. For pressure swing adsorption, it ranges from 1250 EUR $Nm^{-3}h^{-1}$ to 3000 EUR $Nm^{-3}h^{-1}$ with an average electricity consumption of 0.2 kWh Nm^{-3} to 0.3 kWh Nm^{-3} and for water scrubbers it ranged from 1200 EUR $Nm^{-3}h^{-1}$ to 5500 EUR $Nm^{-3}h^{-1}$ with an average electricity consumption of 0.21 kWh Nm^{-3} to 0.3 kWh Nm^{-3}. Specific investment cost for organic physical scrubbers is estimated from 1200 EUR $Nm^{-3}h^{-1}$ to 4800 EUR $Nm^{-3}h^{-1}$ and for the membrane from 1800 EUR $Nm^{-3}h^{-1}$ to 5800 EUR $Nm^{-3}h^{-1}$ with electricity demand of 0.1 to 0.2 kWh Nm^{-3} and 0.2 to 0.3 kWh Nm^{-3} respectively. It was also observed that specific investment costs of all technologies are almost equal for plant capacities in the range of 1500 $Nm^{-3}h^{-1}$ to 2000 $Nm^{-3}h^{-1}$. However, some of the cost implications due to heat demand in some technologies such as amine scrubbers, gas cleaning prior to upgrading unit and off gas treatment were not considered in this analysis.

For the non-upgrading technologies, the major challenges of gas cleaning units are high capital and maintenance costs and poor reliability [199]. The technologies which can clean the gas to the required impurity level of fuel cells are fully developed but the high cost is a real challenge for their practical application, especially in small scale biogas

systems. Cost analysis indicate that removing impurities from biogas can be as high as 40% of the total operational and maintenance costs of the entire power plant and this can increase the capital cost of biogas-fuel cell power plant by 22% [199]. The same report indicates that 42% of the clean-up cost is attributed to labour where as 25% account for the cost of media used for impurity capture. Some studies have indicated that the cost of the cleaning system for biogas based energy system can potentially increase the capital investment cost of the system by 6%–8% and the annual operation cost by 110–120% [102,103]. Therefore, a cost reduction in the clean-up system would significantly reduce on both the overall capital and operational costs and this would increase the fuel cell market share, especially for the small-scale systems.

Pipatmanomai et al. [102] analysed the influence of small scale biogas cleaning systems on the economy of the entire system. They assumed a small system with 86 m^3 daily biogas production coupled to a 6.1 kW generator, which was used to generate electricity at 80% plant utilisation. It was observed that introducing a cleaning unit in small scale biogas system can increase the payback period to twice as much as that without the cleaning unit in the system. However, detailed cost analysis of the impact of H_2S to both the energy system and to the environment needs to be considered in order to justify the cost implication of a cleaning system to the overall cost of the small-scale biogas energy system. From the cost analysis, it was observed that about 40% annual operational costs of a small-scale biogas system goes for maintaining the biogas cleaning unit in terms of sorbent consumption. Also Mehr et al. [200] has recently reported that for biogas-SOFC energy system, the investment cost for the cleaning unit is currently 1000 $ kW^{-1} of electric power. Near and long-term future scenarios of 500 $ kW^{-1} and 200 $ kW^{-1} are expected. It is important to note that the same long term cleaning unit cost projections had earlier been reported in the gas clean-up workshop proceedings [199]. It was also
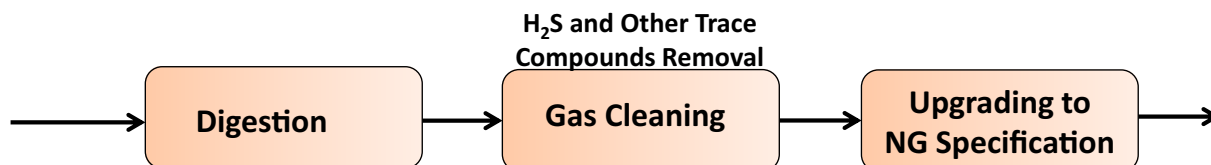

Fig. 5. Schematic flow of most biogas upgrading technologies [198].

Table 7
Cost of different biogas cleaning technologies.

Cleaning technique and media	Level of concentration in the cleaned gas	Energy consumption/ Requirement	Adsorptions capacity kg of H_2S/kg sorbent	Cost of sorbent EUR kg^{-1}	Other equipment cost to be considered	Cost of cleaning (Cost of Sorbent/kg of H_2S Adsorbed)	Notes
H_2S Removal							
Sulfa Treat (Mixture of iron oxide)	< 1 ppm of H_2S [99]	Process conditions adsorption pressure 1050 mbar, adsorption temperature 30 °C [201]	0.15 [73] 0.065[205]	0.28 [206]	Cost of the reactor/Vessel cost of disposal	1.87–4.31 EUR kg^{-1} of H_2S	-Iron oxide use is an old technology - Commonly used method for desulphurisation of biogas -Reaction is exothermic and water is required to cool down the reactor -Recommended to have two reactor vessels for continuous operation during the sorbent recharging - Can remove the H_2S down to the level of < 1 ppm required by the SOFC
Impregnated activated carbon(2% KI, potassium iodide)	< 0.1 ppm of H_2S [99]	Ambient temperature	0.077–0.093 [207], 0.062 [102], 0.015–0.045 [144]- -0.1[22]	1.00 [102]-5 [22]	-Cost of the reactor/Vessel (Estimated to be 900 EUR/kW for 100 kW biogas-SOFC system [22] and 300 EUR for 5 kW Biogas-Engine generator System [102]) -Cost of Disposal	10–70 EUR kg^{-1} of H_2S	- The technology is widely used in biogas cleaning -Regeneration is possible with nitrogen or steam at 400–500 °C but this is not widely done in practice.
Non impregnated activated carbon	10–100 ppm [201]	Ambient temperature	0.15 [73] 0.02–0.2 [73]	19 [208] 0.35–2.83 [209,210]		3.85* EUR kg^{-1} of H_2S [99] 50 EUR kg^{-1} of H_2S 127 EUR 11–140 EUR kg^{-1} of H_2S	Supplier quotation to TU Delft 2018 If non impregnated activated carbon is used, a second cleaning system is required to bring down the H_2S down to < 1 ppm
Dosing of Fe_2O_3(Hematite) in the digester	< 100 ppm [103]	Ambient temperature	0.2 [103]	0.07 [103]	- Cost of the reactor - Cost of Disposal	0.35 EUR kg^{-1} of H_2S	For SOFC, an additional cleaning system is required
Dosing of the digester with FeCl	100–150 ppm [99]	Ambient temperature	–	–	- Automatic dosing equipment - Cost of Cleaning and disposing of the chemicals accumulated in the digester	0.85 EUR kg^{-1} of H_2S* [99]	For SOFC application, additional cleaning system is required
Air/Oxygen dosing	< 50 ppm [121]		–	–		0.0019–0.0049 EUR m^{-3} of biogas cleaned [204]	For SOFC application, additional cleaning system is required
ZnO sorbents	< 1 ppm [105]	Temperature of 250 °C-400 °C is required	28–49 [105]	1.2–266.25 [208,211]		0.03–10 EUR kg^{-1} of H_2S	It can clean the gas to required levels of SOFC
ZnO-CuO sorbents	< 1 ppm [115]	Temperature of 250 °C-400 °C is required	45–77 [212]	125[208]		1–3 EUR kg^{-1} of sorbent	It can clean the gas to required levels of SOFC
Biological filters	< 50 ppm [99]		–	–		0.1–0.25 EUR kg^{-1} of H_2S* [99]	Additional cleaning system is required for SOFC application

Table 7 (*continued*)

Cleaning technique and media	Level of concentration in the cleaned gas	Energy consumption/ Requirement	Adsorptions capacity kg of H$_2$S/kg sorbent	Cost of sorbent EUR kg^{-1}	Other equipment cost to be considered	Cost of cleaning (Cost of Sorbent/kg of H$_2$S Adsorbed)	Notes
Siloxane removal Silica gel	< 0.4 mg/m^3 [101]		0.1 [101]	40–50 [208]		400–500 EUR kg^{-1} of siloxanes	
Activated carbon	< 0.87 ppm [99]					81–113 EUR kg^{-1} of siloxanes, 188–565 EUR kg^{-1} of siloxanes [99]	
Cooling followed by activated carbon bed (other impurities are assumed to be also adsorbed)						Capital $107,000 for 110 m^{-3} h^{-1} and annual maintenance of $16,300* [59]	
Biogas Drying Silica gel		Ambient temperature		40–50 [208]			
Refrigeration/ Condensation		Electrical energy is required for refrigeration				Capital cost of refrigeration is 36,000 $* Un installed [35]	

1USD = 1.44 EUR, *Figure Extracted directly from literature, otherwise it is re-calculated.

observed that the investment cost of a cleaning unit for biogas-SOFC energy systems can be as high as 10% of the total investment cost of the energy system [200]. However, operational and maintenance costs of a cleaning unit will depend more on the type of the sorbent used (media used for impurity capture), the impurity level of the fuel gas and the cost of labour of a given location of the power plant.

Sorbents such as iron oxide have been widely used for H$_2$S removal from biogas although in some cases Iron Hydroxide and ZnO are used [201]. For example, to clean the biogas with Sulfa Treat (mixture of iron oxide), an annual operational cost of 6000 Euros has been reported in literature, for a plant with the capacity of up to 2000 m^3 h^{-1} of biogas and 0.5 m^3 h^{-1} of H$_2$S [201]. This cost includes cost of reacting agent of Sulfa Treat, energy cost of compression work, and labour cost for recharging the adsorption reactor. If a 24 h and full year operation at maximum capacity is assumed for such a plant, it would imply that the cleaning of biogas today would approximately cost 0.034 Euro cents m^{-3}, if the time value of money is neglected.

Chemical and air dosing during AD can be a practical approach to save on the costs of the cleaning systems in small scale biogas systems. Siefert et al. [103] reported that the addition of chemicals to the digester during AD could potentially reduce on the clean-up costs of biogas. In addition to this, it was also reported that some chemicals such as iron oxide can potentially enhance the kinetics of methanogenesis process hence could increase the rate of biogas production [202]. Arespacochaga et al. [100] investigated the cost reduction of bulk sulphur capture as opposed to all sulphur capture by stand-alone adsorption. It was observed that capturing the sulphur before the main adsorption unit can potentially reduce on the operation cost of the cleaning unit and hence, increase the profitability of biogas-SOFC energy system. This is also re-affirmed by Williams et al. [72]. However, Hagen et al. [201] reported that dosing the digester with chemicals to reduce H$_2$S could be expensive if input materials are rich in protein and sulphur compounds. It is important to note that, although pre-treatment methods such as air and chemical dosing are effective in reducing high sulphur levels, they are less effective in maintaining low and stable H$_2$S concentration in the fuel gas [121,203]. Diaz et al. [204] investigated the economic benefits of dosing the digester with chemicals, oxygen and air. They observed that dosing the digester with concentrated oxygen to reduce on sulphur levels is economically attractive as compared to dosing it with FeCl$_3$. Also, the investment and running costs of chemical dosing is often higher as compared to air dosing [19]. This therefore implies that for small scale biogas-SOFC energy systems, if pre-treatment is to be used, air dosing would be preferred to increase on the economic returns of the energy system.

For biogas-SOFC energy system, it has been reported that the cost of gas clean-up represents approximately 20% of the electricity cost [35]. However, this cost depends more on the source of the gas and impurity level of that particular gas [35]. Cost review of the commonly used cleaning media for biogas reported in Table 7 gives an insight of the different technology operation cost implications to the overall biogas-SOFC energy system. Fig. 6 also gives cost comparison (cost of sorbents) of different cleaning technologies from selected literature and quotations from suppliers to Delft University of Technology. For instance, cleaning of biogas from H$_2$S using iron oxide can cost as low as 4.31 EUR kg^{-1} of H$_2$S removed and as high as 10 EUR kg^{-1} of H$_2$S removed when ZnO based sorbent is used, if only the cost of sorbents is considered. It is important to note that the S$_{cap}$ has a great influence on the overall cost of the sorbent even though the initial cost of the sorbent could be low. For example, the initial cost of activated carbon sorbent is generally lower than the ZnO based sorbents but the unit cost of cleaning the gas is lower for ZnO sorbents due to its high S$_{cap}$ (Fig. 6) if thermal energy requirement of ZnO based sorbent is ignored. Although H$_2$S removal within the digester during anaerobic digestion by either biological treatment or addition of chemicals such as FeCl$_2$, would be the most cost competitive technology, with a cost as low as 0.1 EUR kg^{-1} of H$_2$S removed for biological filters and a cost as low as 0.35 EUR
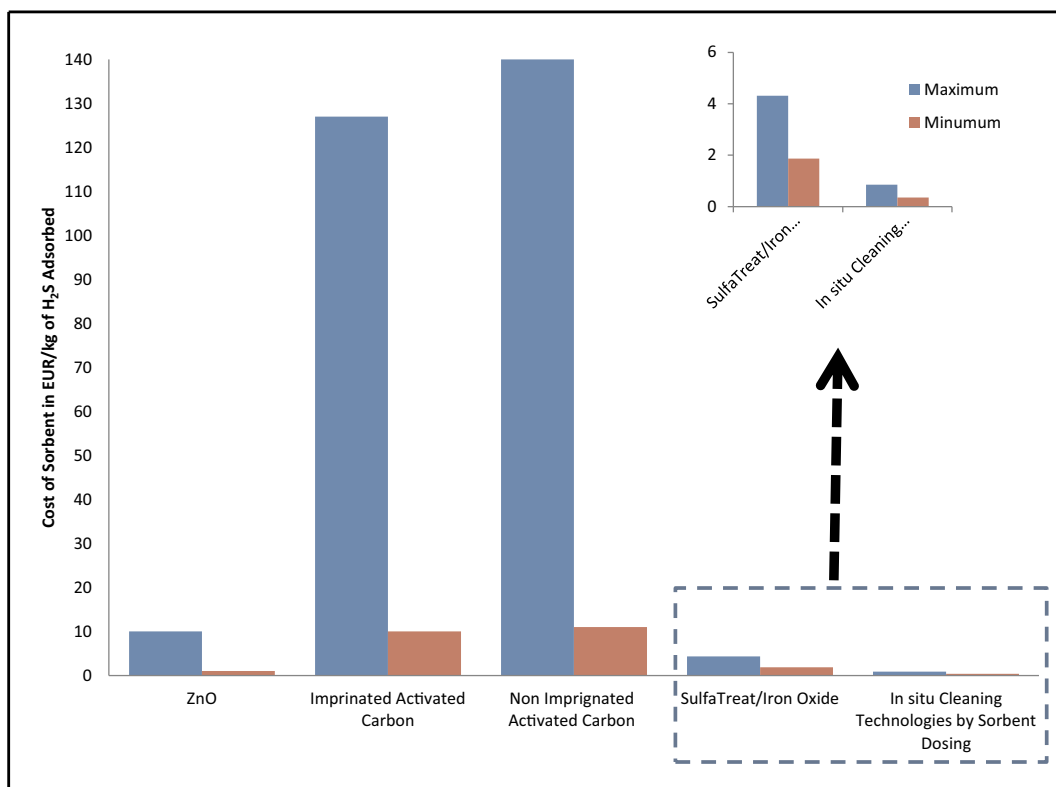
Fig. 6. Cost comparison of commercial sorbents for H_2S adsorption.

kg^{-1} of H_2S removed for $FeCl_2$. Their application to small scale biogas-SOFC energy system would require secondary gas cleaning since they can't clean the gas to a recommended level of < 2 ppm(v) of H_2S. Other impurities removal like siloxane can cost as high as 500 EUR kg^{-1} of siloxanes removed when silica gel is used and as low as 81 EUR kg^{-1} of siloxanes removed when activated carbon is used. To the authors' knowledge, cost of drying of biogas is not commonly reported in literature.

In biogas-SOFC energy system, sometimes the gas is required to be pre-conditioned by methods such as drying and heating before it is fed to the gas cleaning bed. The cost of such pre-conditioning of the gas should also be considered such that a cost-effective choice is made.

Therefore, for a small-scale biogas-SOFC energy system, selection of the cleaning technology needs to be carefully chosen. A clear balance should be determined between the cost and the purification levels of the technology to be applied, if such an energy system is to be economically competitive as compared to other conventional energy sources.

7. Conclusion

Biogas–SOFC energy system can potentially provide both electrical and thermal energy needs for the off-grid communities using waste materials as input resource, which can in turn enhance sanitation among such communities.

However, biogas cleaning technologies can have a great effect on the overall system capital investment and operational costs, hence hindering the technology uptake among the rural off grid communities. Therefore, selection of a cleaning system technology especially for small scale biogas-SOFC energy system need to be carefully evaluated in terms of initial capital and operational costs and also its effectiveness to meet the impurity levels required by SOFC which are typically below 2 ppm(v) for H_2S and a few ppb levels for siloxanes. From literature, there is no single solution for biogas cleaning for SOFC system application. Different technologies need to be integrated together, as proposed in Fig. 7 to come up with an efficient and cost-effective cleaning system for a small-scale biogas-SOFC energy system application.
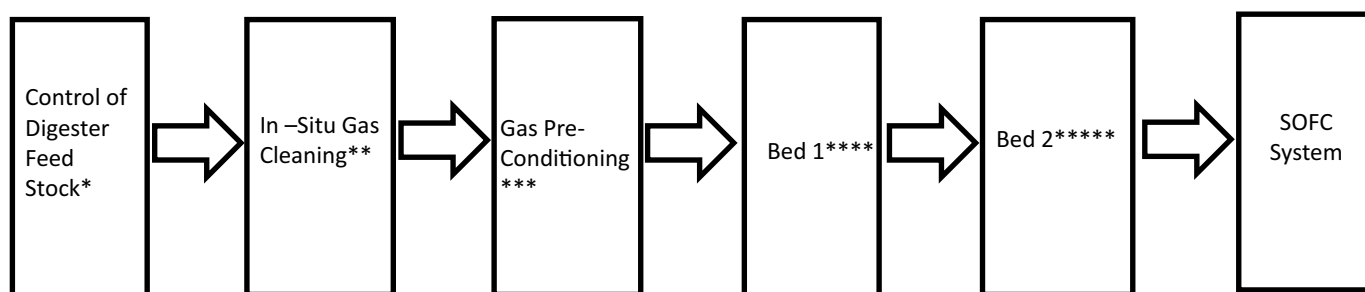
*This can combined with feed stock pre-treatment. ******This can be biological/chemical elimination of H_2S and VOCs during Anaerobic Digestion. *******This could be pre-heating. ******** For removing remaining impurities. *********Can be used as a guard bed for SOFC protection. It can also be used during adsorbent changing.

Fig. 7. Proposed flow scheme of a small-scale biogas–SOFC energy system cleaning unit.

In summary, this review has revealed the followings;

- Apart from H_2S and siloxanes, other sulphur compounds such as CH_4S, CS_2, C_2H_6S exist in raw biogas in a significant amount which could have detrimental effects to SOFC. Their effects on SOFC need to be studied, and removal mechanisms need to be investigated in detail.
- Other trace elements such as halocarbons, alkanes, aromatics, cyclic and other VOCs exist in raw biogas depending on the source. Their effect to the biogas reforming process and SOFC performance needs to be studied in detail, especially on long-term basis.
- Among the metal oxide sorbents, ZnO based sorbents seem to be highly efficient sorbents and can effectively clean the gas to the required levels of H_2S for SOFC applications, but their initial cost is very high compared to other sorbents such as impregnated activated carbon. Although the cost per kg of H_2S removed seem to be competitive, they may not be effective at ambient temperatures. This may hinder their application in small-scale biogas SOFC energy systems in the nearby future. Also, the kinetics of ZnO based sorbents still need to be studied in detail, their effectiveness of simultaneous removal of H_2S and other biogas impurities such as mercaptans need to be considered too. Iron oxide seems to be economically competitive, but details research and development is still required to understand the efficiency of this sorbents in the varying gas composition from anaerobic digestion. Investigations of the role of doping and supports on these sorbents as far as absorption and regeneration are concerned will increase their economic feasibility in small scale applications.
- Sorbents S_{cap} may be affected by the presence of other biogas trace compounds such as VOCs. The influence VOCs to the sorbent S_{cap} needs to be studied in detail.
- Liquid adsorption technologies may not be technically feasible for small scale applications due to operational challenges. Moreover, most of these of technologies are hindered by CO_2 reaction which would be required during envisaged dry reforming process.
- Adsorption technologies seems to be economically and technically promising for small scale biogas-SOFC application. However, further research and development is still required to understand effectiveness of such technologies under real anaerobic digestion conditions.
- Other physicochemical cleaning technologies such water scrubbing and membrane separation are limited by CO_2 absorption for biogas-SOFC application. Cryogenic condensation and adsorption cooling is likely to increase the system capital and operational cost for small scale application. If cooling is to be used as one of the cleaning technology, research and development is required to develop an adsorption cleaning system which can utilise the available waste heat from biogas-SOFC energy system.
- Biological cleaning technologies seem to be economically suitable for small scale application, however they may be limited to slow response time with varying gas compositions and may need additional cleaning technologies to clean the gas to the required level of SOFC system.
- The use of in-situ cleaning technologies such micro aeration may be useful to reduce on the external cleaning capital and operation costs for small scale SOFC application. The extent to which this cost can be reduced needs to be extensively evaluated depending on the technology applied.
- Research focus has been so much on the H_2S removal from biogas for SOFC application and to some extent siloxanes. However, other VOCs could have a negative effect not only to the SOFC operation but also to the efficiency of the cleaning media such as sorbents. Therefore, the performance of sorbents under varying gas compositions should be carefully investigated. The extent to which sorbents can simultaneously remove more than one impurity from biogas should also be considered.
- For biogas-SOFC energy system applications, some sorbents can be

cost effective and efficient if they are applied in parallel, either using the same sorbent in each bed or using a different sorbent in in a mixed bed. For H_2S removal, S_{cap} capacity could have a significant effect on the operation cost of the cleaning unit. The higher the S_{cap}, the lower the operation costs even though the initial cost per unit of sorbent could be higher.

- Cleaning cost of biogas can potentially increase the system operating cost by 40%, and therefore the choice of cleaning technology to be applied in small scale biogas energy system needs to be carefully chosen. Further research and development of a reliable and cost-effective biogas-SOFC cleaning system is still required.

For small scale biogas-SOFC energy systems, an ideal gas cleaning unit needs to be very efficient to meet the stringent impurity levels required for safe SOFC operation and also cost effective for small scale application. Sorbent regeneration might result in reduced operational costs, thus making these systems economically competitive with other technologies currently available for off-grid energy supply but requires co-creation to ensure a value sensitive design.

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