Biogas-Solid Oxide Fuel Cell (SOFC) Energy System for Rural Energy Supply
A field based study on the role of local materials on operation and capital system cost

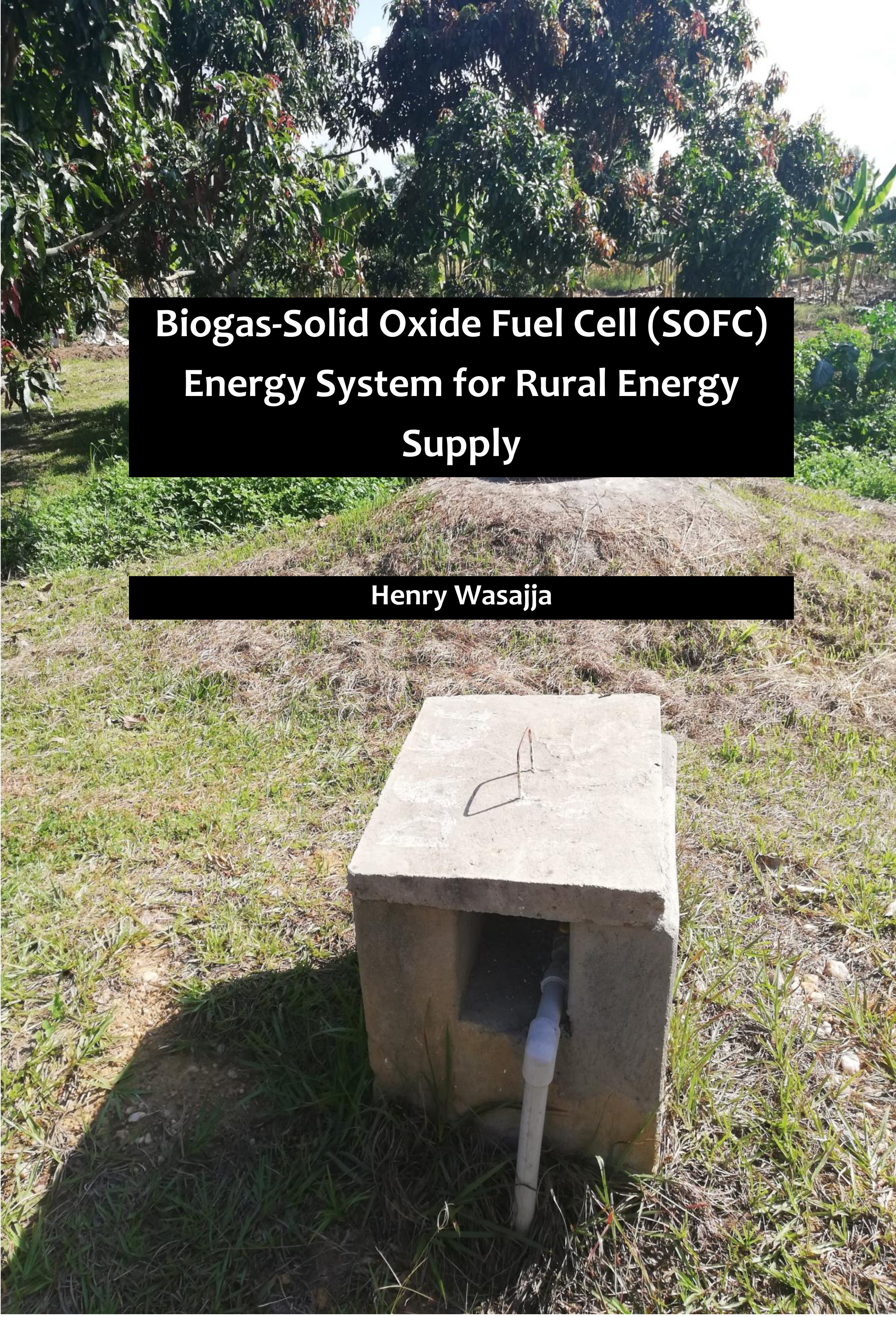
Wasajja, H.

DOI
10.4233/uuid:73945ebd-7e39-459f-a566-50d446b745b2

Publication date
2023

Document Version
Final published version

Citation (APA)
Wasajja, H. (2023). *Biogas-Solid Oxide Fuel Cell (SOFC) Energy System for Rural Energy Supply: A field based study on the role of local materials on operation and capital system cost*. [Dissertation (TU Delft), Delft University of Technology]. https://doi.org/10.4233/uuid:73945ebd-7e39-459f-a566-50d446b745b2



Biogas-Solid Oxide Fuel Cell (SOFC) Energy System for Rural Energy Supply

Henry Wasajja

Biogas-Solid Oxide Fuel Cell (SOFC) Energy System for Rural Energy Supply

A field based study on the role of local materials on operation and capital system cost

Dissertation

for the purpose of obtaining the degree of doctor

at Delft University of Technology,

by the authority of the Rector Magnificus, prof.dr.ir. T.H.J.J. van der Hagen,

Chair of the Board for Doctorates,

to be defended publicly on

Tuesday 22 November at 17:30 o'clock

by

Henry Wasajja

Master of Science in European Renewable Energy, Carl von Ossietzky University of Oldenburg,

Germany

born in Kalungu, Uganda

This dissertation has been approved by the promotors.

Composition of the doctoral committee:

Rector Magnificus	chairperson
Prof. dr.ir Jules van Lier	Technische Universiteit Delft, *promotor*
Dr. Ir. R.E.F Lindeboom	Technische Universiteit Delft, co-*promotor*
Prof. dr. A. Purushothaman Vellayani	Technische Universiteit Delft, co-*promotor*

Independent members:

Prof. dr. Cees van Beers	Technische Universiteit Delft
Prof. dr. ir. G.J.W. Euverink	Rijksuniversiteit Groningen (RUG), The Netherlands
Prof. dr. ir. R. Dewil	KU Leuven, Sint-Katelijne-Waver, Belgium
Dr. Jari Kiviaho	VTT Technical Research Centre of Finland Ltd
Prof. dr. ir. Damir Brdjanovic	Technische Universiteit Delft (reserve member)

Dr. ir. Henri Spanjers, Technische Universiteit Delft, as a supervisor, contributed significantly to the preparation of this dissertation.

The research presented in this thesis was performed at the Sanitary Engineering Section, Department of Water Management, Faculty of Civil Engineering, Delft University of Technology, The Netherlands. The research was financially funded by TU Delft Global Initiative, fellowship number 15DGF214.

Printed by Proefschrift-aio.nl

Keywords: Anaerobic digestion, Biogas impurities, Sorbent cleaning systems, Biogas-SOFCs, Dry reforming, In-situ H_2S reduction, Biochar, Techno-economic analysis.

ISBN/EAN: 978-94-6384-506-9

To my extended family, the Wasajjas’ and the Ssenyimbas’,
your support throughout this academic journey is invaluable

Contents

Summary

Biomass is predominantly the major source of energy in the global south. It is the readily available source of energy in global south and is used in rural energy households in the form of wood, charcoal and agricultural residues. However, biomass energy source is not utilised in the most efficient way and hence there is still a gap in achieving the SDG 7 target. The growing global population has increased the global demand of energy and other basic resources like water and food. But also, has resulted in increased need of sanitation services which are not readily provided to rural communities.

The biogas-solid oxide fuel cell (SOFC) energy system for rural energy supply is an envisaged energy system which aims at enhancement of not only off-grid energy supply but also sanitation services among the rural communities. Such a system utilise waste from faecal sludge to generate biogas which act as fuel to SOFCs to generate electricity and heat energy. SOFCs have been reported to have an electrical efficiency of 50% which is higher as compare to 25-30% of conventional internal combustion engines. This enhances efficient energy generation from scarce biomass resources.

Coupling a biogas system to a SOFC comes with a number of challenges both technical and economic challenges. The initial cost of a SOFC system is very high which is over $9,000 per kW for a 5 kW as compared to cost of internal combustion engines which cost less than $300 per kW of a comparable system. Also, biogas contains impurities like H2S which require cleaning of the gas before it is fed in the fuel cell, this increases the operation cost of the biogas-SOFC energy system.

This dissertation therefore has looked at increasing the economic feasibility of a biogas-SOFC energy system in the rural energy mix. This has been done by looking at cost reduction strategies such as using locally available materials like urine to act as in-situ H2S reduction to reduce on the operation cost of upstream gas cleaning. Using of locally produced biochar from agricultural residues for H2S gas cleaning as opposed to conventional activated carbon. The use of internal dry reforming as opposed to external dry reforming to reduce on the auxiliary equipment. Literature review was conducted to find out the most effective strategies for reducing the operational expenditures related to removing H2S from biogas. Subsequently, a field study was conducted to find out the practices and locally available materials which can be for both in-situ and upstream H2S gas cleaning. Experiments were then conducted to study the effect of H2S on SOFCs during dry reforming and the effectiveness of locally available materials to reduce H2S in biogas. And finally, the economic analysis was conducted to analyse the extent to which the strategies can increase the economic viability of a biogas-SOFC energy system as compared to already existing technologies like solar. The dissertation comprises two main parts, which are subdivided into multiple contributing chapters;

I. Theoretical, experimental and modelling study of available cost reduction strategies

Chapter 2 investigates different cleaning technologies with a view of identifying the most cost-effective strategies to design a cleaning unit of a biogas-SOFC energy system.

Chapter 3 investigates the effect of H2S on the dry reforming of CH4 using Ni already in SOFC as a catalyst. This would result in internal reforming as opposed to the current practice of external reforming. Internal dry reforming is envisaged as one of the cost reduction strategies of the CAPEX of SOFC since an external reformer is excluded on balance of plant (BoP). Results show that H2S content has to be below 0.125 ppm for efficient internal dry reforming.

Chapter 4 is the field study aimed at investigating the practices which can be bench marked on to reduce the cleaning requirements and improve on the efficiency of the AD process in small scale biogas digesters. The theoretical study coupled with field results show that locally available materials such as urine coupled with user practices can potentially improve biogas quality and quantity. Thus, reducing on cleaning requirements of biogas fuel for SOFC. Hence reducing on the CAPEX and OPEX of a biogas-SOFC energy system.

Chapter 5 investigates the effect of using locally available materials like urine on the resultant H2S in the biogas. Experimental and modelling results shows that urine with high metal content and low sulphate content below 400 mg/l can potentially reduce H2S in biogas. Thus, reducing the cleaning requirements and hence reduce the CAPEX and OPEX of a biogas-SOFC energy system.

Chapter 6 is a research note on the use of locally available biochar as opposed to commercially available activated carbon as adsorbent for upstream H2S cleaning. Preliminary results show that biochar can clean the gas to the required level of H2S for SOFC.

II. Effect of available cost reduction strategies on the overall economic feasibility of the biogas-SOFC energy system.

Chapter 7 is the economic study on the effect of the use of biochar, internal reforming and other non-technical strategies like policy/tax intervention on the overall economic feasibility of the biogas-SOFC energy system. Results show that locally available biochar can accelerate the economic feasibility of a biogas-SOFC energy system in off-grid energy mix.

Nomenclature

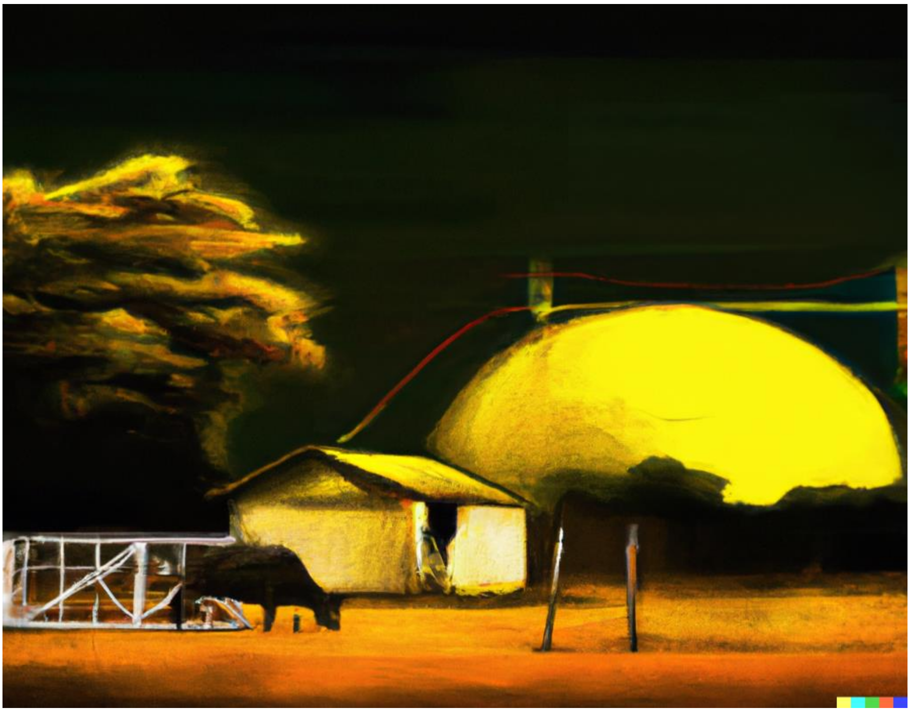
List of Abbreviations

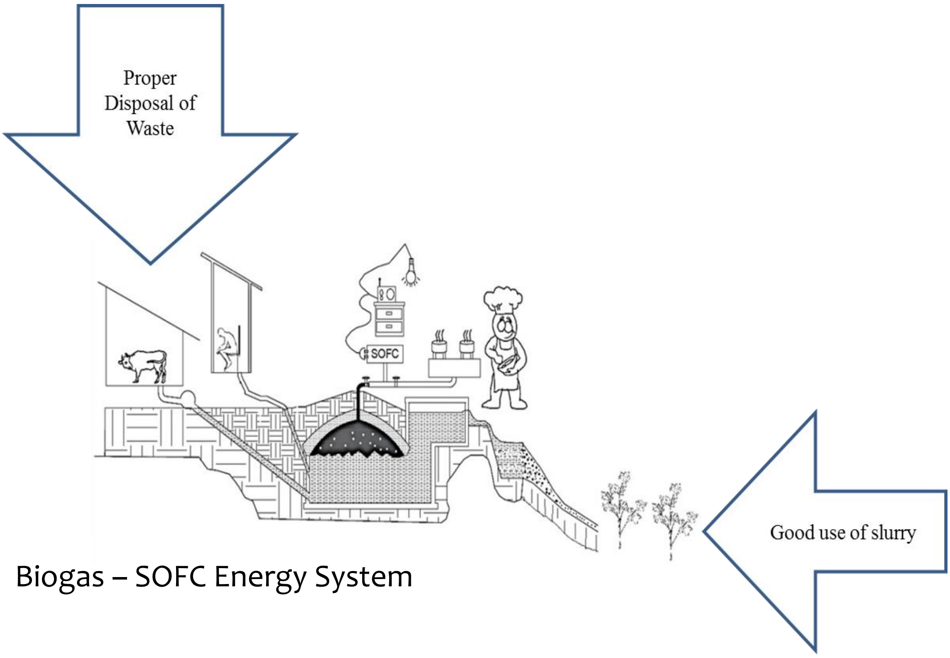
Nomenclature	
AD	Anaerobic Digestion
ADG	Anaerobic Digestion Gas
HC	Hydro-Carbon
ICEs	Internal Combustion Engines
LFG	Land Fill Gas
NG	Natural Gas
NPV	Net Present Value
PEM	Proton Exchange Membrane
rSOFC	Reversible Oxide Fuel Cell

Nomenclature and definitions

Nomenclature	
BSP	Biochemical gaseous H_2S Potential
CAPEX	Capital Exploitation Cost
GIZ	German Corporation for International Cooperation
OPEX	Operation and Maintenance Exploitation Cost
SOFC	Solid Oxide Fuel Cell
SVN	Netherland Development Organisation
VOCS	Volatile Organic Compounds
WASH	Water, Sanitation and Hygiene.

Subscripts	
S_{cap}	Sulphur Capture Capacity
H_2S_{ads}	H_2S adsorbed





Biogas – SOFC Energy System

1

Introduction

1.1 | BACKGROUND AND PROBLEM STATEMENT

While over the last century the resource-affluent nations shifted away from biomass to fossil fuel for their energy supply, biomass has remained the major source of energy for most countries in the global south. It has been estimated that over 80% of the African rural people still depend on biomass for both energy and income gains. Biomass contributes to over a third of primary energy supply in most developing countries and is predominantly used through combustion to supply heat in rural households for cooking and water heating, as well as for heat supply to small scale industries [1]. In contrast, electricity access in developing countries in Asia and Africa is alarming, with estimated 1.64 billion people without access to power, 80% leave in Asia and Africa [2].

In this socio-economical context, a wide variety of biomass sources is used ranging from primary woody biomass to organic waste. This is while the use of primary woody biomass potentially results in the negative side-effect of deforestation. Yet the use of already existing wastes to recover energy through the production of biogas by anaerobic digestion AD is considered to have positive side-effects from an environmental point of view. The Organic waste to biogas route is considered to be attractive since it controls the organic waste disposal which would otherwise cause public health problems and at the same time produce fertilisers for agricultural applications [3,4].

There has been a growing concern of sanitation related diseases such as schistosomiasis among the rural communities and those who reside along shore of lake bodies, and it has been proven that 92% of those who require treatment of schistosomiasis live in Africa [5]. It should also be noted that fishing and agriculture are the major economic activity among these rural communities, due to which exposure is a serious concern.

Also, poor sanitation among rural communities has led to diseases like diarrhoea which result into high mortality rate among the infants [6–8]. For example, in Rwanda, 13% of all children under the age of five years die annually due to diarrhoea caused by poor sanitation among rural communities [6]. Since biogas uses waste materials including faecal matter as input material, its encouragement among rural communities may enhance sanitation among those communities. It has been reported that anaerobic waste treatments may partially remove harmful bacteria such as faecal pathogens [9]. Also, the biogas embracement could accelerate the rate of toilet usage among rural communities. This can reduce the risk of improper human waste disposal which in most cases end up in water bodies posing a healthy risk to human.

From a technical point of view, biogas can be used to substitute primary woody biomass for production of heat for cooking purposes. Biogas also has a high potential for electrical production. If carefully harvested especially from waste, it can also be utilised to generate electricity through conventional biogas internal combustion engines.

Worldwide electricity generation from biogas was 331 TWh in 2010 (8% of the total electric energy generated from renewable energy sources) and it is projected that this figure could reach 696 TWh (10% of the total electric energy generated from renewable energy sources) by 2020 and is targeted to reach 1,487 TWh by 2035 (13% of total electric energy generated from renewable energy sources) [10]. 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 [10]. Generation of energy from waste can potentially reduce the CO_2 emission by over 30% of global emission [11].

However, the efficiency of internal combustion engines (ICEs) is quite limited as it is restricted by the Carnot efficiency. Fuel cells, reach much higher biogas to electricity conversion efficiencies because they are not limited by thermodynamic Carnot efficiency [12]. Biogas-fuelled power plants can replace conventional fossil-fuelled power plants [13]. Small–scale biogas plants are important to replace the common fossil fuel base energy sources of off-grid communities which is growing with increased demand of energy for agri-food systems [14]. Efficient renewable based energy sources have a potential to decrease emission from fossil fuel-based energy sources in agri-food systems which represent 30% of the world's total energy demand [14].

Hence, the substitution of ICEs for fuel cells (FCs) has a very large potential and should play an important future role in accelerating the energy transition towards the 2030 and 2035 targets by enabling the production of more electricity from the same amount of biomass resources. In order to materialise this potential, it is paramount to identify key challenges within the research fields of: biogas digesters and their potential for rural electrification in off-grid settings, the state-of-the-art fuel cells, and the integration of both into a biogas-SOFC system. Section 1.2-1.4 are dedicated towards this purpose. Then in section 1.5 and 1.6 the overall objective and scope of this thesis and each chapter are presented.

1.2 | BIOGAS DIGESTERS AND THEIR POTENTIAL FOR RURAL ELECTRIFICATION IN OFF GRID SETTINGS

Anaerobic digesters have been developed for developing countries to produce biogas in small-scale for meeting local thermal energy needs. Biogas development has registered success in some of the Asian countries, but this is contrary to most of the African countries, where many of the biogas systems were abandoned by users [15]. For African countries, this has been attributed to a number of social, technical and economic challenges faced by the biogas industry [16].

Nonetheless, there is a vast potential of biogas in developing countries and in African countries in particular as shown in Table 1. For this reason, with the support of development partners such as SNV (Netherland Development Organisation) and the world bank, there has been an emphasis in the global south on both the construction of biogas plants as well as the promotion of the use of biogas.

Table 1. Biogas production potential in developing countries [17].

Region	Animal waste available for digestion (million dry metric tons/year)	Potentially available biogas (million Nm^3/ year)	Energy production potential of biogas (Peta Joule, PJ/ year)	Kerosene equivalent of 20% of biogas (million L/ year)	Firewood equivalent of 80% of biogas (million dry metric tons/ year)	Electrical Potential* available in MWh/year
Africa Total	215	54,671	1,143	8,166	143	355,362
Caribbean	9	2,495	52	373	7	16,218
South America	233	56,200	1,175	8,394	147	363,300
Eastern Asia (less Japan and China)	10	3,003	63	447	8	19,520
China	216	61,817	1,293	9,233	162	401,810
Southern Asia (less India)	98	25,522	534	3,812	67	165,898

Table 1 continued…

Region	Animal waste available for digestion (million dry metric tons/year)	Potentially available biogas (million Nm^3/ year)	Energy production potential of biogas (Peta Joule, PJ/ year)	Kerosene equivalent of 20% of biogas (million L/ year)	Firewood equivalent of 80% of biogas (million dry metric tons/ year)	Electrical Potential* available in MWh/year
India	191	48,178	1,007	7196	126	313,157
South-Eastern Asia	95	26,338	551	3934	69	171,197
Total	**1,068**	**278,224**	**5,818**	**41,555**	**727**	**1,808,456**

*on average, $1m^3$ of Biogas = 23,400 kJ m^{-3}, assuming methane content of approximately 60% in the biogas [18]

With the support of development partners such as the Netherland Development Organisation (SNV) and the world bank, there has been an increase in the installed biogas plants in most of developing countries in Asia and some African countries. According to SNV, the total biogas plants it had installed together with its partners by 2012 in Africa and Asia was 504,599 [19]. Table 2 shows the cumulative increase in biogas plant in Africa installed by SNV and other development partners such as world bank. To the authors knowledge, the precise number of biogas plants currently installed in Africa and Asian countries is not known due to limited published data in literature. It is reported that in China alone over a million biogas plants had been installed by 2006 [20]. Recently, biogas is receiving much support from most of the governments of developing countries. As an example, in Uganda the government had a target to increase the number of household and institutional biogas plants and increase the biofuel production to 2,160,000 m^3 per year by the end of 2017 [21]. Although the achievement of this target is rather doubted, tremendous progress in the biogas and biofuel sector has been registered in the past few years [19,22].

Policies and technologies have been reported as the two major factors which can promote biogas usage and development [23]. A survey on renewable energy policies of selected African countries has revealed that most of the African countries are in support of sustainable energy research and development, although as reported earlier, they are currently facing a number of challenges such as limited access to finances [24]. It is also reported that laws, regulations and policies on biogas energy are being updated globally [23]. With such plans in place, the number of biogas plants installed is expected to increase in the nearby future.

Furthermore, with the introduction of water, sanitation and hygiene (WASH) programs by development partners such as SNV, recently the number of people with access to improved toilets has been growing (Figure 1). Therefore, the resources for biogas in terms of human waste is also expected to increase in the nearby future, especially with forecasted population increase in developing countries.

Lastly, if properly exploited, biogas can increase the rate of access to electricity, especially to the rural people in Asia and Africa which currently count for 80% of the global people without access to electricity [2]. As many digesters are being abandoned, it could be hypothesized that biogas as a thermal energy source may not add sufficient value to operate a bio-digester in the rural context. Which is consistent with the fact that thermal energy either through solar irradiation or readily available combustible biomass is abundant in many countries in the global south. Promoting the conversion of biogas to electricity, that is scarce, as an alternative to heat, may thus be an additional driver that could boost biogas production from existing digesters.

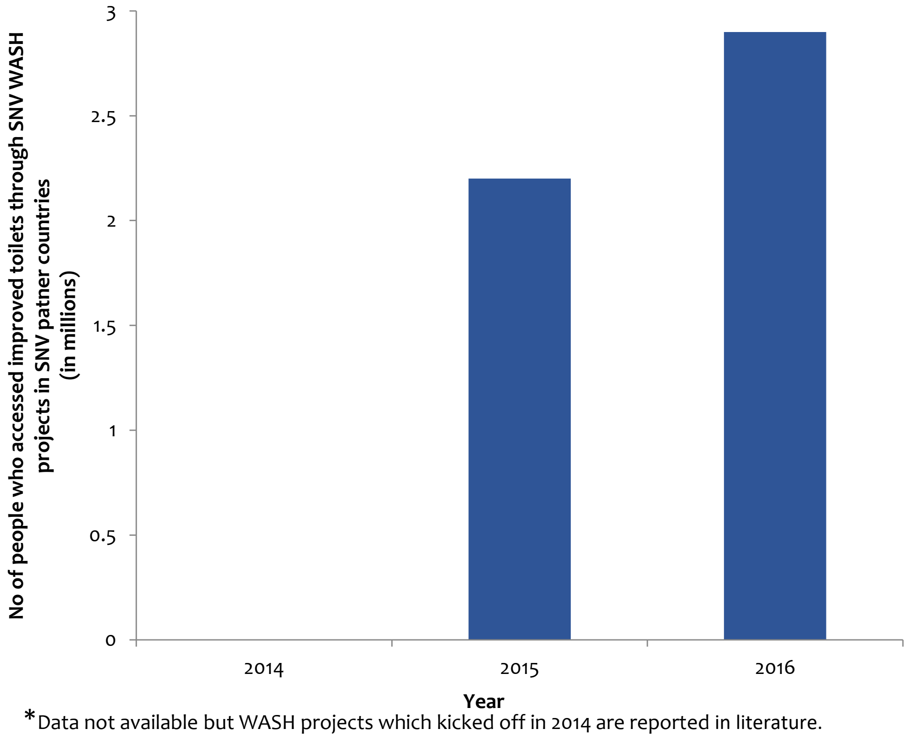
Table 2. Biogas development and status of national energy policy on biogas development of selected African countries [16,19,25–34]

Country	Cumulative number of biogas plants installed by SNV					Status of energy policy on biogas development
	2008	2009	2010	2011	1st half of 2012	
Uganda	N/A	40	583	1,276	2,325	Supports the development of biogas.
Rwanda	120	213	627	785	2,171	Supports the developments of biogas.
Kenya	N/A	3	837	2,399	4,917	Supports the development of biogas.

Table 2 continued…

Country	Cumulative number of biogas plants installed by SNV					Status of energy policy on biogas development
	2008	2009	2010	2011	1st half of 20 12	
Tanzania	3	103	1,021	1,444	3,334	Policy supports the development of biomass but not specific for biogas.
Ethiopia	98	30	731	1,641	3,232	Policy not specific about biomass development but supports the development of renewable energy.
Burkina Faso	2008	2009	2010	2011	1st half of 20 12	Policy not specific about biomass development but supports the development of renewable energy.
Cameroon	N/A	23	49	33	111	Policy supports the development of renewable energy.
Benin	N/A	N/A	22	20	42	Policy supports the development of biogas.
Senegal	N/A	N/A	14	225	334	Policy supports the development of biomass though not specific for biogas.
Total	**221**	**413**	**3,996**	**8,432**	**17,643**	

*N/A - Data Not Available in References. No data could be traced for countries such as South Sudan and Burundi, however their energy policies support development of biomass energy sources.



*Data not available but WASH projects which kicked off in 2014 are reported in literature.

Figure 1. Improved access to modern toilets from 2014 to 2016 in SNV partner countries [8,35,36]

1.3 | FUEL CELLS AND RECENT DEVELOPMENTS

The invention of the fuel cell dates back to the mid-19th Century [37]. One major factor that is attributed to the development of fuel cells is the environment concern of fossil fuel in vehicles propulsion and electricity production [37]. Fuel cell are preferred since they have higher efficiencies compared to conventional engines, with H_2 used as a fuel, only H_2O is emitted to the environment. Furthermore, H_2 can be produced from a renewable resource like wind making the whole energy chain sustainable [38].

Fuel cells are either classified by electrolyte type with exceptional of the Direct Methanol Fuel Cells (DMFCs) or by the operating temperature, thus high and low temperature fuel cells. Low temperature fuel cells include Alkaline Fuel Cells (AFCs), the Polymer Electrolyte Fuel cells (PEMFCs), the DMFCs and Phosphoric Acid Fuel Cells (PAFCs) with operating temperature 100–220°C [37]. High temperature fuel cells including Solid Oxide Fuel Cells (SOFCs) and Molten

Carbonate Fuel Cells (MCFCs) which operate at a temperature range of approximately 600°C to 1000°C [37].

Among the two types (high and low temperature fuel cells), high temperature fuel cells are preferred in rural settings since both H_2 and CO can be used by reforming hydrocarbon fuels and alcohols thus they are more flexible as far as input fuel is concerned [39]. Among the high temperature fuel cells, SOFCs are preferred to MCFCs as far as power plant applications is concerned. This is because SOFCs have relatively higher power density as compared to MCFCs, they are less corrosive and are not susceptible to loss of electrolyte during long term operation [40,41].

Development efforts of SOFCs are being focussed on lowering the operational temperature range which would provide the advantages of internal reforming while reducing internal problems and capital expenditures which are associated with operations in very high temperature ranges [42]. Research on different materials has been conducted and is all geared towards reducing on the SOFC challenges. Such challenges include extended start up times due to high operating temperatures, exert sealing problems which require highly expensive interconnects and integration of materials stacks and reduction on thermal stresses and high resistance to coking and sulphur poisoning [41]. Due to the increased interest to the use of hydrocarbon fuels especially from gasification and AD, SOFC research is also directed towards development of catalytic anode materials that are less susceptible to carbon deposition (coking) and more resistant to sulphur poisoning. The ceria impregnated Ni-YSZ appear to be one of the high performing anodes since it has a high melting point (1,453°C) and it can sustain / or has a higher resistance towards sulphur poisoning [41]. However, some earlier research revealed that also Ni-GDC has high resistance towards sulphur poisoning [43].

There is also increased research on catalytic materials and operating conditions which can enhance internal dry reforming [44][45][46]. This can potentially reduce on the use of external reformers and water gas shift reactors and minimise the use of steam during the SOFC operation.

Fuel cells are currently being developed to replace conventional energy converters such as internal combustion engines because of their high efficiency. And also, they have a possibility to work in a reverse mode (producing H_2) which leads to possibilities of energy storage. This can potentially be a solution to major problems in the field of energy storage and grid stability.

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 [47]. BOSCH is also developing a small-scale modular plug and play SOFC system [48]. 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 liquefied petroleum gas (LPG) or natural gas [49]. 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 1kW 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 [50]. 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 3. 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 [51,52]. The major challenge is still the high upfront costs which is expected to go down with mass production. Currently a cost of 3,000-32,000 USD/kW has been reported for systems from 1 kW to 25 kW of installed capacity [53,54]. Cost is expected to come down once mass production would get started.

Elcogen has also developed 1 kW and 3 kW stacks which are operating at relatively low temperatures of about 650°C [55]. Such systems 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 [56].

Table 3. Specifications of systems manufactured by Watt Imperium, Kyocera and Elcogen [49,50,55].

Parameter	WATT Imperium	Kyocera	Elcogen
Rated output of power generation (AC)	1 kW	3 kW	1 kw 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 x 317.5 D x 304.8 H (mm)	1,150 W x 675 D x 1,690 H (mm)	190(W) x 315(L) x 90 (H) for 1kw and 190(W) x 230(L) x 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

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

1.4 | BIOGAS-SOFC ENERGY SYSTEMS

Currently small-scale solid oxide fuel cells (SOFCs) of less than 10 kW capacity are being promoted by a number of companies already [49,50,55]. 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 (Figure 2) 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) [57]. Small scale biogas-SOFC energy systems (Figure 2) have the potential to evolve into the next off grid energy generation technology for both developed and developing world due to the high achievable efficiencies of fuel cells. Therefore, biogas-SOFC energy system could significantly contribute to rural heat and electricity demand in the most efficient and sustainable way as compared to the current technologies which are being used for rural and off grid energy supply. The working principle of SOFCs and anaerobic digestion are well described in literature [58]. SOFCs have added advantages as compared to other fuel cell types such as proton exchange membrane (PEM) to be integrated with biogas due to their relatively high tolerance to fuel impurities and flexibility [59]. 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 [60]. 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 [20] 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. Also, such a system has ability to enhance sanitation in rural communities.

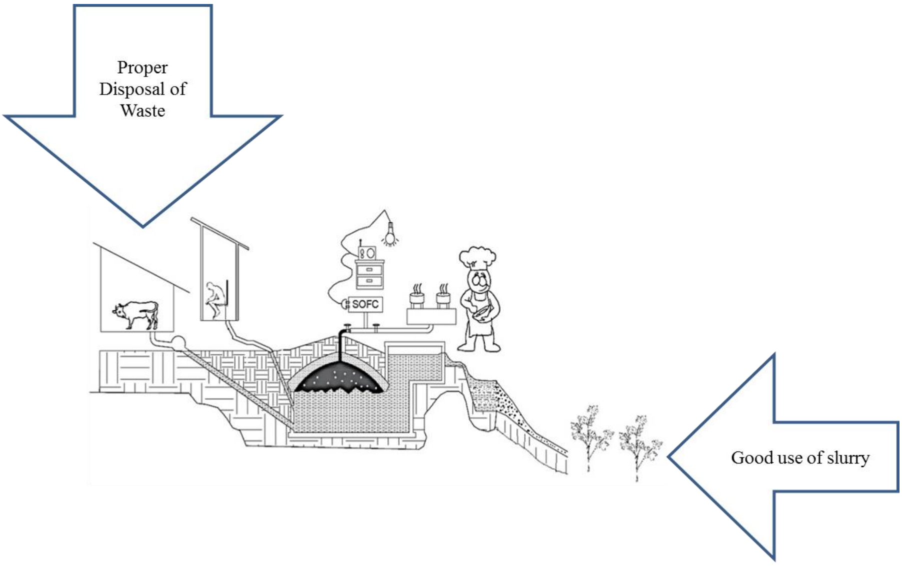


Figure 2. Biogas-SOFC energy system.

A biogas-SOFC energy system is an envisaged State-of-Art technology which can simultaneously solve the power access problems and enhance sanitation among the rural communities. Possibly it could also enhance agricultural activities as it could provide a low-cost substitute for commercial fertilisers among the hard-to-reach communities.

The critical 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 [12,61]. 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 [62]. Another challenge of SOFCs is the high initial capital and operational costs [63–65]

Therefore, the research will focus on developing concepts for both capital and operation cost reduction through a techno-economic study of the biogas-SOFC energy system. Substituting critical parts with locally available materials, such as the use of biochar as possible sorbent for gas impurities, and determining the change in total system efficiency and cost is a core object of this research.

It is envisaged that if locally some of the parts and process materials of biogas-SOFC energy system are replaced with locally available materials, the overall initial and operation cost of the entire system could decrease. For example, locally available biochar and soil can be used as cleaning sorbents to reduce on the cost of sorbents [66][67]. Also utilising as much internal dry reforming as possible instead of steam reforming could increase the system efficiency and therefore increase the economic returns of the system [68][69].

1.5 | MOTIVATION AND OBJECTIVE OF THIS THESIS

They are three growing society problems in Sub-Saharan Africa and these include limited access to sanitation facilities, energy and water. Biogas energy can be generated from waste and hence it can be used as a motivation to enhance sanitation among the rural people. With the growing advancement in technology, small scale decentralised biogas digesters can be coupled to a SOFC and hence contributed to rural energy mix. Therefore, a small-scale biogas-SOFC energy system can potentially enhance sanitation and as well supply both thermal and electrical energy needs to the off-grid communities.

However, the major barrier of using a SOFC as an energy converter has been the cost. Cost per kWe even goes higher when small scale (less than 5 kWe) generation is considered. Hence there is a need to re-think on cost reduction strategies if biogas-SOFC systems are to be integrated in off-grid energy mix. Cost reduction can be both in terms of frugal innovation of materials used in construction of SOFCs and biogas systems, eliminations of some materials by redesigning the system and operation costs reduction in terms of cleaning the gas.

First, study of the system is required with a view of identifying cost reduction potentials. Field studies are also required to further identify the cost reduction strategies during operation. Capital investment cost can be reduced by reducing the complexity of the biogas-SOFC energy system. The proposed strategy is to use internal reforming as opposed to dry reforming. It should be noted that biogas contains impurities like H_2S which is detrimental to proper performance of SOFC. Therefore, for the biogas-SOFC energy system, cleaning of the gas is a significant operation cost. The operation costs can be reduced by using locally available materials like biochar and reducing on in-situ cleaning requirement. Feasibility of the cost reduction strategies need to be studied in detail by gathering and analysis of both literature and field collected data.

Secondary, experiments are required to test theoretical preamble the likely outcome of the strategies proposed. The internal reforming requires a cell to be used as the catalyst. However, since dry reforming is envisaged, using the cell as a reformer need to be experimentally studied since Ni catalyst in the cell is affected by the H_2S presence in biogas. Therefore, experiments are required to determine the extent to which H_2S affect reforming on the cell. Also, experiments are required to determine the extent to which in-situ and upstream H_2S reduction strategies are effective to meet the impurity required level of SOFCs.

Thirdly, economic analysis of proposed strategies is required to determine the extent to which the proposed solutions affect the economic feasibility of the biogas-SOFC energy system.

Based on the motivation, the main goals of this thesis are;

- To theoretically study the cost reduction strategies for both capital investment and operation of the biogas-SOFC energy system.
- To experimentally study the technical feasibility of the proposed strategies.
- To carry out an economic analysis to compare the biogas-SOFC energy system with other alterative off-grid energy systems like Solar PV - battery systems.

1.6 | SCOPE OF THE THESIS

Given the aim and objectives of the thesis, as described in 1.5, chapter 2 will explore potential cost reduction strategies of biogas-SOFC energy systems. It will be done so through a literature study that focuses on the stringent fuel cells requirements for gas cleaning of impurities such as H_2S, as it is anticipated that this would significantly contribute to the capital and operational costs of the biogas-SOFC energy.

Since the use of internal dry reforming would significantly reduce the system complexity and consequently the cost, by omitting a methane reforming unit, chapter 3 presents the studies of boundary limit of H_2S for internal dry reforming.

Chapter 4 is a field study that aims at identifying the feasibility of in-situ H_2S reduction strategies during biogas-SOFC operation in rural Uganda as a potential route to reducing the cost of gas cleaning.

Chapter 5 is a laboratory and field-based study of in-situ H_2S reduction using locally available materials such as urine since this is envisaged to reduce on the gas cleaning costs during biogas-SOFC energy system operation.

Chapter 6 presents the laboratory and field-based study of the effectiveness of using locally available bio-char as an adsorbent for H_2S.

Chapter 7 is the economic study of the envisioned biogas-SOFC energy system putting into consideration different scenarios such as the use of locally available materials such as biochar instead of activated carbon.

Chapter 8 aims at combining the concepts in chapter 2-7 and hence focuses on the road map to practical applications and identifies research gaps for further studies.

Gas cleaning column

2

Techno-Economic Study of Potential Cost reduction Strategies for Biogas-SOFC Energy System Application.

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

Published as: H. Wasajja, R.E.F. Lindeboom, J.B. van Lier, P. V Aravind, Techno-economic review of biogas cleaning technologies for small scale off- grid solid oxide fuel cell applications, Fuel Processing Technology. 197 (2020) 106215.
DOI: https://doi.org/10.1016/j.fuproc.2019.106215

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 more than 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 energy systems in off-grid applications in developing as well as developed world.

Keywords: Biogas impurities, Sorbent cleaning systems, Biogas-SOFC

2.1 | INTRODUCTION

As reported before, the major challenge of using biogas as a fuel for SOFCs is that it contains a number of impurities such as H_2S, siloxanes and other volatile organic compounds (VOCs) which have to be removed to the required impurity level of 2 ppm(v) of the SOFC [12,61][62]. Secondary, challenge of SOFCs is the high initial capital and operational costs [63–65] of SOFCs could be an obstacle in their application. Since biogas contains a number of impurities, cleaning of the gas is considered to be a significant cost during operation and maintenance. 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. Hence the economic use of biogas as a fuel for SOFC cannot be achieved without a proper and sustainable cleaning technology [70]. Operation costs can be reduced by using locally available materials like biochar or using techniques such as in-situ H_2S reduction by air dosing. 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 [65].

A proper biogas cleaning system prior to biogas-SOFC should meet both the stringent gas requirements of the SOFC system and tolerate varying gas composition from anaerobic digestion. The removal of H_2S has been reviewed [71] 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 chapter 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.

2.2 | 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 [17,58,72]. Their presence beyond recommended quantities can be detrimental to thermal and thermal catalytic biogas conversion devices, and also harmful to the environment in form of emissions [73–75]. 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 [20]. As reported earlier, apart from the typical composition of biogas, compounds such as H_2S, volatile organic sulfur 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 [76,77]. All these compounds together are commonly referred to as impurities and their suggested lower threshold limits are shown in 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 [78]. A brief description on how each compound could theoretically affect SOFC performance depending on fuel composition and operating conditions is presented in 2.3.

2.2.1 | 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-} (Figure 3) by sulphate reducing bacteria (SRB), depending on the feed stock composition. Table 4 lists some typical sulphate reduction energetic reactions and methanogenic reactions. In general, it can be deduced from Table 4 that SRB have a much wider substrate spectrum where they have kinetic and thermodynamic advantage compared to methanogens [79]. Therefore, during anaerobic digestion H_2S will always be produced by SRB if sulphate is present.

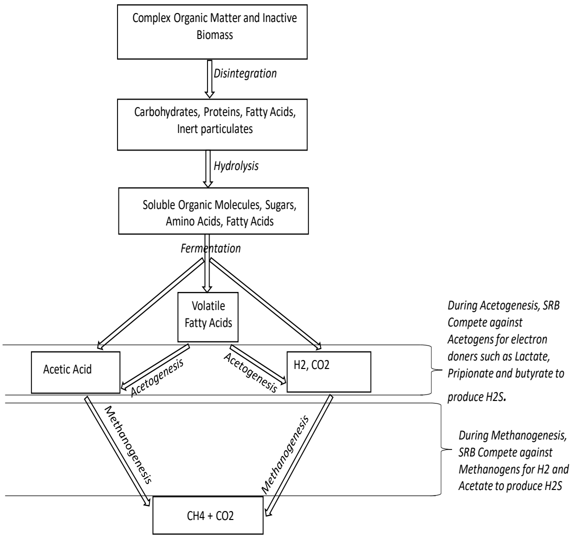


Figure 3. H_2S production during anaerobic digestion [79]

Table 4. Typical SRB Energetic reaction feasibility on comparison to Methanogenic reactions. Adapted from [79]

Sulphate–Reducing versus Methanogenic reactions	$\Delta G_r^{o'}$ 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$^-$ + $SO_4^{2-} \rightarrow$ 1.33Acetate$^-$ + $1.33HCO_3^- + 0.75HS^- + 1.33H^+$	-50.3
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

Biogas may contain H_2S concentrations of up to 5400 ppm depending on the feed stock of the digester [80]. 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) [80,81].

2.2.2 | 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 [82,83]. 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 [84].

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 [85,86]. 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 [86]. 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 [86]. 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 [80–82]. A maximum of 4-9 ppm is expected for LFG, for biogas from WWTP it can be as high as 41 ppm, whereas biogas from the farm digesters is expected to contain the least number of siloxanes [80,81,84]. As far as the author is concerned, no information could be found on the presence of siloxanes in small scale digesters. Common types of siloxanes found in biogas and their typical concentrations are shown in Table 5.

Table 5. Common siloxane types [80,84,87,88]

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*	TMS	$C_3H_{10}OSi$	90	1.65	0.02

* Quantified as toluene equivalent

2.2.3 | 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 [87]. Some of these VOCs have been generally referred to as tars when coming from biomass gasification by many researchers which are often further categorized as light and heavy tars [61,89]. In biogas, VOCs are in the form of organosulfur compounds (mercaptans, sulphides, disulphides), organosilicon compounds (siloxanes, already discussed in previous section), halocarbons, aromatics, and cyclic compounds [80]. Nevertheless, aromatics in the form of benzene, toluene and halogenated hydrocarbons are more common, with toluene being the dominant compound among them [81,90]. 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 [80]. 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 [80]. Biogas from farm digesters contains the least number of VOCs, followed by land fill gas and biogas from WWTPs, respectively [80,90]. Other VOCs in the form of alkanes, aromatics, poly cyclic compounds also exist in biogas in small quantities depending on the source as presented in Table 6. 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 6.

2.3 | EFFECT OF IMPURITIES ON SOFC PERFORMANCE

2.3.1 | 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 [91]. 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. [61] 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. [92]. General effect of H_2S on the performance of SOFCs is reported in Table 6.

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 [43]. 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 [43,91,93]. Also, Papurello et al. [76] recently reported that even at less than 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 [56,94,95]. Matsuzaki et al. [56] 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. [95] 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 level as compared to other SOFC anodes, like Ni/YSZ [43,61]. 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 [96]. Other Ni free anodes have been recently reviewed by Sadabaadi et al. [58], 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 [97–100], 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 (less than 2 ppm(v) is recommended in literature [62]) 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 [101].

2.3.2 | 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 [102]. 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 [103]. Veyo [94], 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. [102] 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. Post-test 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 [104] 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 non-reversible effect to the SOFC [104]. 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 [85,86].

2.3.3 | 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 [76]. VOCs can be generally categorised as siloxanes (organosilicon), organosulphur, halocarbons and hydrocarbons. Siloxanes have been already discussed in the previous sections of this chapter and therefore, they will not be considered in this section.

Organic Sulphur Compounds: Haga et al. [105] 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 polarisation 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 [106] 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.

Halocarbons: The same research group [105], 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.

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. [80] 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 [90] 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. [76] 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. [107] 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 hours duration. The same authors [108] did a similar study considering the VOC load of more than 10 g Nm^{-3} and still no significant effect on the performance was observed for SOFC operated again for 7 hours. 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.

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 [109–113]. Its effect could be outside the SOFC in terms of corroding the equipment like gas pipes [114,115]. 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 more than 16.5 ppm in the gas for 24 hours, they may wear out the process equipment and plug the gas system [116].

2.3.4 | 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 [76]. 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 author's 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.

Table 6. 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, 100-1,000 ppm 0-10,000 ppm(v) 0-8,000 mg m^{-3} [80,90,117–119]	< 1 ppm [12,61,120]	-Odor threshold < 0.014 mg m^{-3} [101] -< 1 ppm for at least few days for eye irritation, respiration irritation etc… [121]	-Causes bad smell [71] -Unhealthy, causes eye irritation [101,121,122] -Environmentally hazardous since it leads to formation of SO_2 and H_2SO_4 [121,123]	Highly corrosive [74,124]	Inhibits the fuel molecules from adsorption and hence affects fuel oxidation [76,91] Affects fuel reforming [125,126] Causes mass transport resistance [76], through the electrodes caused by the sulphur blocking the sites
NH_3	0-500 ppm(v/v) [72,118]		Maximum emission rate < 50 ppm(v) [109].	Leads to formation of NO_x emissions in engines [72,119]	Can be corrosive although less	Considered harmless to SOFC since it can crack to H_2 and N_2 during

			Conversion of NH_3 to NOx is less than 10% during combustion, however this conversion depends on the % of Ammonia in fuel gas and the mode of combustion [127]			corrosive than H_2S [114,115]	operation [109,110,113]
Siloxanes	0-50 ppm [80,81,84] < 1 ppm(v) [76] <0.01-100 ppm [116] 0-5.0 mg Nm^{-3} [119] < 400 mg m^{-3}	< 10 ppb [70] < 100 ppb(v) [86]		Siloxanes may not have a negative effect to the environment [128], however they may be responsible for fouling post-combustion emissions control- catalytic systems [86]		They lead to the formation of glassy micro-crystalline silica which reduces the life span of process equipment [70,86]	Silicon deposits on the interconnects of the cell, forming an insulating layer resulting in increased ohmic resistances [70,102] Reduce the porosity and flow of the fuel towards the active sites [76]
N_2	0-5% (v) [72]					Considered harmless [117]	Considered harmless

			Nitrogen is considered harmless to the environment		
Water Vapour	1-5% (v/v) [72]	Water vapour is considered harmless to the environment		Considered harmless [117]	Operation of SOFC with humidified gas does not affect the cell performance [129], 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 ppm* [80]		Could result in various diseases if exposed for long time [130]	Could result into corrosion, although the effect is less severe than H_2S [131]	Since they contain sulphur, they could have the same corrosion effects like those of H_2S. Increases the rate of cell degradation [105]

Halocarbon such as CH_2CL_2	1.9 – 98.24 ppm* [80]	< 0.5 ppm as ppm in Biogas [70]		If ends up in the environment, it contaminates water and can result in healthy effects [132]	It is highly corrosive in the presence of water [116] Can result into dioxins and furans which are highly toxic [116]	Could result in formation of $NiCl_2$ which has a sublimation temperature of 985 ^{0}C which is near the typical SOFC operating temperatures [105]
Alkanes Such as Ethane	184.13–222.86 ppm* [80]					Could increase polarization resistance [76] Could influence reforming and fuel oxidation reactions
Benzene	0.85 – 21.3 ppm*					
Toluene	2.27-108 ppm					
Other aromatics such as Ethylbenzene	14.94 - 166.64 ppm* [80]		Emission limit is < 0.0004 mg L^{-3} in water, < 0.6 mg m^{-3}	If present in the fuel, could result in		Could increase polarization resistance [76]

		in soil and < 0.2 mg m^{-3} in air [133]	increased emissions on NO_x for engines [134] Could results into increased particulate emission and could cause respiratory effects [134]		
Cyclic Such as Cyclohexane	49.42 - 84.9 ppm* [80]			Could have a detrimental effect on process catalysts [135]	Could increase polarization resistance [76] Could influence reforming and fuel oxidation reactions
Alcohols (Ethanol and 2-prapanol)	7.02 ppm* [80]				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	<10µm particle size	< 20µg/m^{-3} for 24hrs for particles < 2.5µm [136]		Could ware down the equipment and could plug the gas system [116] Could plug the pores of adsorbents [116]

**Cumulative maximum.*

2.4 | 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 [80]. 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 [80]. 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 section. Such technologies are most suitable for biomethane production for gas grid injection and models for biomethane prediction are being investigated [137]. 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 [45,68,138–140]. Moreover, so far, there is no solid evidence about the impact of methane purity and efficiency of the fuel cells [141]. 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 [78]. These technologies are classified as physical, chemical and biological processes [142]. For utilisation of biogas, the contaminants which are considered detrimental are H_2S, volatile organic sulphur compounds, halides and silicon containing compounds [143]. It is important to note that their harmful effect depends on the biogas application. For biogas-SOFC application, generally less than 2 ppm(v) of H_2S is required as discussed in section 2.3 of this thesis. This may not be the case for internal combustion engines which can tolerate as high as 150 ppm of H_2S [52].

2.4.1 | 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 [144,145]. There are various sorbents that have been studied by different researchers as discussed in the subsequent sections. 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 [146]. There are various technologies involved in biogas cleaning and their applications depend on the goal of biogas use. As reported earlier [142], 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 [71]. 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 subsequent sections of chapter 2 of this thesis.

2.4.1.1 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.

ZnO: Among the many metal oxides, ZnO has been widely used for more than 30 years as H_2S removal agent from natural gas [147]. 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 equation 1 [148];

$ZnO + H_2S \rightarrow ZnS + H_2O$ *(Equation 1)*

Sulphur removal to less than 1 ppm using ZnO for inlet gas with sulphur concentrations of over 2,000 ppm(v) has been reported in literature [146,149,150]. Its use has been limited to desulphurisation of low sulphur content gas due to its difficulty to be regenerated [148]. 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 [150]. 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 [146,150]. However, Torkkeli et al. [151] 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 7.

Table 7. Parameters which affect the sulphur capture capacity of ZnO based sorbents

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 [147].
Space velocity	The lower the space velocity the higher the S_{cap} [146,150].
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 [146].
CO_2	Decreases S_{cap} if varied from 0-12% in the presence of steam [147].
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 $ZnO (s) + H_2S (g) \leftrightarrow ZnS (s) + H_2O (g)$ towards ZnO and H_2S [146,147].
Particle size	Optimal particle size range 150-250μm [146].
H_2 (g)	H_2 (g) accelerates the reaction of H_2S in the presence of H_2O at 500°C [149].
CO	CO can potentially inhibit the reaction between ZnO and H_2S according to the following equation; $ZnO + CO \rightarrow Zn + CO_2$ [149,152].

**The behaviour of ZnO and ZnS in the presence of very low water concentration eg < 1% is still not clear* [147].

When pure metal oxides are used as H_2S sorbents, they have a number of physicochemical limitations such as sintering, mechanical disintegrations, loss of surface area and porosity, which affect their life time and performance [153]. 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. Hussein et al. [154], 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 [149], although SiO_2 was found to be a better support than Al_2O_3 [155]. 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 (2-400°C) [151]. This low temperature desulphurisation capacity for such sorbents is important to protect the fuel cell during the cold gas start up [151]. 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 [147].

$Cu\text{-}ZnO/SiO_2$: Among metals, Cu doped with ZnO/SiO_2 has the highest sulphur saturation capacity [151]. Karvan et al [153], 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) [156]. $Cu\text{-}ZnO/SiO_2$ can be easily regenerated in air at a lower temperature range of 300–550°C, better than the available commercial ZnO sorbents which are regenerated at a much higher temperature [148]. Its sulphur capture capacity can fully be recovered at 550°C in 1 hour with limited capacity loss for up to 10 desulphurisation-regeneration cycles [151]. 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 8.

ZnO-CuO/AC: Balsamo et al. [157] 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 [154] 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 [147]. However, its limited extent of regeneration [148] 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 [145].

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 [151,158]. The advantage of such sorbents to biogas desulphurisation is that they are not affected by CO_2 [158] (Table 8). However, CuO oxide-based sorbents have been reported to potentially cause formation of larger volatile sulphides from mercaptans in biogas[159].

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. [160] 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 8). 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 [159]. 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 [152,161]. Eventually, they were not given focus in subsequent research and development.

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. [78] 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 [162].

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 [163]. During absorption, H_2S is first chemosorbed on the surface by molecular adsorption followed by dissociative adsorption on inner surface [164]. For iron oxide-based sorbents, a three dimensionally ordered macropore (3DOM) structure has been reported to increase its sulphur capture capacity [165]. 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 [165]. 3DOM iron oxide are therefore more effective sorbents as compared to conventional ones and can be regenerated at relatively low temperature of 100°C [165]. Early research showed that addition of supports like Al_2O_3 and SiO_2 can influence the reactivity of iron oxide with H_2S [166]. Such supports can also enhance regeneration capability [167] and sulphur capture capacity of iron oxide [168]. Also, when iron oxide is added to ZnO with a support, it can result in a more efficient and mechanically stable sorbent [169]. Therefore, as it is with ZnO based sorbents, doping of iron oxide-based sorbents can greatly influence their absorption capacity [170]. 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 [171]. 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 [163]. 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 [172]. And it can simultaneously absorb more than one impurity [173]. Other advantages and disadvantages of this technology to small scale biogas-SOFC system are reported in table 8.

2.4.1.2 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.

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) [117]. This method has not gained much attention because of reactivity of CO_2 with alkaline reactants such as NaOH and CaO [117].

Sulphuric acid and nitric acid: Sulphuric acid can be used to remove siloxanes but this is effective only at high temperatures [85,143]. 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 [143]. Other advantages and disadvantages of this technology to biogas-SOFC energy system are reported in Table 8.

Fe-chelated solutions: This technique involves the use of the redox reaction [117],

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

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

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 [117]. Also, the technology is fairly complex to be applied on a small-scale basis.

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 [117],

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

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

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2HSO_4^- \rightarrow 2Fe^{3+} + H_2O + 2SO_4^{2-} \qquad \text{(Equation 6)}$$

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O \qquad \text{(Equation 7)}$$

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_2SO_4, its application to small scale biogas system is rather difficult [117]. Furthermore, due to generation of H_2SO_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.

Organic solvents: Organic amine solvents are commercially used for H_2S removal from gas streams. The initial research of this technologies focused on simultaneously cleaning of the gas from H_2S and absorb CO_2 [174–176]. However, their major challenge was high energy consumption and low adsorption rates [177]. 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 thesis.

2.4.1.3 Adsorption gas cleaning processes

These technologies have been investigated for their effectiveness to adsorb H_2S 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 [178].

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 1,100°C to increase its surface area available for adsorption [178,179]. The adsorption capacity depends on surface structure and surface characteristics of a given activated carbon [73]. Activated carbon can be available in three types *(i)* catalytic–

impregnated (regenerable) *(ii)* impregnated and *(iii)* non-impregnated [117]. It has been used as an adsorbent in either granular or powdered form, the latter could have high adsorption capacity than the former [180]. Commercially available activated carbons have been proved to effectively remove H_2S and siloxanes from biogas to less than 1 ppm [181]. Studies by Yu et al [73] show that activated carbon can effectively remove siloxanes from biogas, although the adsorption capacity is greatly reduced by the presence of H_2O [182]. This has been recently re-affirmed by Calbry-muzyka et al. [159] and Papurello et al. [183]. Activated carbon is so far the most common adsorbent which is utilised for removal of halides and H_2S and its adsorption capacity for impurities is normally improved by impregnating it with liquid or solid chemicals [71]. The majorly used chemicals for impregnating activated carbons are KI, NaOH, KOH, $NaHCO_3$, $NaCO_3$ and $KMnO_4$ [71,160,184]. Also, it is important to note that sometimes a mixture of these chemicals is used to impregnate activated carbon [71]. Other chemicals such as K_2CO_3 have been used to successfully impregnate activated carbon [185,186]. 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 equation 8 and 9 [160];

$$KI \quad H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O \qquad \text{(Equation 8)}$$

$$NaOH \quad H_2S + 2NaOH \rightarrow 2NaS + 2H_2O \qquad \text{(Equation 9)}$$

As reported earlier, impregnating activated carbon can potentially improve its affinity to sulphur containing compounds in the biogas [118,187], hence increasing its adsorption selectivity. Lazini et al. [92] reported that impregnating activated carbon can improve its sulphur capture capacity to as high as 300 g of H_2S per kg of adsorbent. However, for impregnated activated carbon, the adsorption capacity depends on the availability of oxygen [188]. Isik-Gulsac [189] 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 [159] and what was reported by Yu et al. [73]. Other factors such as surface pH and diameter of micropores can as well affect the adsorption capacity of activated carbon [92].

Mescia et al. [118] also studied the effectiveness of H_2S 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_2S 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. [190] 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 hours. The results revealed that commercially available activated carbon can efficiently remove H_2S and other sulphur compounds such as CH_4S, C_2H_6S 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. [191]. 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. [192] reported that silica gel was more superior for removal of D4 siloxanes as compared to activated carbon and zeolites. The same group [191] 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. [193] 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. [194] 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. [195] 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. [73].

Although it is possible to regenerate any type of activated carbon, regeneration is considered not feasible for small scale applications [117]. 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 [184], 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 8. It is important to also note that apart from activated carbon, ashes and biochar are potential adsorbents for biogas contaminants [92,196].

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 [197]. Zeolites have uniformly sized pores through the crystal structure [198]. 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 [178]. Molecular simulations by Cosoli et al. [199] revealed that zeolites are potential adsorbers for H_2S in biogas. Also, novel molecular sieves are being developed by some research groups [200], 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 8.

Papurello et al. [201] recently analysed the performance of commercially available Na-X pellets Zeolite (1/16 inch, 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 less than 70 ppbv for over 250 hours. 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 [202], 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 less than 2 ppm(v) H_2S concentration required by SOFC, and this could potentially increase both the capital and operation costs of the cleaning system.

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 [190]. Zeolite effectively removes H_2S from the gas to an even greater extent [201]. However, sulphur compounds such as C_2H_6S (Dimethyl sulphide) was reported to be relatively difficult to be removed by activated carbon [203]. This also can be the case with several other sulphur containing compounds such as COS and halogenated compounds [204]. 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 [205]. 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 [204]. 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 [206].

Silica Gel: Siloxanes could be completely removed by using silica gel and activated carbon at the same time. Schweigkofler [143] 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 [143]. Adsorption capacities of silica gel exceeding 100 mg of siloxanes per gram of silica gel has been reported by the same research group [143]. 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.

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 [178]. Contrary to zeolites, polymers have a high adsorption capacity under high vapour pressure [178]. 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.

Sludge–derived adsorbents or Activated sludge: The use of activated sludge as H_2S sorbent has been also investigated by a few researchers [71,207]. Xu et al. [66] 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.

2.4.1.4 Other physicochemical biogas cleaning systems

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% [143]. Other compounds such as H_2S and halogens can also be removed at a temperature of approximately -25°C [208]. 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 [78,85]. 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 [143]. 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 [209].

Adsorption cooling systems have been investigated by a number of researchers. Solid desiccant cooling system can be categorised into two [210]; 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 [210]. Physical adsorption-based chillers such as silica gel-H_2O adsorption chillers were investigated by Najeh et al. [211]. 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 not reached with such a system [210]. Therefore, in practice, they are used in air conditioning systems, where relatively high cooling temperatures are required. Other chemical based adsorption chillers which seem to be promising are $CaCl_2$-NH_3 and metal hydrides-H_2, but still their operating temperatures are low [210]. Also, $CaCl_2$-NH_3 based adsorption chillers have problems of expansion, decomposition and corrosion which have hindered their application [212,213]. 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 [213]. Since ammonia–water absorption chillers require a driving temperature as high as 200°C and cooling temperature is as low as -10°C [213], they can presumably match with a biogas-SOFC energy system where high operating temperatures of more than 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 [210,213]. 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 8.

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 [78]. Its major drawback for biogas-SOFC energy system application is the absorption of CO_2 gas and requirement of large volume of water [78]. 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 [214]. The application of such methods on small scale SOFC would result in less CO_2 available if dry reforming is to be used [138]. Other draw backs of this technology are summarised in Table 8. 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 [163]. 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 [163].

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 [70]. The removal of siloxanes by various types of membranes was extensively investigated by Ajhar et al. [215,216]. 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.

2.4.2 | 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. [160] 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.

2.4.3 | 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 odour. 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 [217]. As reported by Duan et al. [218], 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. [219] 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 more than 70%. This is also re-affirmed by Montebollo et al. [220] 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. [221] 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 less than 5 gL^{-1}. Also, Chung et al. [222] 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 [103].

Although some researchers [160] 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 8, slow adaptability to fluctuating gas composition would result in a detrimental effect to the SOFC system [160]. S_{cap} during the start-up is very low [223] 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 are required to engineer a controllable system.

2.4.4 | Combined effect of activated carbon and biological H_2S 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 [218]. 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 [224]. 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 [222].

The effectiveness of combined adsorption and biological removal of H_2S was investigated by Duan et al. [225]. 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 recirculation (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 $Lmin^{-1}$, 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. [226] 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 131-854 ppm down to 3-78 ppm with an average removal efficiency of 90%.

Duan et al. [218], 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 x 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. [221], 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.

2.4.5 | In-situ biogas cleaning and upgrading technologies

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 oxidising micro-organism on the storage surface, this can potentially reduce the concentration of H_2S by up to 95% [163]. 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 [144,163].

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 [163]. 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 [145]. 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. [227,228] 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 less than 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 are 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.

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 [229]. 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 [229]. Such technologies can simultaneously remove more than 65% of VOCs and H_2S from the fuel gas

Table 8. Summary of biogas cleaning technologies.

Gas cleaning technology	Advantages to small scale 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 - It is environmentally friendly [230]	- Efficiency of H_2S is affected by moisture with biogas [146,147] - 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) [146,150] - The effect of co-existing gases during adsorption can result in formation of sulphur compounds such COS which can potentially affect the SOFC [147,231] - Very low S_{cap} at low temperatures [146], therefore not effective during cold start-ups. - High energy is required during regeneration [148]	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 [154,157] - Can be easily regenerated at relatively low temperatures [151] - Efficiency is not affected by humidity at ambient temperature (20 °C) [151]	- Efficiency is highly affected by the aging effect [151]	H_2S	Commercialised and laboratory scale
CuO	- S_{cap} is not affected by CO_2 gas	- Could result in formation of larger volatile sulphides from mercaptans [159]	H_2S	
Activated alumina-V_2O_5/TiO-Alkalized material	- Can simultaneously remove siloxanes and H_2S [78]			Laboratory scale
CuO-MnO	- Relatively better break through time as compared to activated carbon and zeolite [160]	- The adsorption capacity is highly affected by the humidity with in biogas [160] - There could be risk of volatile sulphide formation from mercaptans in biogas [159]	H_2S	Laboratory scale

Iron oxides	- Relatively cheap [163] - Some types are environmentally friendly, they can be disposed of after use without following stringent environmental procedures [202] - Can be easily regenerated [163] - Can simultaneously absorb more than one impurity [173]		H_2S	Commercialised
Liquid Absorption Gas Cleaning Processes				
Nitric and sulfuric acid	- High siloxane removal efficiency [143]	- High potential risk to healthy and environment, and this could result in high operation costs due to safety concerns [143]. - High risks of trace sulphur elements reaching the fuel cell system	H_2S	Laboratory scale
Fe-chelated solutions			H_2S	Laboratory scale

Metal sulphate solution		- Less efficient and high risks of contaminant to strip to solvents at high gas flows [85]	H_2S	Commercialised
Organic amine solvents		- High energy consumption [177] - Low adsorption/desorption rates and amine loss during regeneration [177] - Absorbs CO_2	H_2S	Commercialised
Adsorption Gas Cleaning Processes				
Activated Carbon	- Can efficiently remove siloxanes, linear and aromatic hydro carbons from dry biogas [142] - Can tolerant moisture content of approximately up to 40% of the total gas with negligible effect on adsorption capacity [177,182,232] - Pre-humidification of activated carbon could enhance its adsorption capacity [233]	- Regeneration can potentially reduce the efficiency of activated carbon [181]. - Could require regular change due to low adsorption capacity and this could potentially increase the operations cost [85,200] - Disposal may not be environmentally friendly [78] - Adsorption capacity can be potentially decreased by gas contents such as CO_2 [234] - Activated carbon impregnated by caustic could be difficult to handle and to dispose [116,194]	H_2S, mercaptans, siloxanes and Other VOCs	Commercialised

	- 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 [160] - Relatively less expensive as compared to zeolites and metal oxides [160,178].			
Zeolites	- They are effective at ambient temperature [200]. - Due to narrow pores, it has good selectivity to CO_2 and CH_4, hence little effect to the SOFC reforming process [201].	- Since they are selective to CO_2 and CH_4 [201], 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	- Adsorption capacity is reduced by H_2O content in the gas [143,192].	Siloxanes	Commercialised

	downstream gas cleaning [143]. - Easy and cost effective to regenerate [143], although adsorption capacity decreases significantly when regenerated [192]. - Could be cost effective for small scale biogas applications [85].	- Adsorption capacity is reduced by increase in temperature [192].		
Polymeric adsorbents	- Less sensitive to humidity as compared to carbons [178]. - They can easily be regenerated [178].		VOCs	Laboratory scale/ commercialised
Activated sludge	- Cheap source and readily available. - Adsorption capacity is not affected by high moisture content in the gas [66].		H_2S	Laboratory scale

Other physicochemical biogas cleaning systems				
Water scrubbing technology		- Requires high volumes of water [78]. - Absorbs CO_2 [78] which can affect fuel cell internal reforming. - Results into formation of corrosive acids [78] which can potentially increase operation cost. - Poor removal efficiency of other siloxanes compounds due to their low solubility in water [78].	H_2S	Commercialised
Cryogenic condensation		- Very low efficiency [143] - High operation costs [78]	H_2S, siloxane, and halogens	Commercialised
Membrane separation technique		- Cannot selectively remove impurities [215,216]	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	- Slow adaptability to gas composition and slow response time during start up [160]. - Maintenance of pH would require the use of extra chemicals like NaOH and this	H_2S and mercaptans	Laboratory scale

	mercaptans [103,219,220]		would increase the operation costs of the system		
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
Solar-photo-oxidation in combination with biological treatment	Can simultaneously remove all impurities from the gas [229]	-	Depends on solar light which may not be available all the time	H_2S and VOCs	Laboratory scale

2.5 | INDUSTRIAL BIOLOGICAL DESULPHURISATION

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 [163]. 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.

THIOPAQ O&G desulphurisation technology. This technology combines the gas purification along with sulphur recovery within a single gas cleaning unit [235]. During the gas cleaning process, H_2S rich gas is passed through a scrubber (absorption section in Figure 4, 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 Figure 4) 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 less than 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.

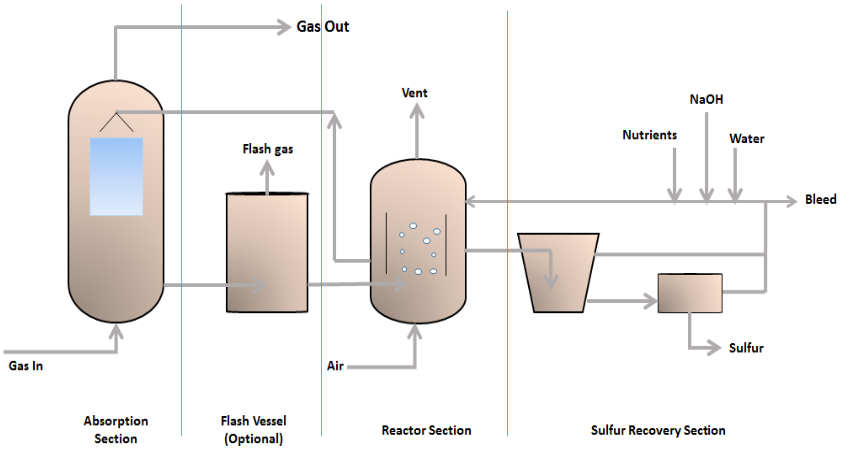


Figure 4. Schematic flow of THIOPAQ O&G desulphurisation technology [235]

Sulfothane desulphurisation technology. This technology consists of two steps [236] (Figure 5). During the first step, biogas is passed through a scrubber column in which H_2S is absorbed by NaOH according to equation 10.

$$H_2S + NaOH \longrightarrow NaHS + H_2O \qquad \text{(Equation 10)}$$

During the second step, NaHS is biologically oxidised to elemental sulphur and also the washing liquid is regenerated according to equation 11.

$$NaHS + \tfrac{1}{2}O_2 \longrightarrow S + NaOH \qquad \text{(Equation 11)}$$

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 [235], since washing liquid is regenerated, less chemicals are used. However, for small scale application, such a system may not be readily applicable since only standard units from 100 to 1,500 $Nm^3\ h^{-1}$ 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 less than 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.

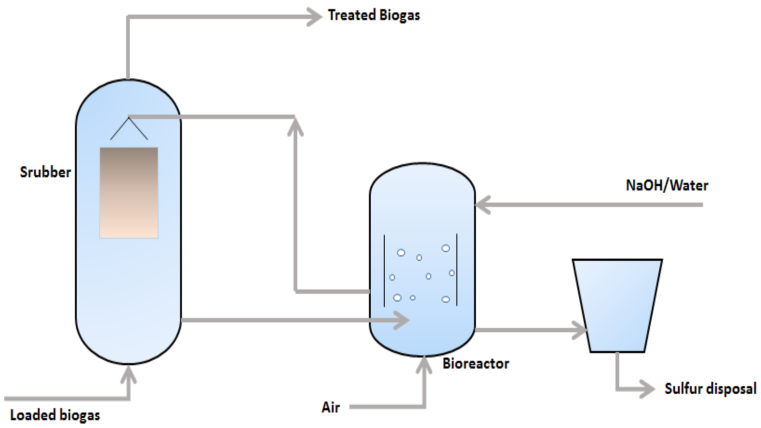


Figure 5. Schematic flow of Sulfothane desulphurization technology [236]

2.6 | ECONOMIC STUDY 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 it 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. [52] 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 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 [237].

To get an insight on the economic status of different upgrading technologies, a few papers were surveyed which seem to follow the same approach (Figure 6), although some of them combine gas cleaning and upgrading in one single step [238]. Bauer et al. [208] analysed the specific investment costs of different biogas upgrade technologies. In their analysis, the specific investment cost of amine scrubbers is in the range of 1,400 EUR Nm^{-3} h^{-1} to 3,400 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 1,250 EUR Nm^{-3} h^{-1} to 3,000 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 1,200 EUR Nm^{-3} h^{-1} to 5,500 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 1,200 EUR Nm^{-3} h^{-1} to 4,800 EUR Nm^{-3} h^{-1} and for the membrane from 1,800 EUR Nm^{-3} h^{-1} to 5,800 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 1,500 Nm^{-3} h^{-1} to 2,000 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.

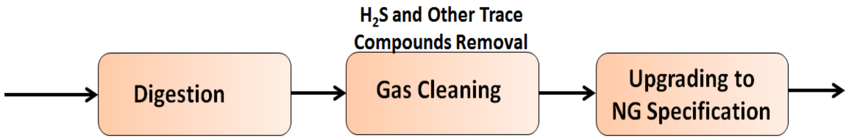


Figure 6. Schematic flow of most biogas upgrading technologies [239]

For the non-upgrading technologies, the major challenges of gas cleaning units are high capital and maintenance costs and poor reliability [240]. 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% [240]. 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% [144,145]. 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. [144] 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 go for maintaining the biogas cleaning unit in terms of sorbent consumption. Also, Mehr et al. [241] has recently reported that for biogas-SOFC energy system, the investment cost for the cleaning unit is currently \$1,000 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 [240]. It was also 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 [241]. 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_2S removal from biogas although in some cases Iron Hydroxide and ZnO are used [242]. For example, to clean the biogas with Sulfa Treat (mixture of iron oxide), an annual operational cost of 6,000 EURs has been reported in literature, for a plant with the capacity of up to 2,000 $m^3\ h^{-1}$ of biogas and 0.5 $m^3\ h^{-1}$ of H_2S [242]. 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 hours 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 EUR 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. [145] 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 [243]. Arespacochaga et al. [142] 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. [116]. However, Hagen et al. [242] reported that dosing the digester with chemicals to reduce H_2S 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_2S concentration in the fuel gas [163,244]. Diaz et al. [245] 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 [70]. 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 [80]. However, this cost depends more on the source of the gas and impurity level of that particular gas [80]. Cost review of the commonly used cleaning media for biogas reported in Table 9 gives an insight of the different technology operation cost implications to the overall biogas-SOFC energy system.

Figure 7 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_2S using iron oxide can cost as low as 4.31 EUR kg^{-1} of H_2S removed and as high as 10 EUR kg^{-1} of H_2S 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} (Figure 7) if thermal energy requirement of ZnO based sorbent is ignored. Although H_2S 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_2S removed for biological filters and a cost as low as 0.35 EUR 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 less than 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.

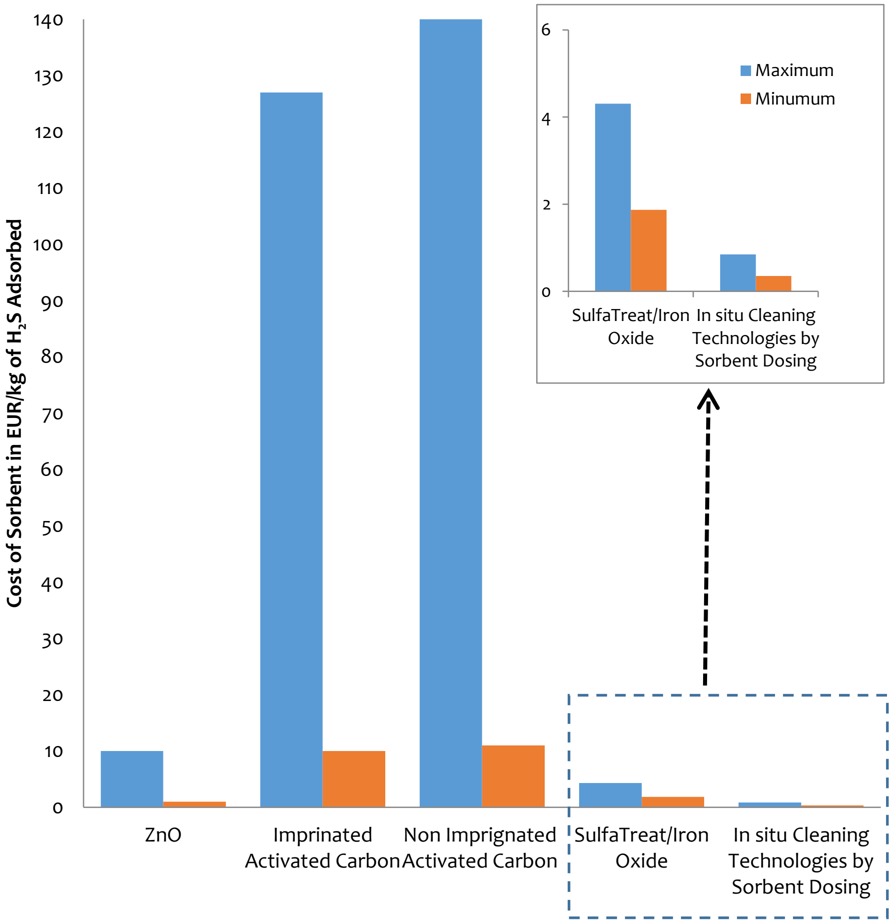


Figure 7. Cost comparison of commercial sorbents for H_2S adsorption

Table 9. 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)	< 1ppm of H_2S [246]	Process conditions adsorption pressure 1,050 mbar, adsorption temperature 30 °C [242]	0.15 [117] 0.065 [247]	0.28 [248]	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 less than 1ppm required by the SOFC
Impregnated activated carbon (2% KI, potassium iodide)	< 0.1 ppm of H_2S [246]	Ambient temperature	0.077-0.093 [249] 0.062 [144], 0.015-0.045 [250]-	1.00 [144]	-Cost of the reactor/Vessel (Estimated to be 900 EUR/kW for 100 kW biogas-SOFC system [52] and 300 EUR for 5 kW Biogas-Engine generator System [144]) -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.

						3.85* EUR kg^{-1} of H_2S [246]	
			-	-		50 EUR kg^{-1} of H_2S	
			0.1 [52]	5 [52]			
			0.15 [117]	19 [251]		127 EUR	Supplier quotation to TU Delft 2018
Non impregnated activated carbon	10-100 ppm [242]	Ambient temperature	0.02-0.2 [117]	0.35-2.83 [252,253]	- Cost of the reactor - Cost of Disposal	11 – 140 EUR kg^{-1} of H_2S	If non impregnated activated carbon is used, a second cleaning system is required to bring down the H_2S down to less than 1 ppm
Dosing of Fe_2O_3(Hematite) in the digester	< 100 ppm [145]	Ambient temperature	0.2 [145]	0.07 [145]	- Automatic dosing equipment - Cost of Cleaning and disposing of	0.35 EUR kg^{-1} of H_2S	For SOFC, an additional cleaning system is required

					the chemicals accumulated in the digester		
Dosing of the digester with FeCl	100-150 ppm [246]	Ambient temperature	-	-		0.85 EUR kg^{-1} of H_2S* [246]	For SOFC application, additional cleaning system is required
Air/Oxygen dosing	< 50 ppm [163]		-	-		0.0019-0.0049 EUR m^{-3} of biogas cleaned [245]	For SOFC application, additional cleaning system is required
ZnO sorbents	<1 ppm [147]	Temperature of 250 °C-400°C is required	28-49 [147]	1.2-266.25 [251,254]		0.03-10 EUR kg^{-1} of H_2S	It can clean the gas to required levels of SOFC
ZnO-CuO sorbents	<1 ppm [157]	Temperature of 250 °C-400°C is required	45-77 [255]	125[251]		1-3 EUR kg^{-1} of sorbent	It can clean the gas to required levels of SOFC
Biological filters	<50 ppm [246]		-	-		0.1–0.25 EUR kg^{-1} of H_2S* [246]	Additional cleaning system is required for SOFC application

Siloxane Removal				
Silica gel	<0.4 mg/m^3 [143]	0.1 [143]	40-50 [251]	400-500 EUR kg^{-1} of siloxanes
Activated carbon	< 0.87 ppm [246]			81–113 EUR kg^{-1} of siloxanes, 188–565 EUR kg^{-1} of siloxanes [246]

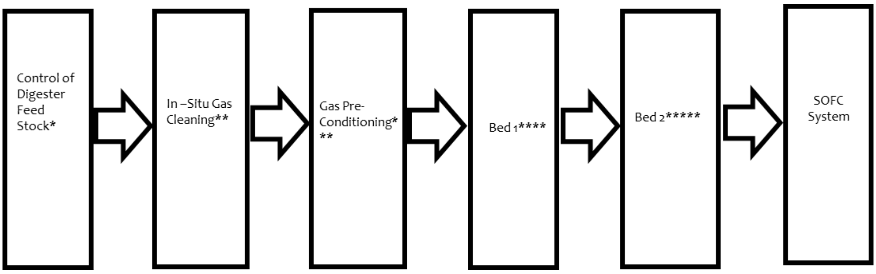
Cooling followed by activated carbon bed (other impurities are assumed to be also adsorbed)			Capital $107,000 for 110m^{-3} h^{-1} and annual maintenance of $16,300*[103]
Biogas Drying			
Silica gel	Ambient temperature	40-50 [251]	
Refrigeration/ Condensation	Electrical energy is required for refrigeration		Capital cost of refrigeration Is 36,000 $* Un installed [80]

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

2.7 | 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 Figure 8 to come up with an efficient and cost-effective cleaning system for a small-scale biogas-SOFC energy system application.



*This can combine 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.

Figure 8. Proposed flow scheme of a small-scale biogas–SOFC energy system cleaning unit.

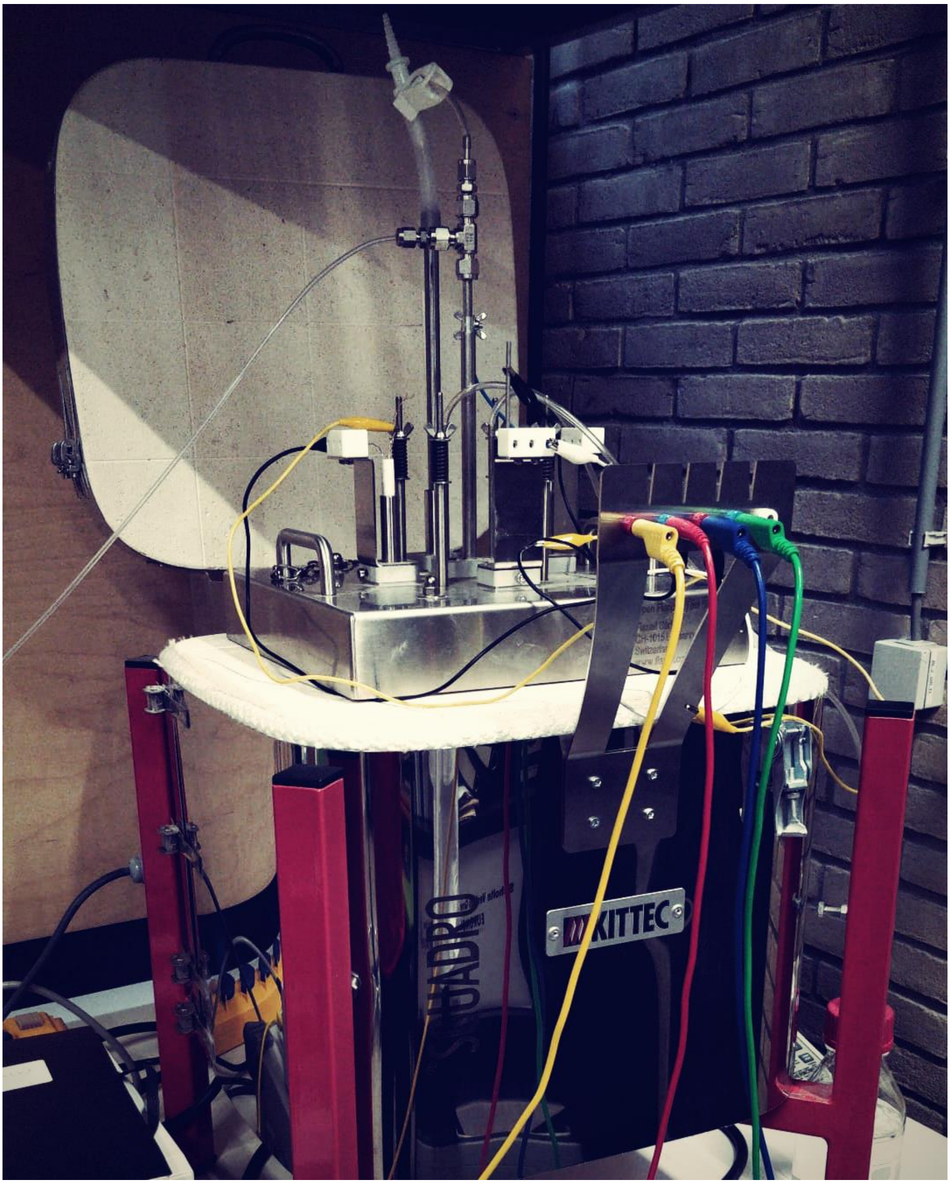
In summary, this study has revealed the followings;

- 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 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.



Fiaxel SOFC test bench

3

Laboratory study on the boundary limit of H2S feasible for biogas dry reforming as an envisaged cost reduction strategy

The effect of H2S on internal dry reforming in biogas fuelled solid oxide fuel cells

Published as: H. Wasajja, S.A. Saadabadi, B. Illathukandy, R.E.F. Lindeboom, J.B. van Lier, P. Vellayani Aravind, The effect of H2S on internal dry reforming in biogas fuelled solid oxide fuel cells, Energy Science and Engineering. 10 (2022) 374–383. DOI: https://doi.org/10.1002/ese3.1021.

ABSTRACT

Internal dry reforming of methane is envisaged as a potential solution for reducing on capital and operation costs of biogas fuelled Solid Oxide Fuel Cells (SOFCs) system by using the CO_2 present in the biogas. Due to envisaged internal dry reforming, the requirement for biogas upgrading becomes obsolete, thereby simplify the system complexity and increase its technology readiness level. However, impurities prevailing in biogas such as H_2S have been reported in literature as one of the parameters which affects the internal reforming process in SOFCs. This research has been carried out to investigate the effects of H_2S on internal dry reforming of methane on nickel–scandia stabilized zirconia (Ni-ScSZ) electrolyte supported SOFCs. Results showed that at 800°C and a CH_4:CO_2 ratio of 2:3, H_2S at concentrations as low as 0.125 ppm affect both the catalytic and electric performance of a SOFC. At 0.125 ppm H_2S concentration, the CH_4 reforming process is affected and it is reduced from over 95% to below 10% in 10 h. Therefore, future biogas-SOFC energy system cost reduction seems to become a trade-off between biogas upgrading for CO_2 removal and biogas cleaning of impurities to facilitate efficient internal dry reforming.

Keywords: SOFC poisoning; Internal dry reforming; H_2S; Ni-based catalyst

3.1 | INTRODUCTION

Biogas is one of the most common energy carriers recovered from waste. It is mainly composed of CH_4 and CO_2. In the presence of heat and a catalyst, CH_4 reacts with CO_2 to form H_2 and CO which are potential SOFC fuels. SOFCs operate often with Ni-based anodes at temperatures between 600-1000°C [59]. Ni can catalyse CH_4 and CO_2 reforming reaction at temperatures as low as 400°C [256]. SOFCs are reported to be tolerant to CO containing fuels [12]. This provides an opportunity for internal reforming in SOFCs, since Ni is also a catalyst for CH_4 reforming [257]. Hence, possibility to use biogas as a fuel for SOFCs [58]. However, there are still technical challenges such as carbon deposition, thermal stress and gas contaminant poisoning for direct biogas fuelled SOFCs [258]. Therefore, currently research is being directed to develop more efficient Ni-based catalysts for electro-catalytic reforming [259].

Possibilities of methane internal dry reforming in SOFCs were investigated by Goula et al. [260]. Authors observed that internal dry reforming is indeed feasible in SOFCs. However, full dry reforming is still a challenge especially if Ni-based SOFC anodes are used due to the risk of carbon deposition and nickel re-oxidation in the H_2-lean portions of the anode [261]. The possibility for internal dry reforming can greatly reduce the overall system costs by 6% if external reformers can be eliminated from the system [262]. Also, Schubert and Kusnezoff [263] reported that direct internal reforming of SOFCs fuelled with biogas is preferred due to its foreseeable cost reduction in the overall plant investment. It is important to note that currently the major drawback of SOFC application in the energy sector is high upfront capital expenditures [65]. Therefore, for small-scale systems, internal dry reforming could also reduce the overall system costs, which is critical especially for systems less than 10 kW capacity.

However, gas impurities are generally considered to be detrimental to the reforming process and general operation of the SOFC system [61]. Among the impurities in the biogas, H_2S is considered as the most detrimental and thermodynamically stable gas at the common operating conditions of SOFCs [117]. It is generally agreed that H_2S may have an influence on both the chemical and electro-chemical reaction on the Ni-anodes [264][265]. These effects can be potentially influenced by a number of parameters ranging from fuel composition to materials from which SOFC anodes are developed [266]. In SOFCs, biogas dry reforming would be preferred to steam reforming since it is seen as a possible mechanism of cost and system complexity reduction [267]. Moreover, small scale SOFCs are being promoted by a number of companies [49][50][55] and such system would be suitable for internal dry reforming if they are to be fuelled by biogas.

It has been reported that H_2S content in the gas as low as 2 ppm already has an effect on the internal SOFC steam reforming process [268][269]. However, this effect could be different during dry reforming process in the presence of CO_2 [68]. Moreover, even with reformed gas, H_2S as low as 0.5 ppm has been reported to affect the electro-chemical performance of SOFCs at 750°C [270].

Under syngas operation, nickel-gadolinium doped ceria (Ni-GDC) anode material showed good performance as compared to other materials like nickel-yttria stabilised zirconia (Ni-YSZ) [97]. Ni-GDC has been reported to have an enhanced tolerance of H_2S in the presence of hydrocarbon (H/C) fuels and this is attributed to CeO_2 which enhances reforming and as well as H_2S tolerance [266]. Also, addition of Cu to Ni anodes could stabilise the active surface of the anode by limiting the rate of carbon deposition [271]. Therefore, the effect of H_2S on dry reforming could also be influenced by material composition of the anode [261].

Under steam reforming conditions, H_2S has been reported to have a larger effect on reforming activity than on the electro-chemical activity even at H_2S concentration of 2-4 ppm levels [268]. This is also in agreement with Aravind et al. [272]. This could be due to the different reforming and electro-chemical sites within the cell. H_2S has been reported to decrease the rate of the water gas shift reaction [270]. Therefore, the effect of H_2S on the performance of SOFCs generally depends on material composition of the anode and operating parameters such as temperature [273][274][275]. H_2S effect on the catalytic performance of a catalyst varies depending on the material composition [276]. Hence in the presence of reforming gases, H_2S could have an effect on both chemical and electro-chemical process and this effect would vary depending on the specific operational conditions of the SOFC, its material composition and fuel gas composition [277].

The effect of H_2S on dry reforming was investigated by Shiratori et al. [278]. In their experiment they used an electrolyte supported Ni-ScSZ cermet SOFC of 8x8 mm^2. A simulated biogas of CH_4/CO_2 = 1.5 at SOFC operating temperature of 1000°C was used at a current density of 200 mA cm^{-2}. Under these conditions, a 9% drop in voltage and 40% drop in reforming reaction rate was observed during poisoning of the cell by 1 ppm of H_2S. They observed that under these conditions, a concentration of 1 ppm H_2S is feasible during internal dry reforming. With real biogas, a constant voltage above 0.9 V was attained during the 50 h of operation with no observation of carbon deposition. Attempts to study the effect of H_2S on dry reforming by Xu et al. [279] was hindered by carbon deposition, therefore, no results were yielded from the experiment. Johnson et al. [280] studied the effect of H_2S on dry reforming under catalytic conditions. They found out that the effect of H_2S was more severe under steam reforming as compared to dry reforming. This is also re-affirmed by Lakshminarayanan et al. [281]. Also, it was reported that H_2S appears to increase the chances of carbon deposition [282]. Table 10 represents H_2S tolerance for different anode materials with varying gas composition and experimental conditions from selected literature.

It is generally agreed that H_2S may have an effect on the dry reforming process depending on the type of catalysts and operating conditions [283][284]. But detailed analysis is still required to investigate the H_2S concentration limit for SOFCs and the performance of the cell close to real operating conditions of normal sized SOFCs. Therefore, this research has given focus on investigating the effects of H_2S on dry reforming under both current load and open-circuit voltage (OCV) operating conditions of SOFCs. To the authors knowledge, no attempt has been done to investigate the effects of H_2S on dry reforming under typical SOFC operating conditions (800-850°C) of relatively large surface area SOFC (close to real operating conditions of normal sized SOFC) under current and OCV. Moreover, the boundary limit of H_2S concentration in fuel gas at a typical SOFC operational condition of 800-850°C with internal dry reforming has not been investigated.

Table 10. Studies on Sulphur poisoning during methane reforming process.

Cell/Catalyst	Fuel	Experimental Conditions	H_2S tolerance limit	Ref.
Planar SOFCs with (Ni/YSZ) anode support and an active Ni/YSZ anode, a YSZ electrolyte, and a lanthanum-strontium-manganite (LSM)/YSZ cathode. (Total area 5x5 cm^2, active area 4x4 cm^2)	13-46% H_2, 17-29% CH_4, 37-58% H_2O, 2-9 ppm H_2S (57-60% Fuel Utilisation)	T = 850°C, OCV and under current load 1 A/cm^2	Under current load, just below 7-9ppm is feasible for 24 hours period	[285]
Planar SOFC Ten Cell Stack (12x12 cm^2)	11.5% H_2, 10.5% CO, 12.5% CO_2, 1.5% CH_4, 63.2% N_2	T = 700°C, 800°C	10 ppm at 800°C	[286]
Anode supported SOFCs with Ni/YSZ anodes, YSZ electrolytes and LSM/YSZ cathodes (denoted as Ni, YSZ, LSM). The active area was 4 cm × 4 cm	13% H_2, 29% CH_4, 58% H_2O 2-24 ppm of H_2S.	T = 850°C. OCV and under 1 A cm^{-2} (0.44)	2 ppm for Ni/Sc-YSZ and less than 2 ppm for Ni/YSZ for 500 h	[269]
Ni/GDC, electrolyte supported, 100 cm^2 active area	Different percentages of H_2, CO, CH_4, CO_2,	T = 850°C, T = 920°C	Less than 2 ppm of sulphur deactivates the Ni/GDC anodes for methane reforming but not for oxidation of H_2 and CO	[272]

	N_2, H_2O0 – 2ppm of H_2S			
Ni-YSZ (uncoated and coated with Ni-CeO) button cells	32% CH_4, 48% H_2O, 20% CO_2, 200 ppm of H_2S	T = 850°C, at 0.5A cm^{-2}	20 ppm caused irreversible loss for uncoated cell and reversible loss for the coated loss	[279]
Anode supported cells with Ni/YSZ anodes, YSZ electrolyte and LSM/YSZ cathodes, 5x5 cm^2	26% H_2, 32% H_2O, 20% CO, 22% CO_2 at 850°C and 27% H_2, 31% H_2O, 19% CO and 23% CO_2	T = 750°C and T = 850°C, at 0.25-0.5 A cm^{-2}	Less than 8 ppm was possible for CO containing fuel and less up to 90 ppm for H_2/H_2O fuel	[287]
LSV, La0.7Sr0.3VO_3/YSZ and LSV/GDC	24.1% H_2,28.6% CO, 3.2% N_2, 12% CO_2, 27.1% H_2O, 300 ppm	T = 800°C, T = 900°C, electro-catalytic conditions	LSY/GDC showed significant difference between H_2 and syngas/H_2S gas as compared to LSV/SYZ under similar conditions	[288]
La0.4Sr0.5Ba0.1TiO3 (LSBT) anode-based solid oxide fuel cell/SYZ electrolyte YSZ (LSBT powders)	0.5% H_2S, CH_4 (C:H ration1.9-2.5), 3% H_2O	T = 900 K-1100 K	In the presence of H_2O, H_2S appear to increase the effect of carbon deposition.	[282]
Ni/8YSZ planar anode supported SOFC 5x5.8 cm (active area 4x4 cm)	31% H_2, 42% CO, 12% CO_2, 12% N_2, 3% H_2O (H_2O was increased from 3-10%), 12.5 ppm	T = 800°C	CO_2 and H_2O content appear to be beneficial to mitigate the H_2S poisoning effect. However, the effect is higher as compared to H_2/N_2 fuel	[289]

Ni/YSZ, 12.5x12.5 cm (121 cm^2 active area)	25%, 35%, 50% DIR of CH_4 with H_2O, 1 ppmv H_2S	T = 750°C, CD = 0.5 A cm^{-2} fuel utilisation and air utilisation 60% and 35% respectively.	1 ppmv of H_2S caused increased degradation as the percentage of direct internal reforming (DIR) increases.	[257]
Ni/8YSZ cerment with LSCF cathode with CGO inter diffuser barrier	11.43-15.8% H_2, 9.12- 11.82% H_2O, 44.75-55.15% N_2, 14.12-16.24% CO, 10.18-11.39% CO_2	T = 750°C, CD = 1 A cm^{-2}	0.1 ppm of H_2S caused a 20% performance loss. There was performance degradation delay of 20 h followed by stabilised performance of the cell after 20 h.	[270]
Ni/8YSZ anode with LSCF cathode and CGO inter layer (50 x 50 mm^2)	0.15% H_2, 0.15% H_2O, 0.15% CO, 0.13% CO_2 and 0.45% N_2	T = 800°C, pO_2 cathode = 0.12 atm	With 0.1 ppm H_2S in the gas, no significant degradation of the polarisation was observed for 100 h. However, for 0.5 ppm H_2S, considerable increase of the polarisation resistance of the cell was observed. A decrease in the water gas shift reaction is reported.	[290]
Ni/8YSZ with $La_{1-x}Sr_xMnO_3$/YSZ cathode (4 x 4 cm) active area	4% CH_4, 5% CO, 13% CO_2, 48% H_2, 30% H_2O, H_2S 2 ppm	T = 800°C, OCV and CD = 0.625A cm^{-2}	At 2 ppm of H_2S, methane reforming process was inhibited both at OCV and under current conditions	[291]
Ni/YSZ powder catalyst (250 mg)	5% CH_4, 10% H_2O, 35% N_2 and 50% He, 5% CO_2, 5% O_2, 40% N_2, 50% He	T = 700°C	50 ppm caused a drop in methane reforming under catalytic conditions, however the effect of H_2S on methane reforming is more severe under steam reforming as compared to dry conditions.	[281]
Electrolyte supported Ni-ScSZ cermet	CH_4/CO_2 = 1.5	T = 1000°C, CD = 200 mA cm^{-2}	1 ppm of H_2S caused 9% voltage drop and about 40% decrease in the reaction rate of internal dry reforming.	[278]

Anode supported Ni-ScSZ with LSM cathode	S/C =1.5 (also octane fuel)	T = 800°C, CD 40 mA cm^{-2} for 5 h	5 ppm of H_2S in the gas increased the methane concentration in the anode off gas from less than 10% to 40%	[292]
Reformax®	58% CH_4, 39% CO_2	T = 650°C – 850°C	0.5 mol % of H_2S cause a decrease in reforming from 67% to 19%	[283]
250				

3.2 | MATERIALS AND METHOD

It is hypothesised that the effect of H_2S on dry reforming will vary depending on operating conditions. Hence, experiments were conducted under different operating conditions.

3.2.1 | Experimental setup

Experiments have been conducted to evaluate the performance of a SOFC under dry reforming in the presence of H_2S at 800°C. The setup used is shown in Figure 9. In this experiment, commercial Ni-ScSZ electrolyte supported cells with an active area of 81 cm^2 were used.

The gases were supplied from gas bottles. Composition and flow rate were varied using mass flow controllers (MFC) (Bronkhorst High-Tech BV). The inlet gas to the anode was trace heated to 130°C. Temperature of the oven was maintained by 4 electrical heaters controlled by the furnace control unit. The performance of the cell was analysed by Gammry FC-350. Outlet gas composition was analysed by micro gas chromatograph device. The anode outlet gas was dried using silica gel for analysis in Agilent 490 micro-GC columns (Molsieve 5A and PoraPLOT U). The cell temperature was measured by the k-type thermo couple (RS PRO, −50°C/+1200°C) closely placed at the anode side. The cells were placed between two ceramic blocks. To ensure gas tightness, mica (thermiculite) sheets were placed in the anode side and in the cathode side. To enhance gas sealing, extra weights were added on the top of the block as represented in Figure 9. For further details of the set up the reader is referred to Saadabadi et al [293].

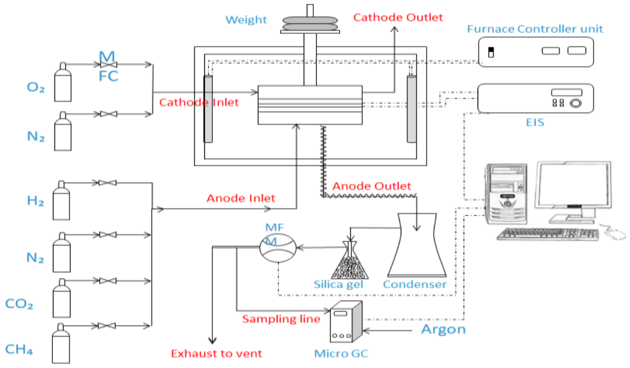


Figure 9. Schematic of the experimental test station (Reproduced with permission from Saadabadi et al. [293]*).*

3.2.2 | Experimental procedure

The cells were preheated by heating the furnace to 1000°C at a ramp rate of 50°C h^{-1} with N_2 gas flowing at a rate of 1200 mL min^{-1} to the anode and cathode. At 950°C, the NiO of the anode was reduced by feeding H_2 to the anode and simulated air (O_2 and N_2) to the cathode. During cell reduction, the concentration of H_2 gas was gradually increased from 2% to 100% in 4 h. The current–voltage measurements were carried out after the cell reduction procedure.

The cells were fed with CH_4, CO_2 and N_2 mixture with different compositions. H_2S injection was carried out by including H_2S in the gas mixtures which was in N_2 bottle. The concentration of H_2S in the fuel gas was varied by changing the flow from H_2S/N_2 (H_2S concentration of 50 ppm) bottle and compensating it with the flow from N_2 bottle to maintain a total of 1200 NmL min^{-1}. The ratio of CH_4:CO_2 in this experiment was 2:3. The ratio was chosen to have enough CO_2 which can supress carbon deposition [69][294]. After poisoning with H_2S, the cells were recovered using pure H_2 balanced with N_2 gas for 12 h.

To determine the effect of H_2S on dry reforming under current conditions using a Ni-ScSZ cell, a constant current of 2 A (250 A m^{-2}) was drawn from the cell using CH_4:CO_2 of 2:3 as fuel at 800°C. Starting with H_2S concentration of 0 ppm, the cell was poisoned with 0.125 ppm and the percentage of CH_4 reformed was monitored by samples analysed in the Agilent 490 micro-GC columns until the cut off voltage of 0.6 V which was monitored by Gammry FC-350. The percentage of CH_4 reformed was calculated based on the carbon balance of outlet gas composition described in Saadabadi et al [293]. The experiment was repeated by increasing the H_2S concentration to 0.5 ppm and 1 ppm. To determine the effect of H_2S on dry reforming under OCV conditions (purely dry conditions), the experimental conditions were maintained and the cell was poisoned by H_2S concentration of 0.125 ppm.

In order to determine the contribution of the cell material (catalyst) to the H_2S effects on reforming, the experiment was repeated using dummy cell mica (thermiculite) sheet. The effect of H_2S on reforming was evaluated at CH_4:CO_2 of 2:3 and at 800°C dummy cell temperature.

3.3 | RESULTS AND DISCUSSION

3.3.1 | Effect of H_2S on dry reforming on Ni-ScSZ under current

Using the Ni-ScSZ electrolyte supported cell under a current of 2 A (250 A m^{-2}) at 800°C cell temperature and CH_4:CO_2 ratio of 2:3, it was observed that with no H_2S in the fuel gas (0 ppm), CH_4 reforming was more than 95%. If H_2S is gradually introduced in the gas, then the reforming efficiency (methane conversion) is reduced with time. Figure 10 shows how the concentration of H_2S in the gas affected both the cell voltage and the dry reforming process. With H_2S concentration of 0.125 ppm in the gas, there was no effect observed in the percentage of CH_4 reforming (X_{CH4}) for 4 h. Also, the cell voltage was stable for the first 4 h. After 4 h, CH_4 reforming started decreasing and a decrease in the cell voltage was observed. Between 4 and 10 h, a gradual decrease in the CH_4 reforming process and a decrease in cell voltage was observed. At the cut off voltage of 0.6 V, CH_4 reforming process had decreased to 10%. The decrease in cell voltage can be attributed to the decrease in CH_4 reforming. These results suggested that the effect of H_2S is more pronounced at the reforming sites. A similar trend was observed when the H_2S concentration in the gas was increased to 0.5 ppm and 1 ppm but in a shorter period. This trend suggested that the decrease in cell voltage resulted from a reduction in H_2 and CO due to the reduced percentage of CH_4 reformed. It was reported that sites for reforming (catalytic sites) are different from electro-chemical sites [286]. It seems that under dry reforming conditions, H_2S is adsorbed to the reforming sites. Similar to steam reforming, H_2S has an effect on the electro-chemical activity during dry reforming [268][286]. These results have a good agreement with what was reported by Shiratori et al. [278]. They observed that H_2S can affect the reforming and electro-chemical performance of the cell but the performance of the cell was tolerant to 1 ppm at 1000°C. However, present research has revealed that 1 ppm of H_2S is not feasible in internal dry reforming at temperatures of 800°C. Results showed that H_2S concentration in the gas as low as 0.125 ppm can affect the cell voltage and the internal dry reforming process in SOFCs operating at 800°C within only 4 h of operation [278].

It was also observed that after poisoning the cell with 0.125 ppm of H_2S, the initial cell voltage slightly dropped (Figure 10). This can be attributed to incomplete sulphur desorption during cell recovery. The current-voltage (IV)-

curves were obtained with pure H_2 after recovering the cell, and before the next reforming process. The IV curves (Figure 11) showed that H_2S caused a small drop in performance.

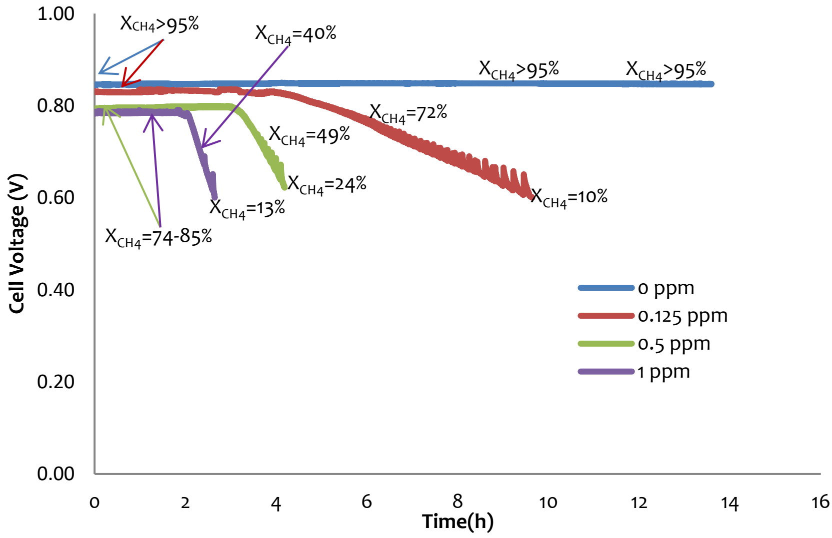


Figure 10. The effects of H_2S on dry reforming (X_{CH4} is percentage of CH_4 reformed) and performance of the Ni-ScSZ cell under current of 2 A at 800°C and CH_4:CO_2 of 2:3

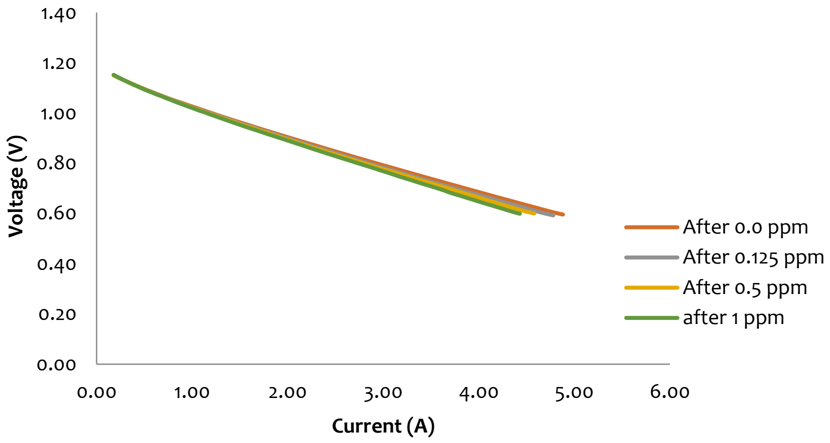


Figure 11. Current-Voltage curves of the cell during different points of the experiment at 800 °C and CH_4:CO_2 of 2:3.

3.3.2 | Effect of H_2S on dry reforming on Ni-ScSZ at OCV

The experiment was repeated when the cell was at OCV. A decrease in the CH_4 reforming process was observed after two hours of injecting 0.125 ppm of H_2S in the fuel gas (Figure 12). The CH_4 reforming process and cell OCV decreased from 47% to 4% and 0.96 V to 0.85 V respectively in 3 h. When H_2S injection was stopped, methane reforming and OCV were recovered from 4% to more than 41%. This is also in agreement with Chattanathan et al. [283] who observed that 0.5 mol% of H_2S caused a decrease in dry reforming to 19% using a Reformax 250 catalyst in a bed reactor. This research has revealed that even at purely catalytic conditions, H_2S as low as 0.125 ppm cause a severe decrease in dry reforming at operating conditions of SOFCs. While Johnson et al [68] has reported that 25 ppm affects dry reforming on crashed anode catalyst (Ni-ScYSZ and Ni-ScYSZ/Pd-CGO), we report that even 0.125 ppm can affect dry reforming on an electro-chemically performing complete solid oxide fuel cell with Ni-ScSZ anode.

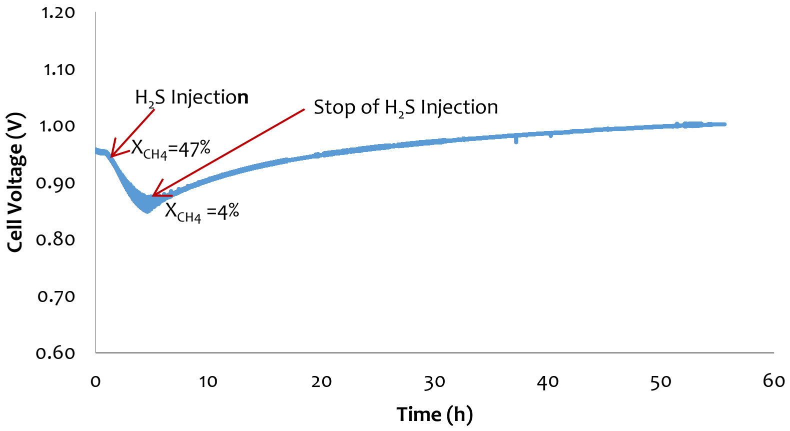


Figure 12. The effect of 0.125 ppm H_2S on dry reforming and performance of the cell with a Ni-ScSZ cell at OCV at 800°C and CH_4:CO_2 of 2:3.

3.3.3 | H_2S effect on dry reforming with and without a catalyst

Reforming has been assumed to take place on the cell and to a small extent on the current collector [46]. However, it is possible that other process equipment such as stainless steel may contribute to catalytic dry reforming [295]. Therefore, to test the catalytic reforming effect of H_2S purely on the cell, the experiment was carried out using the mica sheet (dummy cell) and the real cell without a current corrector.

To test the reforming and the effect of H_2S on reforming without catalysts (Ni-ScSZ cell and Pt current collector), the experiment was conducted using a dummy cell (mica sheet) in a ceramic block without platinum mesh (as the current collector) at 800°C. The same procedure was repeated using a real cell in a ceramic block without platinum mesh for comparison. It was observed that even when the cell was taken out (with mica sheet as a dummy cell), CH_4 dry reforming took place though lower than in presence of the cell. Figure 13 shows the effects of H_2S on dry reforming with and without the cell. With a dummy cell, the percentage of CH_4 reformed (X_{CH4}) was 8%. When 0.125 ppm H_2S was injected, X_{CH4} decreased to 0.5% in 1 h. These could imply that H_2S could also affect the reforming reaction even without a cell. However, when H_2S was stopped, the CH_4 reforming was recovered. A similar trend was observed when a real cell (without platinum wire mesh) was used. A percentage of over 90% of CH_4 reforming was observed before injection of 0.125 ppm of H_2S in the fuel gas. When H_2S was injected, the X_{CH4} decreased to below 20% and it was recovered when H_2S injection was stopped.

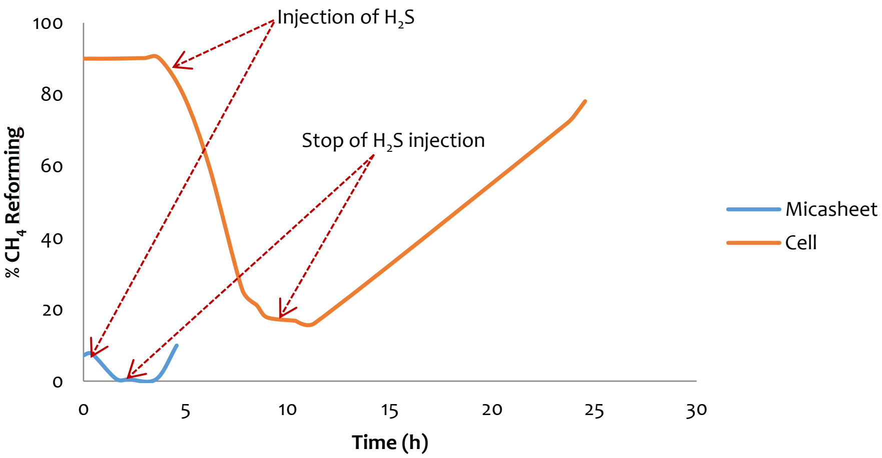


Figure 13. Effect of H_2S on CH_4 reforming without and with a catalyst at 850°C.

From Table 10, it appears from different authors that 1-2 ppm H_2S concentration is feasible for steam reforming using carbon containing fuels. Also, Johnson et al. [68] observed that dry reforming was more tolerant to H_2S poisoning than steam reforming. However, from this research, dry reforming is greatly reduced by H_2S poisoning even at very low ppm levels, i.e., a 0.125 ppm H_2S concentration in the gas resulted in a significant decrease in the reforming process. This suggests that H_2S as low as 0.125 ppm affect the catalyst on the reforming sites of SOFCs.

3.4 | CONCLUSIONS

It has been observed that methane dry reforming in biogas fed SOFC is affected by H_2S even at concentrations as low as 0.125 ppm H_2S in biogas with Ni-ScSZ cell. This H_2S concentration is far below the threshold of 1 ppm which is normally reported in literature. H_2S appeared to influence the reforming in the cell chamber even when the mica sheet (dummy cell) was used. Therefore, if biogas is to be used as fuel for SOFCs and internal dry reforming is envisaged, a stringent cleaning system is required, which can clean the gas to nearly zero ppm of H_2S level. With up-to over 2000 ppm of H_2S concentration in biogas reported in literature, such a stringent gas cleaning system needs to be carefully designed to meet the conditions of internal dry reforming in SOFCs. Otherwise, an external reformer for dry reforming of CH_4 is required.

While the results obtained from experiments are presented, it appears that the influence of H_2S on different types of anodes under different fuel conditions including dry reforming need detailed studies. Therefore, further studies are required to investigate the effect of H_2S in the presence of hydrocarbon fuels to facilitate SOFC systems design for real life applications and material selection for systems components.

Off-grid informal settlements

4

Field based Study of cost reduction strategies

Improvement of Biogas Quality and Quantity for Small-Scale Biogas-Electricity Generation Application in off-Grid Settings : A Field-Based Study

Published as: H. Wasajja, S.A.A. Al-muraisy, A.L. Piaggio, P. Ceron-chafla, P.V. Aravind, H. Spanjers, J.B. Van Lier, R.E.F. Lindeboom, Improvement of Biogas Quality and Quantity for Small-Scale Biogas-Electricity Generation Application in off-Grid Settings : A Field-Based Study, Energies. 14 (2021) 3088. DOI: https://doi.org/10.3390/en14113088.

ABSTRACT

Electrical power generation on small scale (< 100 kW) from biogas plants to provide off-grid electricity is of growing interest. Currently, gas engines are used to meet this demand. Alternatively, more efficient small-scale solid oxide fuel cells (SOFCs) can be used to enhance electricity generation from small-scale biogas plants. Most electricity generators require a constant gas supply and high gas quality in terms of absence of impurities like H_2S. Therefore, to efficiently use the biogas from existing decentralized anaerobic digesters for electricity production, higher quality and stable biogas flow must be guaranteed. The installation of a biogas upgrading and buffer system could be considered, however, the cost implication could be high on small-scale as compared to locally available alternatives such as co-digestion and improved digester operation. Therefore, this study initially describes relevant literature related to feedstock pre-treatment, co-digestion and user operational practices of small-scale digesters, which theoretically could lead to major improvements of anaerobic digestion process efficiency. The theoretical preamble is then coupled to the results of a field study, which demonstrated that many locally available resources and user practices constitute frugal innovations with potential to improve biogas quality and digester performance in off-grid settings.

Key words: Biogas quality; biogas quantity; anaerobic digestion; electricity generation; pre-treatment; co-digestion; user practices

4.1 | INTRODUCTION

Biomass is a traditional source of energy for resource-constraint communities, which are disconnected from the central grid [19]. However, combustion in low-cost furnaces often leads to health and environmental concerns [296]. Biogas production from biomass could mitigate these negative health and environmental effects, while safeguarding energy access for disadvantaged communities, especially if local residues such as faecal matter and animal waste are utilised as feedstock. Until recently, biogas from small-scale digesters has been predominantly used for thermal energy generation for cooking purpose application. However, concomitant with the demand for rural electrification, there has been a growing interest for small-scale electrical power generation from biogas as a complementary solution to PV-battery based systems [19].

Electricity production from small-scale biogas installations using conventional technologies such as internal combustion engines (ICEs) can be economically advantageous compared to subsidised costs of electricity from fossil fuels, which require large-scale infrastructure [297]. With the introduction of the state-of-the-art small-scale solid oxide fuel cells (SOFCs) with a power output of less than 5 kW [298], a significant electrical efficiency gain could be made that could accelerate the integration of biogas in rural electrification schemes. However, from literature reviews [58,299], small-scale electricity generation using biogas as a SOFC fuel would require a different biogas quality compared to ICEs. For the SOFC, macro-pollutants like CO_2 and water vapour have no negative impact and may be used for dry and steam reforming, thereby omitting the need for biogas upgrading. However, the SOFC is much more sensitive to trace impurities such as H_2S, siloxanes and other volatile organic compounds (VOCs) compared to conventional electrical generators including its process equipment. For example, ICEs have a reported tolerance as high as 150 ppm for H_2S [52,124], whereas a 2 ppm(v) for H_2S and ppb level for siloxanes, have been reported to negatively affect SOFC performance, depending on the operational conditions [62,80]. It should be noted that both technologies will require biogas cleaning since reported H_2S concentrations in biogas may reach values as high as 2,000 ppm, depending on the used feedstock [80,300].

Quantitatively, electricity generation from biogas through a SOFC and other technologies such as ICEs also has different requirements [58,299] compared to biogas for cooking [301]. This is because, constant power supply is usually required as compared to cooking, which is done in intervals. Likely, more biogas production is required if biogas is used for power generation.

So, to further explore the potentials of biogas-electricity generation systems for rural electrification schemes, both the required stringent biogas quality levels and continuous biogas supply for SOFC and other technologies like ICEs operation should be secured in a local resource-constraint context. Many of the biogas cleaning and upgrading techniques that are commonly proposed in literature are based on technologies developed in affluent societies and/or research environments [299]. The same is true for many of the feedstock pre-treatment methods for enhanced biogas production [302]. The current study, takes a new direction and emphasizes the role of local operational practices on digester performance [299] as a first step to prevent or minimize the dependency on additional process equipment, while not compromising on biogas quality and quantity.

In order to do so, pre-treatment and other operational practices that could enhance biogas quantity and quality for small-scale electricity generation from biogas have been identified from literature. With these operational practices in mind, a field study with 48 Ugandan digesters was performed to identify promising local operational practices and resources. Afterwards, field observations have been compared to literature and the most beneficial opportunities were derived and integrated into a proposal for a frugal biogas-electrical generation system.

4.2 | MATERIALS AND METHODS

4.2.1 | Identification of operational practices and reactor designs suitable for small-scale digesters

The study was carried out through literature review of potential feedstock pre-treatment, co-digestion and user operation practices that can potentially enhance the anaerobic digestion (AD) process efficiency. Innovative design and operations in small-scale digesters that can potentially enhance the AD process efficiency were also reviewed.

4.2.2 | Observation of local operational practices and reactor designs through field study

The theoretical framework is coupled with the field survey of 48 digesters (Table 11) in central and western Uganda to investigate the locally available opportunities for enhancing the AD process efficiency in small-scale digesters. Common user practices were monitored during one-multiple day site visits and observations were classified based on the parameters defined in results section 4.3.

During these site visits, digester users were asked inquiry questions, meanwhile their operational practices such as feedstock storage were observed and digesters were visually inspected. Analysis of feedstock and slurry pH and biogas composition in terms of H_2S, CH_4 and CO_2 was also performed during field visits. The H_2S content in the biogas from various digesters was measured at the cooking side using a hand sampling pump (Dräger accuri, Luebeck, Germany) equipped with various H_2S measurement tubes (Dräger, Luebeck, Germany). The measurement range of the different H_2S Dräger tubes was from 0-2,000 ppm and 0-7%. The biogas major composition of CH_4 and CO_2 was also analysed using a portable gas analyser (Geotec Biogas 5000, Chelmsford, United Kingdom). Gas samples from the cooking side, which were taken from a disconnected gas pipe normally connected to the stove, were captured using gas lock-syringes which were connected to the portable gas analyser for analysis. Temperature and pH of feedstock and slurry were measured using two portable pH meters. One was Greisinger G 1500 series, Regenstauf, Germany with pH resolution of 0.01 and temperature of 1°C. Second was Ohaus ST10, Nänikon, Switzerland with pH resolution of 0.1 without a temperature sensor.

Samples of feedstock, slurry and urine were collected in the field and their sulphur and elemental content were analysed in the laboratory using ICP-OES 5300DV (Perkin Elmer Optima, Waltham, Massachusetts, USA). Samples were diluted to 50 mL with demineralised water and HNO_3 to facilitate the destruction process. All 50 ml samples were destructed in the microwave. The destruction time in the microwave was 60 minutes at a maximum power of 1300 W.

Table 11. (a) Type of feedstock used and (b) the size of the digesters visited during the fieldwork in Uganda.

(a) (b)

Type of feedstock	Number of digesters depending on the type of feedstock	Size of the digesters (m³)	Number of digesters depending on the size
Pig dung with water as solvent	6	6	11
Pig dung with urine as solvent	1	9	24
Chicken droppings	1	13	9
Cow dung and human waste*	4	30	1
Cow dung with urine as solvent	15	40	2
Cow dung with water as solvent	21	60	1
Total	**48**		**48**

* Toilet linked digesters

4.2.3 | Towards a conceptual frugal small-scale design for Uganda/ East-Africa context

Evaluation of the observations were compared to literature and the consequences for reactor performance were deduced qualitatively. For each aspect, one or multiple modifications were proposed, culminating in a conceptual frugal design of a small-scale digester adapted to the resource - constraints of the local situation.

4.2.4 | General description of Ugandan and East African climate conditions affecting bio-digestion

The rural areas in Uganda that were chosen for this field study are characterized by abundant solar irradiation reaching 4-6 kWh m^{-2}/day, few clouded days, and an ambient temperature between 20 and 25°C year-round [303]. Precipitation ranges between 1 and 60 mm daily [303]. These areas are home to many farmers that have cattle, but also agricultural production of crops is common. There is ample vegetation and agriculture such as plantation of cassava, banana, mango and jack fruit. Biomass residues of such plantations are easily accessible for co-digestion. Some farmers have their own pastures and practice zero-grazing, while for others, their cattle roam freely, but often can spend the night together in a kraal (shade where cows sleep) near homesteads. Over the course of the years, NGOs have been actively disseminating fixed dome digesters that are commonly used in rural areas. It is considered that the climatic condition is representative of many other global sunbelt locations.

4.3 | LITERATURE IDENTIFICATION OF OPERATIONAL PRACTICES AND AD REACTOR DESIGNS SUITABLE FOR SMALL SCALE DIGESTERS

Literature on biogas is extensive and many parameters have been shown to influence the quality and quantity of biogas produced from AD. The aim of this section is to derive hypotheses for the relevance of parameters given the local physical and socio-economic conditions. The outputs have been summarised in Table 14.

4.3.1 | Pre-treatment

Pre-treatment is mostly applied to feedstock from complex organic sources such as plant waste, whose biodegradability needs to be improved to enhance methane production [304]. Pre-treatment can be categorised as physical, chemical, physicochemical, biochemical and biological pre-treatments [305]. If more than one feedstock is to be used for AD, often only the most complex organic source is considered for pre-treatment to reduce the associated costs [304].

Physical pre-treatment methods include milling, chipping, gridding, ultra-sonication and irradiation. Milling is used to reduce the size of the substrate, which increases the particle surface area available for enzyme attack. Colloid mills, fibrillator, and dissolvers are majorly used for wet materials and fats whereas for dry materials, extruders, rollers, as well as cryogenic and hammer milling are majorly applied [305]. Although, milling pre-treatment methods have some drawbacks which include high energy consumption [305], for small scale application, manual milling can be considered. For small scale biogas applications in Uganda, there is a huge potential of biogas feedstock, especially from plant waste such as locally available banana leaves. If pre-treatment, such as using a simple mechanical grinder is embraced, it would distinctly increase feedstock availability for co-digestion with the usual animal waste.

Irradiation such as gamma rays, electron beam and micro wave can be used as a pre-treatment method for lignocellulosic wastes. Gamma rays pre-treatment helps to increase accessible surface area and pore size, decreases the degree of polymerization and cellulose crystallinity in biomass hence improving enzymatic hydrolysis in lignocelluloses [306]. For this type of pre-treatment to be applied in small scale digesters, the sun can be used as a source of radiation especially for sunbelt countries. Other physical such as ultra-sonication, lysis centrifugation and high-pressure pre-treatment may not be readily applicable in small scale settings due to their high energy consumption which may not be compensated by extra methane yield [304,305,307].

Physico-chemical pre-treatment usually concerns thermal treatment (hot water and steam explosion) and ammonia fiber explosion [308]. Thermal pre-treatment can be categorized as high temperature pre-treatment (150-220˚C), which sometimes involves steam explosion and mildly elevated temperature pre-treatment (60°C-90°C) [304]. High temperature pre-treatment requires a reliable source of heat if it is to be applied in AD which may not be readily available especial for small scale digesters.

Pasteurization methods or relatively low temperature pre-treatment have been investigated by a number of researchers. An increase in the methane yield by 30-40% has been reported when low temperature pre-treatment is applied to feedstock [309]. For some feedstocks, such as waste activated sludge (WAS), this type of pre-treatment, has shown a positive impact on the AD process [307], however, feedstock with high concentration of carbohydrates may not be suitable for pre-treatment at temperatures exceeding 70-80°C [310]. The low efficiency at these temperatures was attributed to the occurrence of the Maillard-reaction, creating refractory organic matter from carbohydrates with proteins [307,310]. The availability of easily harvestable solar energy, especially in tropical countries, may facilitate thermal pre-treatment by means of solar thermal concentration. This could provide an alternative pre-treatment method for small scale applications. In addition, for a biogas-electricity generation system, the waste heat from devices such as SOFCs with a typical operating temperature above 700°C, can also be used as a thermal source for feedstock pre-treatment.

Chemical pre-treatment may include alkali pre-treatment, alkali peroxide pre-treatment, organosolv (lignocelluloses is mixed with organic solvent and water, the mixture is then heated), wet oxidation, diluted acid at high temperature or concentrated acid at low temperature (acid hydrolysis) [305]. This pre-treatment is reported to be effective in enhancement of methane production and feedstock bio-digestibility [311–313]. However, it should be noted that the use of chemicals may have a negative effect on the quality and quantity of biogas due to inhibition caused by, for example, the accumulation of cations [314]. Alkalis such as NaOH may result into excess Na^+ concentration which may slow down microbial growth [314]. Therefore, chemical pre-treatment methods may distinctly increase the operation cost of small-scale biogas-electricity generation system since it involves the use of chemicals. Moreover, the logistic management associated with chemical dosage need to be carefully considered against its merits.

Biological pre-treatment using different species of fungi generally enhances biodegradation of feedstock and hence improves biogas yield [305,315,316]. Utilization of biological methods is attractive from the economic point of view however these methods are slow and require a large area as well as careful control of bacterial or fungal growth [317]. Although this pre-treatment is cost effective, it may not be technically feasible in small scale biogas-electricity generation applications.

4.3.2 | Co-digestion

Co-digestion is the simultaneous treatment of two or more waste streams with complementary characteristics [318][319]. Traditionally, co-digestion was focused on common feedstocks such as cow dung and pig manure and less attention were given to other feedstocks. However, recently research is being carried out on various types of feedstocks in order to develop a more efficient waste treatment strategy and widen the scope of energy generation by AD depending on feedstock availability in a particular location.

Different feedstocks have different properties and composition and even cow dung from different breeds may have different composition [320]. Co-digestion can potentially counter solve drawbacks linked to feedstock properties in single feedstock AD, apart from improving the quality and quantity of biogas [304]. Such drawbacks include low content of biodegradable organic matter for substrates like WAS and animal dung, high concentration of N in substrates such as animal manure, which may inhibit methanogenesis; the presence of heavy metals in substrates such as municipal solid waste (MSW), and seasonal availability as in the case of agricultural waste [304]. Therefore, co-digestion is likely to balance the feedstock composition with in the non-toxic ranges for microbial growth.

Co-digestion of various organic feed stocks has been reported to enhance biogas yield from anaerobic digesters by over 60% [321]. Feedstocks, such as mixed food waste were reported to have a high methane yield [322]. Co-digestion may enhance the economic returns of small energy systems through increased biogas production. Kaparaju et al. [323] reported that co-digestion could have both economic and bio-technical advantages as far as energy generation from biogas is concerned. They further reported that co-digestion helps in maintaining the pH in optimal ranges during methanogenesis and overcoming ammonia inhibition, which is associated with pure manure digestion. This in turn, increases the methane yield and hence reduces the investment costs of biogas-based power plants.

Callaghan et al. [324] investigated the effect of co-digestion on the methane yield on a laboratory scale digester at a loading rate of 3.2 to 5.0 kg VS m^{-3} d^{-1} and hydraulic retention time (HRT) of 21 days. They found that co-digestion of cow dung with food and vegetable waste in a ratio of up to 1:1 (cow dung: food and vegetable waste) increased the rate of biogas production, whereas co-digestion of cow dung with chicken manure did not yield satisfactory results. This was attributed to the high concentration of free ammonia in the liquor of more than 100 mgL^{-1}. Bothi et al. [325] reported that addition of food waste to cow dung can potentially reduce the H_2S content in biogas and also increase the methane yield depending on the elemental composition of food waste. Co-digestion of cow dung with coffee pulp was studied by Corro et al. [326]. They observed that co-digestion of cow dung and coffee pulp increased the C/N ratio of the substrate from 5 to over 50 and this enhanced methane yield. They also observed that co-digestion of cow dung with coffee pulp can potentially reduce the H_2S content of biogas [326]. This occurs due to a synergistic effect: cow dung contains a high concentration of microorganisms, whereas coffee pulp contains nutrients that are essential for bacterial growth or may precipitate with H_2S [326]. Co-digestion of cow and pig dung was reported to increase the methane yield and an optimal ratio of 1:1 by volume is proposed by these researchers [327]. Moreover, wall paper has been reported to be a potential co-feedstock for cow dung [328]. Even under cold climate conditions where digesters operate at psychrophilic conditions, co-digestion of cow and sheep dung was reported to increase biogas production by 100% in comparison to cow dung mono digestion [329].

The effect of co-digestion of cow dung and organic fraction of municipal solid waste (OFMSW) on methane yield was investigated by Hartmann et al. [330]. They used a continuous stirred-tank reactor (CSTR) under thermophilic conditions (55°C) at HRT of 14-18 days and organic loading rate (OLR) of 3.3-4.0 g VS $L^{-1}d^{-1}$. Their results showed that co-digestion of cow dung with OFMSW at a ratio of 50% (VS/VS) enabled stable operation conditions and increased methane yield. Co-digestion of OFMSW with cow dung and cotton gin waste (CGW) was analysed by Macias-Corral et al. [331] in a two-stage pilot anaerobic digester. They observed that co-digestion of cow dung with CGW yielded 87 m^3 of methane/ton on dry matter basis as compared to digestion of cow dung alone which yielded 62 m^3 of methane/ton. Co-digestion of OFMSW with cow dung had a much higher biogas production rate (172 m^3 of methane/ton) as compared to cow dung alone [331]. They further observed that cow dung contains native cellulose degrading microorganisms and nutrients, which reduces imbalances in single feedstocks and hence improves biodegradation. They also observed that a two-stage digester produces a higher methane content (more than 72% methane) as compared to a single stage digester with typical gas production containing 60% methane. The higher methane content in a two-stage digester could be attributed to more CO_2 production in the first stage and less CO_2 production in the second stage.

Kaparaju et al. [323] analysed the potential of co-digestion of pig manure with potato waste (potato stillage and potato peels) in a laboratory scale digester at a loading rate of 2 kg VS m^{-3} d^{-1} in a CSTR at 35°C. They found that potato waste increased the methane yield from 0.13-0.15 m^3 kg^{-1} of volatile solids to 0.30-0.33 m^3 kg^{-1} of volatile solids if it is co-digested with pig manure in a proportion of up to 15-20%. The increase in methane yield was attributed to the high starch content in potato waste since digestion of pig manure alone results in detrimental effect of the AD process. This waste contains more lignin, a considered refractory compound capable of inhibiting the degradation of other components like cellulose [323]. Liu et al. [332] studied the co-digestion of kitchen waste (fruits, vegetables, meat, fish and staple foods), cow and pig dung under thermophilic conditions (53°C) at controlled pH of 7.5-7.8. They observed that if limited amount of kitchen waste (2-3%) is co-digested with cow and pig dung, it can potentially improve the digestion process of both cow and pig dung. The feasibility of co-digestion of food waste and piggery wastewater was investigated by Zhang et al. [333] in a laboratory scale digester. They found that piggery wastewater has trace elements such as Na, Mg, Al, etc. which supplemented the food waste and enhanced co-digestion performance.

Co-digestion has been reported to potentially enhance biogas yield and therefore increase the economic returns of the biogas-based energy system. As reported before, cow digestion of animal manure with other feedstock such as kitchen waste and plant waste can increase the efficiency of AD process. Kitchen and plant waste is commonly and locally available to small scale digester operators although some waste such as WAS may be difficult to access and possibly costly to transport. Therefore, the usual animal waste can be supplement with other wastes which are available depending on the location and geographical condition. However, care should be taken when choosing the co-substrates since the selection should favour syntropy between different microorganisms, dilute harmful compounds, optimize methane production and maintain digestate quality [304].

The literature survey on the effect of co-digestion on biogas quality and quantity in Table 12 show that biogas composition varies depending on types of feedstocks used for co-digestion. Although, there are other parameters such as hydraulic retention times (HRT) and experimental conditions which may contribute to alter biogas composition, generally the composition depends on the type of feedstock used. It is further noted that co-digestion can have an effect on H_2S content in the biogas. The biogas analysis from both co-digestion laboratory experiments and field measurements (Table 12) showed a lower H_2S content compared to the biogas from single substrate digesters. For example, co-digestion of cow dung with coffee pulp reduced the H_2S content in the gas from 3% to 2% [326]. Co-digestion might be of interest for the biogas-electricity generation system since it can reduce the cleaning requirement of biogas fuel for appliances such as SOFCs when properly selected co-substrates are used.

Therefore, the right co-substrate has to be chosen to avoid drawbacks like unexpected overloads which can result in VFA and ammonia inhibition [304]. Co-digestion substrates need to be carefully selected to guarantee enhanced biogas production but also to lower impurities like H_2S in the biogas. As discussed in this section, co-digestion can potentially enhance biogas quality and quantity. Particularly, for small scale biogas-electricity generation applications, co-digestion may ameliorate system reliability by enhancing biogas fuel production for electrical power generation. Also, co-digestion can potentially reduce H_2S in the biogas and this in turn will lead to lower operational costs of the cleaning unit coupled to such systems [299].

4.3.3 | Additives that enhance biogas quality and quantity

Heavy metals are essential as micro-nutrients for anaerobic bacteria and archaea [334]. Metals are required in a specific amount depending on the AD microbial conversion stage (hydrolysis, acidogenesis, acetogenesis and methanogenesis) and the operating conditions such as thermophilic and mesophilic regime [334]. The commonly added metals in anaerobic growth media include Fe, Cu, Zn, Mn, Ni, Co, Mo, Se and W [317,334]. However, high concentration of metals such as Ni and Co are reported to be detrimental to methanogenic activity [335]. Also, Fe and Ni depletion could lead to a sudden accumulation of VFA due to toxicity of microorganisms [336]. Metals such as Fe have been reported to reduce the H_2S content in the biogas due to the formation of metal sulphides [336]. Apart from lowering the H_2S concentration in the biogas, metals have also been reported to enhance organic matter degradation and biogas production [337,338]. This is because, they support the microbial activity which improves feedstock degradation efficiency and hence biogas production [337]. Metal additives can also help to maintain favourable conditions in the digester such as pH which enhances biogas production [339]. Other additives such as $FeSO_4$, $FeCl_3$, Ca^{2+} and Mg^{2+} salts which enhance bacterial growth and hence improve the overall AD process efficiency [339]. Adsorbents such as charcoal and silica gel can potentially enhance the biogas yield [339], most likely due to their trace metal composition containing elements such as Fe [340,341]. However, it should be noted that inorganic additives can be a source of secondary pollution to the environment and increase the inert suspended solids of the digester, moreover, additives will increase the operational costs [342].

It has been shown that other mineral additives such as bentonite enhance resistance to ammonia inhibition during AD [343]. Moreover, the usage of mafic silicate minerals as additives has been reported to affect CH_4 content in the biogas by scavenging CO_2 and the iron present in the silicate may react with H_2S reducing its content [344].

Additives such as green biomass have been reported to enhance biogas production. Powdered legumes and leaves of some plants are reported to increase the biogas yield by over 18% [339,345]. This could be due to trace elements available within green biomass [346], or due to additional carbohydrates. It should be noted that metal trace elements such as Fe are constitutive components in most leaves of plants [346], therefore, they could be released as essential elements and favourably contribute to enhance biogas yield and quality. As well, it is hypothesized that metal trace elements composition in leaves could also reduce the concentration of H_2S in the biogas, nonetheless, further research is still required to quantify this effect.

Bio-augmentation or addition of microbial strains has also been reported to enhance biogas production by stimulating particular enzyme activity [347]. For instance, microbial strains such as rumen microorganisms can potentially enhance the biodegradability of lignocellulosic waste [342,348].

Additives like green leaves and charcoal would be ideal for small scale biogas-electricity generation applications since they are readily available in off-grid settings. This would not only enhance biogas production but may also reduce the biogas H_2S concentration which in turn, could further accelerate electricity generation from already existing biogas systems. However, research and development are still required to reveal the optimal ratio to be added in the feedstock depending on the type of leaves and feedstock available at a particular location.

4.3.4 | Micro-aeration of anaerobic digester

Micro-aeration has been proposed by a few researchers as one of the pre-treatment methods for feedstock [349,350]. It is suggested that the introduction of limited amounts of air into AD improves several biochemical conversion processes and enhances hydrolysis of hardly biodegradable compounds. Lima et al. [349] co-digested food waste and faeces and obtained a higher COD solubilisation, greater VFA accumulation and conversion of short chain fatty acids to acetate when using micro-aeration as a pre-treatment in AD. Oxidation reduction potential (ORP) values in micro-aeration pre-treatment were comparable to a complete anaerobic reference since they were in the same range.

A few researchers found a positive effect of microaerophilic conditions on the hydrolysis of particulate matter [351]. Díaz, Pérez et al. [352] obtained a shorter lag-phase, and Johansen and Bakke [350] observed an increase in hydrolysis of carbohydrates and proteins, but no difference between the lipid content on the digested sludge. These improvements in hydrolysis can be directly linked to a higher production of biogas due to substrate availability. Even though methanogens are strict anaerobes and oxygen might result toxic for them, some authors suggested that methanogens can adapt and handle different amounts of oxygen [353–355].

Micro-aeration can reduce the H_2S content in the biogas [351]. At full scale, micro-aeration can remove up to 99% of H_2S from biogas [356,357]. Jenicek et al. [358] reported that micro-aeration increased specific methane production and decreased H_2S content in the biogas. The enhanced specific methane production was attributed to suppressed H_2S inhibition, due to oxidation of sulphide to elemental sulphur. They further noted that micro-aeration resulted in a better quality of sludge liquor in terms of lower soluble COD [359]. Although micro-aeration is a low-cost intervention for H_2S removal, it can result in clogging of the walls of the digester and gas pipes with elemental sulphur [360] if air is dosed in the digester headspace. Therefore, the location of air dosing point needs to be carefully selected. Also, for the removal of very high H_2S concentrations in the range of 12,000 ppm, the applied air dose could result in biogas dilution with N_2 [360]. In such cases, pure oxygen should be used instead of air. In the particular case of small-scale digesters, the efficiency of H_2S oxidation during micro-aeration is correlated with the installed size of the digester liquid-gas surface area from 0.099 – 0.150 m^2 [361].

Addition of limited air might have several beneficial impacts on small scale digesters. Firstly, air can be added directly to the headspace in order to oxidize H_2S, minimizing its concentration in the biogas and thus improving the biogas quality. This has been effective to reduce the H_2S levels of biogas from small scale digesters [361]. Secondly, limited aeration can be introduced directly to anaerobic sludge. As mentioned before, aeration might lead to an improvement of hydrolysis, which is considered one of the bottlenecks in AD when the influent has a high content of particulate matter. Furthermore, micro-aeration can also promote areas where aerobic degradation of organic matter occurs in the digester, with an increase in bicarbonate availability as end result [362]. Due to this, the expected methane-CO_2 ratio of 40-60 % in complete anaerobic conditions might change, however, an equal distribution of these gases in biogas could be optimal for SOFC cells if dry reforming is envisaged [363–365]. Finally, adding aeration is cost demanding if active aeration of the sludge is considered. While air is easily available, added costs should be considered when planning to introduce air into the system. Hence, it is key to perform an economical assessment of the gained energy or operational performance due to improvements in biogas quantity and quality, in comparison to the energy or additional maintenance needed for aeration.

Therefore, for biogas-electricity generation application, micro-aeration can reduce on H_2S impurity for sensitive devices such as SOFCs and at the same time has the potential to increase the fuel gas production.

4.3.5 | Other operational parameters

Apart from pre-treatment, co-digestion and additives, there are other operational parameters which can influence the biogas quality and quantity and those are discussed in this section.

Temperature regime: Temperature was found to significantly influence the performance of anaerobic digesters in comparison to other factors such as HRT, OLR and substrate characteristics [366]. The AD process is applied in a wide temperature range in which the biochemical conversions follow the Arrhenius equation [367]. Thermophilic AD (50-60°C) has a faster reaction rate and a higher loading capacity compared to mesophilic AD (30-40°C) [342,368]. As a result, higher biogas production rate is expected from thermophilic digesters as compared to mesophilic ones. However, when not properly operated, thermophilic digesters may have drawbacks such as acidification, decreased stability, low quality effluent, increased sensitivity to toxicity, susceptibility to environmental conditions, larger investments, and higher energy input [342]. Moreover, it has been observed that sudden changes in the temperature regime can drastically reduce the rate of biogas production [368].

pH: Although the different microbial sub-populations in AD have different pH ranges and pH optima, the optimal range reported in literature for the process is about 6.5-8.0 [369]. A reactor pH outside the optimal range can potentially affect the quantity and quality of biogas yield. For small scale digesters, an average pH of 6.7-7.3 has been reported [370]. This is within the optimal range proposed in literature [369]. It should be noted that the pH influences the speciation of HS^- and therefore H_2S in the gas phase. An increase in pH decreases the H_2S concentration in the biogas, therefore, a higher operational pH (7.5-8.0) is desired for biogas-electricity generation applications.

Particle size: The particle size of the feedstock also has an influence on the rate of biogas production. A decrease in particle size increases the rate of hydrolysis which is limiting in the AD process [367]. Large particles could result in clogging of the digester, whereas small particles provide a large surface area for adsorption of microorganisms, enhancing microbial activity and hence biogas production [339].

Mixing: Mixing enhances the contact time between microorganisms and substrates and prevents local pH drops or high concentrations of intermediates. Mixing can be done in a number of ways, including daily feeding, using biogas recirculation and mechanical stirring. Proper mixing ensures intimate contact between the microorganisms and the substrate, which results in a more efficient digestion process with increased biogas production [339]. According to Jegede et al. [371] in small scale digesters, mixing depends on the type of the digester. For digesters of Chinese dome-type, mixing is achieved by pressure build-up due to gas storage, usage and influent flow. For plug-flow digesters, mixing is achieved by flow of the feedstock from the inlet to the outlet and gas production. For the biogas-electrical generation application, a high and constant biogas production is preferred, meaning reactor operation at an increased loading rate. Increased biogas production would enhance mixing but this can be coupled with regular active mechanical mixing for a more efficient AD process.

Type of reactor: Optimization in terms of retention time, organic loading, low sludge production for waste water treatment plant digesters and reduced footprint seems to be the focus of current research [342]. The reactor design criteria depend on the location, for example, if psychrophilic conditions are expected, longer HRT is required as compared to mesophilic conditions [366]. Different reactor designs may have an effect on the biogas quality and quantity since reactor configuration affects the overall AD process. Innovative reactor designs are discussed in detail in subsequent sections of this chapter.

Seeding: Seeding is basically done to enrich bacteria into the digester to facilitate/accelerate the start-up process of AD. Re-seeding is considered when intermediate VFA accumulate during digester operation, which results in decreased quality and quantity of biogas production. Even daily-use materials like wood-ash have been reported to enhance biogas production if they are used as part of seeding materials for the digester [372]. It should be noted that, ash also contains earth alkaline and metal elements such as Ca, Mg, Fe, whose concentration depends on the material source and that are often present in the oxidized form [373]. Such elements can also act as additives to the digester to buffer the pH, enhance biogas production and achieve the required quality for electrical production by reducing impurities such as H_2S in the gas phase. Although ash may have elements which can enhance biogas quantity and quality, it may be harmful to AD when dosage is not controlled. Therefore, the use of ash as seed for off-grid digesters needs to be carefully evaluated to understand the optimal condition under off-grid anaerobic conditions, which could vary depending on the available feedstocks.

The effect of modifying some of these operational parameters on biogas quality and quantity needs to be carefully evaluated for small scale biogas-electrical generation applications. Some of these operational practices such as daily feeding and agitation can easily be adapted in small scale digester operation with marginal increase in operational costs. Other operational parameters such as the C/N ratio, organic loading rate (OLR), HRT and solids concentration can influence the biogas quality and quantity. Their effect to the AD process is summarised in Table 14, which shows the effect of operational parameters and their optimal condition for biogas-electricity generation application. It should also be noted that some of the parameters like OLR and HRT are influenced by users' behaviour depending on their respective needs such as fertilizers [374]. Furthermore, HRT can be influenced by the gas pressure [375,376]. Therefore, efforts to optimize small scale digesters should include social-cultural status of the given community, although this is out of scope of this thesis.

4.3.6 | Digester design parameters

For small-scale applications, a self-agitation bio-reactor was proposed [371]. Such a reactor can minimise the need for mechanical mixing and enhance the quantity of biogas generated at the same time. Martí-Herrero et al. [377] proposed the use of Polyethylene Terephthalate (PET) rings from soda bottles in a tubular plug-flow digester to increase solids retention and the effective surface area. The incorporation of PET rings was found to increase COD removal and the specific biogas production rate. Additionally, it enhanced process stability and allowed for a higher loading rate [378].

The integration of solar thermal energy into the AD process was proposed to increase the efficiency of the digesters [377]. Also, the integration of a greenhouse and a solar thermal energy system for AD was effective in enhancement of the digester temperature [378,379]. Application of the greenhouse above the digester was reported to increase the slurry temperature by over 9°C above ambient temperature [380,381]. Also, a simple passive solar design of a low-cost plug-flow digester constructed with double tubular polyethylene layer was able to increase the slurry temperature by 8°C above the ambient temperature [382]. Simple digester modifications in terms of covering the gas holder with transparent polyethylene that acts as a greenhouse can potentially increase the digester temperature and hence, increase the biogas production rate [339,383]. For underground digesters, the slurry temperature greatly depends on the temperature of the soil surrounding the digester [384] and hence keeping this temperature elevated using a greenhouse would, in turn, enhance the digester temperature. Since polyethylene is readily available in most countries, the construction of greenhouses surrounding the digester seems to be a suitable approach for resource-constraint settings. The increase in temperature, which enhances the biogas production rate by the use of solar energy, is likely to increase the economic returns of the biogas digesters. Even at the household level, solar-assisted biogas system was proven to be economically feasible [385]. A temperature increases from 20°C to 35°C can significantly increase the biogas production rate in the case of manure [386]. However, for this feedstock, increasing the temperature beyond 35°C may not significantly enhance biogas production rate [368].

Apart from a greenhouse structure, several researchers have investigated the use of solar thermal in AD using various techniques such as concentrated solar power and rooftop solar collectors. Earlier researchers developed innovative solutions such as the use of a solar collector as a rooftop for the digesters, which they reported as a potential technique to reduce thermal losses [387]. El-mashad et al. [377] investigated the use of a solar water system for thermophilic AD. A solar heating system with a flat plate collector in AD is technically feasible, although it increases the capital and operational costs of the system [377]. Hao et al. [388] studied the feasibility of integrating a concentrating photovoltaic/thermal (C-PV/T) hybrid system into a biogas plant to achieve a more efficient bio-methane production by temperature enhancement. An improvement of 1.7% in bio-methane production was obtained, however, this was less than the regular error margin. Moreover, Colmenar-Santos et al. [389] analysed the hybridisation of concentrated solar power (CSP) and biogas plants, which was found to increase the profitability and environmental advantages. As well, Vidal et al. [390] studied the integrated AD/solar photo-electro-Fenton (SPEF) process for the treatment of slaughter-house wastewater. Results showed that the combined process reduced the costs associated with slaughter-house wastewater treatment and improved the removal efficiency of influent COD by more than 90%. In addition, a solar-driven hydrothermal pre-treatment system was investigated as an alternative energy-saving approach for the digestion of microalgae slurry. This approach improved the bio-methane potential by 57% compared to that of raw microalgae without pre-treatment [391]. A novel integrated solar PV and thermal AD system has been recently proposed by Young et al. [392]. Such a system would meet both the auxiliary and thermal energy demand of the biogas digester, but its economic feasibility in small-scale systems is rather doubted.

Solar energy, apart from enhancing biogas production, can also be used to enhance pathogen removal from the digested slurry, when faecal matter is used as feedstock [393]. Sun drying of the digested slurry was found to increase pathogen (*F. streptococcus*) removal up to 3 log units. Also, in a digester effluent that operated at a temperature of 45°C, *E.Coli* and total coliforms were found to be between 2-3 log units, which is lower than the world health organisation (WHO) guidelines for digested slurries [394]. Solar drying of digestate can reduce its total nitrogen concentration by volatilising ammonia, thus resulting in balanced chemical composition for fertilizer application [393]. As reported before, solar radiation can also be used for pre-treatment to enhance lignin degradation [395] and hence further improve the efficiency of AD. Therefore, countries, which receive a large amount of annual radiation, can consider solar energy as a source of heat to enhance the AD process efficiency and also as a feedstock pre-treatment option. Moreover, the usual feedstock for small-scale digesters, namely cow dung, contains a considerable fraction of lignocellulosic material [396]. Hence, the possibility of using the freely available solar radiation as a pre-treatment method for digester feedstock, seems advantageous to enhance the biogas production rate of small-scale digesters.

Table 12. Quality of Biogas from Lab experiments

Gas Composition	Concentration	Feed stock		Protocol	Analysis Equipment	Ref	pH	Temp	S Concentration in feed stock
CH_4	68.6-71.4%[1]	Fish waste		BMP	GC-2014	[397]			
	62.2%[1]	Brewery grain Waste		BMP	GC-2014	[397]			
	53.1%[1]	Bread Waste		BMP	GC-2014	[397]			
	5-15%	Cow dung	Batch		FTIR spectroscopy	[326]			
	15-25%	Coffee pulp	Batch		FTIR spectroscopy	[326]			
	45-55%	Cow dung + Coffee Pulp (40% Wt coffee pulp, 40% Wt Cow dung, 20% Water)	Batch		FTIR spectroscopy	[326]			
	56.5%[2]	Apple Pomace				[398]			
	71.8%[2]	Cauliflower + Radish				[398]			
	68%[2]	Rotten cabbage				[398]			
	72.8%[2]	Cauliflower + Radish + Cow dung				[398]	6.91[2]		
	70.8%v[2]	Cauliflower + Radish + Cow dung + Apple Pomace				[398]	7.22[2]		
	60-86%	Cow dung				[320]			
	66.6%	Cow dung	Batch	BMP		[399]			
	65.9%	Pig dung	Batch	BMP		[399]			
	76.9%	Sludge	Batch	BMP		[399]			
	63.4%	Fruit/Vegetable waste	Batch	BMP		[399]			
	68.0%	Food waste	Batch	BMP		[399]			
	59.4-60.6%	OFMSW	CSTR			[330]	7.0-7.5		
	62.8-64.6%	OFMSW + Cow dung at a proportion of	CSTR			[330]	7.2-7.5		

		50% (VS/VS)							
	71.4-81.2%	Mixed Sludge	Batch	BMP	Awite Serie analyzer^3	4	[400]		
	67.6-78.4%	Leachate	Batch	BMP	Awite Serie analyzer^3	4	[400]		
	70.9-83.3%	Oil	Batch	BMP	Awite Serie analyzer^3	4	[400]		
	62.1-66.7%	SHW					[401]		
	55.3-67.1%	SHW+OFMSW in ratio of SHW:OFMSW is 1:5 in weight					[401]		
CO_2	$36.1\%^2$	Apple Pomace					[398]		
	$22.5\%^2$	Cauliflower + Radish					[398]		
	$25.1\%^2$	Rotten cabbage					[398]		
	$21.9\%^2$	Cauliflower + Radish + Cow dung						6.91^2	
	$23.1\%^2$	Cauliflower + Radish + Cow dung + Apple Pomace						7.22^2	
	13-28%	Cow dung					[320]		
	33.3-37.9%	SHW					[401]		
	32.8-44.7%	SHW+OFMSW in ratio of SHW:OFMSW is 1:5 in weight					[401]		
H_2S ppm	850-2872	Fish waste					[397]		
	382-2260	Brewery grain Waste					[397]		
	900-3270	Bread Waste					[397]		
	17000-35000	Sea weed + Pig dung					[402]	6.71-7.76	2.60 g S/L
	1500-3000	Pig dung					[402]		0.36 g S/L
	3.01%v	Cow dung			FTIR spectroscopy		[326]	6.5-7.0	

	0	Coffee Pulp	FTIR spectroscopy	[326]	4.5-7.2
	2.12%v	Cow dung+ Coffee Pulp (40% Wt coffee pulp, 40% Wt Cow dung, 20% Water)	FTIR spectroscopy	[326]	5.4-7.2
	7.3%v[2]	Apple Pomace		[398]	
	5.7%v[2]	Cauliflower + Radish		[398]	
	6.9%v[2]	Rotten Cabbage		[398]	
	5.3%v[2]	Cauliflower + Radish + Cow dung		[398]	6.91[2]
	6.1%v[2]	Cauliflower + Radish + Cow dung + Apple Pomace		[398]	7.22[2]
N_2	0.177-11.484%	Cow dung		[320]	
CO	0.001-0.05%	Cow dung		[320]	
Air (N+O)	0.0110-0.05%	Cow dung		[320]	

[1] Weighted average methane content. [2] Averages. [3] automated gas analyzer with infrared and electrochemical sensors

Table 13. Quality of Biogas From field measurements

	Biogas Plat type			Main feed stock for Organic waste Digesters	Measuring Procedure/Equipment	Analysis Conditions	Ref	This Research
Gas Composition	Land Fills	WWTPs	Organic waste digesters/farm/ domestic digesters					
CH_4 (%v)	47-62	60-67	55-70	Cow and pig dung, waste water, industrial and agricultural waste	Infra-red gas analyser	Laboratory	[90]	
	59.4-67.9				Hewlett Packard (HP) 5890 gas chromato- graphy with thermal conductivity detector	Laboratory	[182]	
			41-59	Cow and Pig dung			[403]	
			62.94-67.76[3]	Pig dung	GA5000 multifunctional portable gas analyser (Geotech, Leamington Spa, UK)	On site measurement	[404]	
			59.42-62.46[6]	Cow dung	GC	Laboratory	[325]	
			61.7%[7]	Cow dung	An IR-30M hydrocarbon meter (Environmental Sensors Co.)	On site measurement	[405]	

			61.4-72.5%[7]	Pig Dung	An IR-30M hydrocarbon meter (Environmental Sensors Co.)	On site Measurement	[405]	
			40-59%	Mainly cow dung	Gas Analyser (Geotech, GA 2000 plus)	On site	[370]	47-52
			60%	Pig manure			[144]	
			60%[9]	Cow dung	The ATEX Certified, Portable Gas Detector		[406]	
CO_2 (%v)	32-43	33-38	29-40	Cow and pig dung, waste, industrial and agricultural waste	Infra-red gas analyser	Laboratory	[90]	
	29.9-38.6				Hewlett Packard (HP) 5890 gas chromato-graphy with thermal conductivity detector	Laboratory	[182]	
	35.1-40.0				GC/MS		[407]	
			30-49	Cow and Pig dung			[403]	
			26.59-31.89[3]	Pig dung	GA5000 multi-functional portable gas analyser (Geotech, Leamington Spa, UK)	On site measurement	[404]	
			38.21%[5]	Cow dung	GC	Laboratory	[325]	
			30-49.3%	Mainly cow	Gas Analyser (Geotech, GA	On site	[370]	40-45

				dung	2000 plus)			
			30%				[144]	
			40%^{9}	Cow dug	The ATEX Certified, Portable Gas Detector		[406]	
N_2 (%v)	<1-17	< 2	<1	Cow and pig dung, waste, industrial and agricultural waste	Infra-red gas analyser	Laboratory	[90]	N/A
	4-15.8				GC/MS	Laboratory	[407]	
			1.52%^{5}	Cow dung	GC	Laboratory	[325]	
			10%	Pig manure			[144]	
O_2 (%v)	<1	<1	<1-2	Cow and pig dung, waste, industrial and agricultural waste		Laboratory	[90]	1-3
	0.9-3.7				GC/MS	Laboratory	[407]	
H_2 (%v)	< 0.01-0.01				GC/MS	Laboratory	[407]	N/A
NH_3 (%v)			0.03-0.05^{3}	Pig dung	GA5000 multifunctional portable gas analyser (Geotech, Leamington Spa, UK)		[404]	N/A
Common Trace Elements								
H_2S ppm	27-500	<1-4	3-1000	Cow and pig	-Infra red gas analyser	Laboratory	[90]	

			dung, waste, industrial and agricultural waste	equipped with electro-chemical cell -Draeger and Rae Systems gas tubes -Portable gas chromatograph.			
	15.1-427.5			HP 5890 series II GC with sulphur chemiluminescence detector	Laboratory	[182]	
$mg\ m^{-3}$	220-420			GC/MS	Laboratory	[407]	
		0-312	Cow and pig dung			[403]	3-500 ppm
ppm		130[1]-1,600[2]		Draeger tubes	Onsite measurement	[300]	
%vol		0.07-0.22[3]	Pig dung	GA5000 multifunctional portable gas analyser (Geotech, Leamington Spa, UK)	On site measurement	[404]	100-600ppm
ppm		991-2923[4]	Cow dung	GC	Laboratory	[325]	0-1400 ppm
		4.8[7]	Cow dung	Z-900 hydrogen sulphide (H_2S) meter (Environmental Sensors Co.)	On site measurement	[405]	
		0.37-84.4[7]	Pig dung	Z-900 hydrogen sulphide (H_2S) meter (Environmental Sensors Co.)	On site measurement	[405]	
ppm		149-310[8]		Gas Analyser (Geotech, GA	On site	[370]	

					2000 plus)	measurement		
			2400[9]				[144]	
			100[9]	Cow dung,	The ATEX Certified, Portable Gas Detector		[406]	
			2000-6000	manure, biowaste and food waste			[408]	
				Cow dung+ faecal waste				20-2000 ppm 2000-4000 ppm
Siloxanes (ppm)					Thermal desorption gas chromatograph-mass spectrometry	Laboratory	[90]	
Mercaptans (ppm)	0.7-4	1.5-10.6	<0.4	Cow and pig dung, waste water, industrial and agricultural waste	Thermal desorption gas chromatograph-mass spectrometry	Laboratory	[90]	
	9.3-13.2				HS-GC/MS	Laboratory	[407]	
	12.1-84.9				HP 5890 series II GC with sulphur chemiluminescence detector	Laboratory	[182]	
Other VOCs (TVOCs) (mg m^{-3})	46-173	13-268	5-8	Cow and pig dung, waste water,	Thermal desorption gas chromatograph-mass spectrometry	Laboratory	[90]	

mg m^{-3}	48-728		industrial and agricultural waste Cow and pig dung, human dung	B, GC/MS	Laboratory	[407]	0-30ppm

[1]Mean for measurements every two weeks for 6 months with 95% CI: 95 - 150 ppm, [2]mean for measurements every two weeks for 6 months with 95% CI:1300 - 2000 ppm, [3]maximum upper and minimum lower bound of the mean at 95% CI, [4]daily average with standard deviation of 34 - 277 +/- ppm of H_2S, [5]monthly average, [6]weekly average, [7]average percentages, [8]maximun values and [9]average.[409]

4.4 | RESULTS

4.4.1 | Literature identification of operational practices and AD reactor designs suitable for small-scale digesters

Literature on biogas is extensive and the influence of many parameters on the quality and quantity of biogas produced from AD have been described in various textbooks [409,410]. The aim of this section is to derive hypotheses for the relevance of parameters given the local physical and socio-economic conditions.

4.4.1.1 Pre-treatment, co-digestion and other operational parameters can enhance biogas quality and quantity.

As discussed in section 4.3, a number of parameters enhances biogas quality and quantity. These parameters are summarised in these section as follows;

Physical pre-treatment such as milling, chipping and gridding may lead to diversification of feedstocks for small-scale biogas plants. If pre-treatment, such as using a simple mechanical grinder, is encouraged, then the availability of feedstock for co-digestion with the animal and faecal waste would be increased. Also, irradiation from the sun can be used as a freely available photothermal or photochemical pre-treatment option in small-scale applications. Solar irradiation contains UV radiation that can enhance lignin disruption within the substrate and subsequently enhance its biodegradability [411]. In the presence of a catalyst such as TiO_2, solar irradiation can enhance photo-oxidation of lignin, which yields more easily biodegradable compounds [395]. Even in the absence of a catalyst, UV light pre-treatment has been reported to enhance biohydrogen production [412]. Solar energy can also be utilised to supply thermal energy input for low temperature (55-100°C) pre-treatment [309].

Co-digestion is another freely available technique to increase the efficiency of AD processes and hence improve the biogas production rate and concomitantly reduce H_2S content in the biogas [321,326]. From Table 12, co-digestion can greatly reduce H_2S content in the gas as compared to single feedstock.

Specific heavy metals are indispensable as micro-nutrients for anaerobic bacteria and archaea [334]. Locally available additives, such as green leaves and biochar, contain these trace metals and can supplement microorganisms with these micronutrients [346]. Mentioned additives are freely available in off-grid communities and if they are used in the right proportions, they can indeed enhance biogas production rates and also reduce on H_2S concentrations in the biogas [336–338].

In addition, micro-aeration has been reported to enhance the hydrolysis of hardly biodegradable materials, meanwhile reducing the H_2S content in the biogas [349,350,356,357].

The extensive literature study and systematic discussion on the relevance of specific parameters for small-scale digesters and biogas-electricity generation systems, considering these local socio-economic conditions has been presented. From this analysis the following most relevant topics were derived that have been taken into account in the field study: i) pre-treatment methods, ii) co-digestion, iii) additives for enhanced biogas quality and quantity, iv) reactor pH, v) reactor mixing, vi) substrate particle size, vii) seeding, viii) micro-aeration, ix) temperature and x) design of the reactor. Their theoretical effect on the performance of AD systems has been described in Table 14.

4.4.1.4 Small-scale digester design parameters.

In rural conditions, particular attention should be paid to the digester design to ease operation and prevent unnecessary maintenance. Different small-scale reactor designs that have been reported to affect the efficiency of the AD process and have an influence on the biogas quality and quantity. Digester design such those which integrate solar thermal energy have been reported to enhance the biogas production rate as reported in section 4.3.6.

Table 14. Effect of operational parameter on AD and their optimal conditions

Parameter	Theoretical effect to the AD process /Optimal range	Actual situation described in literature on small scale digesters	Recommendation for improved quality or quantity in small-scale biogas-electricity generation system based on this field study
Physical pre-treatment- milling, chipping and gridding	Increases the particle surface area available for enzyme attack [305]	Not recommended for small application due to some drawbacks which include high energy consumption [305]	For small-scale application, manual milling can be considered. This can result in feedstock diversification
Physical pre-treatment- Irradiation and low-temperature pre-treatment	Irradiation improves lignin degradation [395]	No solution suggested	Solar can be used as a source of irradiation for pre-treatment
	Low temperature (55-100°C) pre-treatment enhances thermal solubilisation of particulate matter thus enhancing hydrolysis [309].	No solution suggested	Solar can be used as a source of heat (thermal energy) for low temperature treatment using parabolic solar concentrators.
Co-digestion	Co-digestion complements feedstock characteristics and hence balances its composition within non-toxic ranges for microbial growth [318,319].	Commonly cow dung and pig dung are used and less attention was given to other feedstocks	Other materials such as plant waste can be used if physical pre-treatment such as milling is encouraged.
Metals	Nutrient to bacteria and increases organic matter degradation and biogas production [334,337,338]	No solution suggested	Additives such as green leaves can be used to increase metals in the feedstock.
pH	6.8-7.8 [370]	pH is not controlled and recommendations are given with focus on microbial performance	Upper limit 7.5-8.0 would be preferred since it also improves biogas quality, in particular it reduces H_2S concentration in biogas. Dilution of feedstock with hydrolysed urine could keep the pH in the upper limit [413]
C/N ratio	High C/N ratio results in insufficient nitrogen for microorganisms and hence lower biogas production. Optimal range	No solution suggested	The use of urine as a dilution can be used to balance the C/N ratio

is 20-35 [54]

Parameter	Theoretical effect to the AD process /Optimal range	Actual situation described in literature on small scale digesters	Recommendation for improved quality or quantity in small-scale biogas-electricity generation system based on the field study
Organic loading rate	Optimal value depends on the type of feedstock and reactor [414]	This is not controlled, but feeding schemes are proposed	For small scale Biogas-SOFC, this can be easily controlled by providing feed bucket with specific dimensions
Hydraulic retention time	Lower retention time results in lower biogas quantity [342].	In fixed dome reactors, this is controlled passively by the pressure	Needs to be more thoroughly controlled as observed feeding schemes are all very different.
Mixing	Ensures intimate contact between feedstock and microorganism [339] and improves biogas production rate	Self-agitation has been proposed in literature [83] through a new design	Mixing was not observed. But can easily be done by incorporating mechanical mixing in the reactor design. This can be complemented by varying gas pressure and flow of feedstock [371].
Substrate particle size	Large particles are very slowly hydrolysed and may lead to clogging	Small particles are preferred since they provide a large surface for microorganism adsorption, but for small scale rural digesters no solution is proposed	Feedstock is usually taken as it is. For plant waste feedstock, manual milling could improve hydrolysis and increase biogas quantity
Solids concentration	Increased biogas yield if it is in optimal range of 7-9% [339,415]	No solution suggested	Co-digestion with plant waste can be used to balance the solids concentration.
Seeding	Enriches microorganisms into the digester to accelerate the start-up [372]	Wood ash is recommended although this is more of an additive [372]	Wood ash is readily available and can be used as additive
Temperature, thermophilic (50-60°C) and mesophilic (30-40°C)	The higher the temperature, the faster the hydrolysis and the higher the loading capacity [342,368]	Mesophilic operation is proposed as it is less intensive in terms of operation and maintenance. The use of solar energy is proposed to increase operational temperature by using a greenhouse (covering the gas holder with transparent polyethylene) [339,383]	Mesophilic situation is not achieved and systems operate typically well below 35°C. Abundant solar energy can be used to enhance the digester temperature. Also, waste heat from electricity generators such as SOFC can be used to increase the digester temperature and increase biogas quantity.
Type of the reactor	Reactor type affects solids retention time	Designed in such a way to optimize organic loading rate and retention time.	If waste heat or solar thermal energy is to be used, it should have good thermal insulation properties

4.4.2 | Field observations that may influence the quality and quantity of biogas from small-scale digesters.

After defining the key parameters, the field survey was carried out to verify the outcome from literature for off-grid small-scale digesters and biogas-electricity systems. A total of 48 digesters across Uganda were visited. The observations carried out during the field visit corresponded to the following categories: i) pre-treatment (irradiation due to feedstock storage), ii) co-digestion, iii) co-feedstock and additives such as passive mixture of feedstock with leaves, soil, and feedstock dilution using urine instead of water, iv) reactor pH, v) reactor mixing regime (feeding frequency and mixing by stirring) vi) substrate particle size (solid materials), vii) seeding, viii) micro-aeration, ix) temperature and x) type of reactor.

4.4.2.1 Current pre-treatment observed

Physical pre-treatment-irradiation and feedstock storage: It was observed that some farmers store the feedstock for several days before it is fed into the digester (Figure 14a). It was noted that the feedstock is normally exposed to open irradiation from the sun. Other farmers, due to limited feedstock, always use fresh dung.

(a) (b)

Figure 14. (a) Stored cow dung and (b) fresh cow dung.

4.4.2.2 Co-digestion observed in the field

It was observed that some farmers were practicing co-digestion. Out of the 48 digesters visited, 11 were co-digesting feedstock. Some of the farmers added toilet waste to the digesters, while others used pig and cow dung due to the presence of more than one type of animal. It was evidenced that co-digestion of animal dung and food or agricultural waste is not practiced in off-grid settings for the visited digesters.

4.4.2.3 Observed co-feedstocks and additives with biogas quality and quantity enhancing potential

It was observed that during cow dung collection, a mixture of leaves and grass is also collected (Figure 15a), however, this depends on the collection site. Sometimes when grass is not present, then soil is likely to be collected together with the cow dung (Figure 15b). If the un-cemented-Kraal[1] (Figure 15b) is located in a clay area, this can constitute a passive clay additive to the feedstock. During field research, it was also observed that wood-ash is readily available and hence can be used as part of additive material.

(a)

---

[1] *A place in which cows sleep at night*

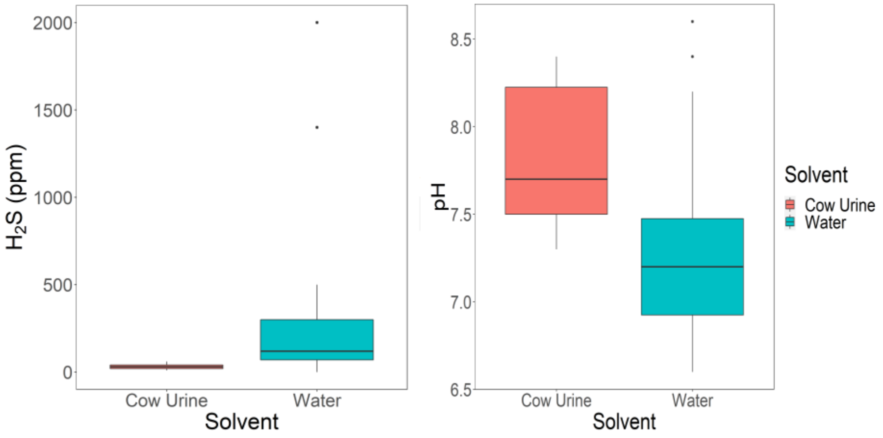
(b) (c)

Figure 15. (a) Cow dung mixed with green grass and leaves, (b) Un-cemented kraal where cow dung mixes with soil and (c) Cemented kraal with minimal chances of cow dung mixing with soil.

4.4.2.4 Other observed digester operational practices which can potentially affect the quality and quantity of biogas

Dilution of feedstock with urine. In Uganda, some farmers dilute the feedstock with urine as opposed to water. This practice is widely spread in the central region where most of the cows are kept on zero-grazing, hence the collection of urine is relatively easy. Famers usually collect the urine in a pond which is then later used to dilute feedstock instead of water. Away from the central region, where animal field grazing is the common practice, farmers usually use water for feedstock dilution.

Analysis of biogas composition presented in Table 13 in terms of CH_4, CO_2 and H_2S showed that they were in the range of 47-52 %v, 40-47 %v and 0-2,000 ppm, respectively. It was observed that digesters, which had urine as solvent, had higher pH as compared to digesters, which had water as the solvent (Figure 16b). Digesters with a higher pH and urine as a solvent had relatively lower H_2S content in the gas as compared to digesters with a lower pH (Figure 16a). Figure 17 shows the variation of H_2S content in the gas with effluent pH. It is shows that a general decreasing trend in H_2S content was observed as effluent pH increased.



(a) (b)

Figure 16. (a) Effect of solvents on H_2S content in biogas and (b) on pH of digesters visited in the field study using either cow urine or water as solvent.

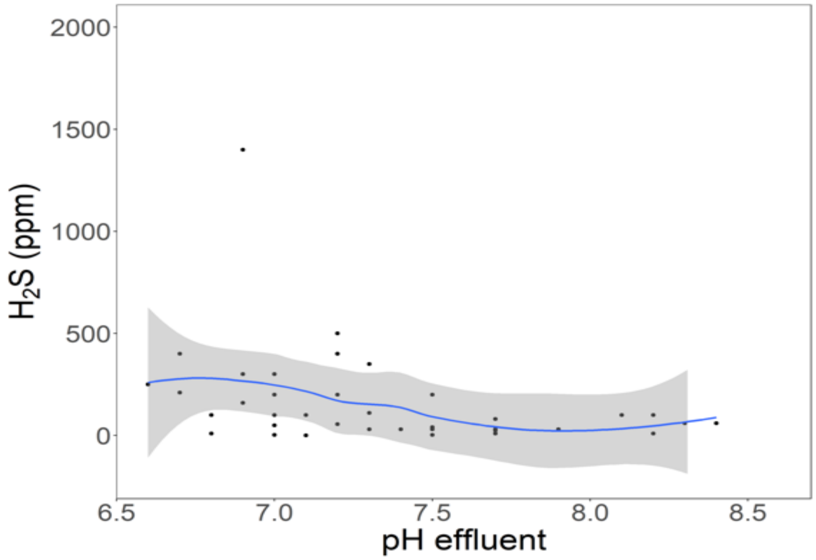
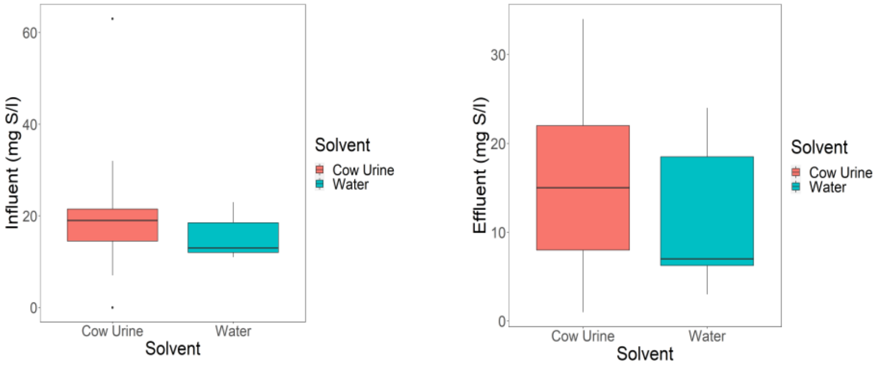


Figure 17. Effect of pH on the H_2S content in the gas

Analysis of the influent and effluent samples (Figure 18) shows that digesters, which had urine as the solvent had a relatively higher sulphide concentration as compared to digesters which had water as a solvent.



(a) (b)

Figure 18. (a) Sulphur (S) concentration measured in the influent and (b) effluent (mg S /L) of digesters visited in the field study using either cow urine or water as solvent.

Feeding Frequency. The feeding pattern is one of the operational practices, which could enhance mixing and result in a more efficient digestion process. However, it was observed that the frequency of digester feeding widely varies between digesters, as well as for the same digester from time to time. All the digesters visited had no standard feeding schedule. Some farmers fed their digesters once a week, whereas others tried to feed them daily. Also, the ratio for feedstock dilution was not standardised and was usually calculated based on assumptions. In most cases, feeding depended on the availability of feedstock and it was not based on protocols related to digester capacity and required retention times.

Mixing by stirring. Mixing by mechanical stirring is generally not frequently practiced in decentralised digesters. All the digesters visited were not agitated by stirring and the operators were not aware of the benefits of such practices. Proper stirring needs to be encouraged since it improves contact between the microorganism and the feedstock, hence enhancing bioconversion.

Solid materials. Solid materials in the concentration range of 7-9% have been reported to enhance biogas production [415]. As mentioned before, it was observed during the field survey that off-grid communities have access to digestible solid material such as banana peels. If such a practice is embraced in small-scale digesters, it is likely to increase the feedstock availability and also enhance biogas production rate of AD.

Seeding materials. Seeding is not a common practice in off-grid small-scale digesters. None of the 48 surveyed digesters used seeding.

Micro-aeration of anaerobic digester. In small-scale digesters, micro-aeration is not a common practice in Uganda. However, it was observed that passive micro-aeration could occur for some digester designs like fixed dome (Figure 19), which have an expansion chamber exposed to the atmosphere. This unintended exposure of the slurry to the atmosphere might result in micro-aeration of the slurry especially during mixing through the expansion chamber.

(a) (b) (c)

Figure 19. (a) Side view of the expansion chamber and inlet (b) Arial view of the inlet and (c) Aerial view of open expansion chamber with slurry exposed to ambient.

Temperature. In small-scale digesters, temperature usually is not controlled and is determined by the environment. In East Africa, most of the visited digesters are fixed-dome (Figure 19), which are usually constructed underground to maintain a constant temperature. However, during the rainy season, it is likely that the temperature will be low due to soil humidity. The average annual temperature which has been reported ranged between 18-25°C [370]. The measured slurry temperature during field visit ranged between 23-25°C. Although common for field digesters, this range is below the recommended mesophilic condition of 30-40°C [368]. Other reactors, such as plastic tubular plug flow digesters, which are usually mounted above the ground, are likely to be affected by temperature variations in the East Africa settings, which range from 17°C at night to 30°C during day time [416].

4.4.2.5 Type of the reactor

It has been observed that most of the digesters which are currently being used in East Africa are of fixed dome type (Figure 19). Such digesters are usually constructed underground to balance potential temperature fluctuations. Other digesters which are currently used are the balloon type (Figure 20) and the plastic digesters. These two types of digesters are usually cheaper as compared to the fixed-dome type, but their lifetime is shorter and are susceptible to damage and temperature variations during cold nights. According to digester owners in Uganda, a tubular digester of 9 m^3 can cost as low as Ugandan Shillings 3,000,000 (USD 842) whereas a fixed dome of similar capacity can cost between Ugandan Shillings 4,500,000 (USD 1,250) and 6,000,000 (USD 1,667). However, although the capital investment is high for a fixed dome digester, it has a life of more than 20 years which is more than 2 times that of tubular [417,418].

Figure 20. Balloon type digester

4.5 | DISCUSSION

It was observed during the field survey that there is potential to improve the biogas quality and quantity for electricity generation with alternatives ranging from physical pre-treatment to user practices such as proper mixing. Note that the observed CH_4 and CO_2 composition is suitable for electricity generation especially if dry reforming in SOFCs is envisaged [363–365]. However, H_2S needs to be removed for efficient electricity generation.

Currently in East Africa, some farmers store feedstock under the sun before it is supplied to the digester. Although this is done passively and in open space, it can potentially increase the rate of biodegradability of lignin-containing material [411], which in turn could increase biogas generation. According to Gong et al. [395], UV radiation from the sun is likely to increase the rate of degradation of lignin material that is present in cow dung. Therefore, solar exposure can potentially affect the rate of biogas production. It should, however, be noted that storing feedstock under open irradiation may require more water for feedstock dilution. In consequence, closed irradiation storage shall be preferred to enhance biodegradability of feed stock. Water loss can be minimised by storing the feedstock in closed storage, which concomitantly could be used to retain heat for additional thermal pre-treatment. Through this improvement, the feedstock temperature would increase leading to better efficiency of the AD process. If pre-treatment by solar radiation is embraced in small-scale digesters, it is likely to enhance the efficiency of the AD process.

Although not currently practiced, solar energy can also be used as thermal energy supply for feedstock low temperature (55-100°C) pre-treatment. This method is favourable for feedstock with low carbohydrates [310]. Since cow dung consists of approximately 20% of carbohydrates [419], the effectivity of this method on improving biogas quality and quantity when using this feedstock needs further investigation. It should be noted that with the availability of solar radiation and the possibility of solar thermal concentrators, low-temperature pre-treatment might be well feasible in small applications in sunbelt countries. Nonetheless, the additional capital and operational costs of its incorporation in small-scale applications need further investigation. Also, sub-Saharan Africa is generally hot with abundant solar irradiance, thus solar energy could be utilised to optimise the temperature control of the digester. However, its implementation needs to be evaluated concerning increased economic benefits and extra requirements such as a thermal insulation system to be used during cold nights.

A frugal[2] CSP system using Fresnel lenses can be proposed to utilise solar energy and provide heat for both pre-treatment and temperature enhancement for a fixed-dome underground anaerobic digester [420]. Fresnel lenses have become one of the top contenders in the field of concentrated solar energy applications [421]. This can be attributed to their lightweight and small volume properties. Furthermore, they are mass-produced at a low cost and can effectively increase the energy density [421]. Fresnel lenses achieve a concentration factor of 350-500 at direct normal irradiation (DNI) of 1 kW/m^2 [422], with a conservative estimate of 86% efficiency [423]. This feature makes them a good heating source for various applications [424–426]. Although solar tracking would generate more thermal energy from the sun as compared to the fixed system [427], if moving parts are used, the operational and maintenance costs for small-scale biogas-electricity generation systems will increase. To enhance actual implementation, the digester should be designed in such a way to minimise the heat transfer area and total costs [428]. Instead of heating the entire digester, heating of the feedstock input on daily basis can be considered as an alternative [386]. As reported before, many researchers have proposed the use of solar water heating system to enhance digester temperature. However, for small-scale applications, such system would require additional auxiliary components like pumps. Overall, this would increase the auxiliary power consumption and the operational and maintenance costs.

Milling, chipping and grinding practices were not observed in the field. This is because animal and human waste are currently used as the only feedstock in small-scale digesters. Out of the 48 digesters, 47 used animal waste as feedstock apart from a few of them in which toilet waste was added in addition to animal waste. It was observed during the field visit that there is under-utilised potential of plant waste, namely banana leaves, as a feedstock for small-scale digesters. If physical pre-treatment is embraced as common practice, this could enhance the use of plant waste as co-digestion feedstock with the usual animal dung in small-scale digesters. Milling, chipping and grinding, although not currently utilised, can be employed as a strategy to diversify feedstock and obtain more biogas. If this practice is embraced in small-scale digesters, it can encourage the

---

[2] *"Frugal Innovation is a design innovation process in which the needs and context of citizens in the developing world are put first in order to develop appropriate, adaptable, affordable, and accessible services and products for emerging markets"*

use of specific plant waste, namely banana leaves as co-feedstocks with the usual animal waste.

Physicochemical pre-treatment as reported before, basically refers to thermal pre-treatment. This pre-treatment is currently not utilised in the visited digesters. High-temperature pre-treatment (150°C-220°C) may not be readily applicable in small-scale application. But low-temperature pre-treatment can be readily applied in small scale applications using solar energy. However, low-temperature pre-treatment (60°C-90°C) was not in use for the visited small-scale digesters, although high solar insolation is available. Nevertheless, the prevailing solar irradiance could be passively applied during open sunlight storage. Other pre-treatment such as ultra-sonication, chemical pre-treatment and biological pre-treatment are currently not used in the investigated small-scale digesters.

In off-grid settings, there is a number of potential feedstock co-digestion alternatives which can be supplemented with the available cow dung. Such feedstocks include plant leaves, food peelings, among others which need further investigation on their possible beneficial effect on biogas quality and quantity. Co-digestion is likely to increase biogas quality and quantity and, therefore, should be encouraged for electricity generation from biogas. However, care should be taken to have the optimal co-digestion ratios depending on the type of available feedstocks. This can have economic and biotechnological advantages for operating small-scale digesters [323]. Research and development is required to determine the optimal ratio for specific feedstock co-digestion depending on the available alternatives.

From the field observations, there is passive co-feedstock of green leaves and additives of soil. As reported before, green grass and leaves may contain micro-nutrients of interest, such as Fe [346], which is also among the trace elements found in soil [67]. Such elements have been reported to enhance biogas yield and possibly reduce the H_2S content in biogas [337]. It was also reported that clay contains a significant amount of Fe_2O_3 and metal elements [429]. Some parts of East Africa are characterized by the presence of clay soils. This can either positively or negatively affect the biogas quantity and quality in terms of H_2S content for electricity generation applications. It should be noted that adding clay and soil in the digester may negatively impact the digester hydraulics and hence result in malfunctioning. Hence, the use of clay soil as an additive and green biomass as a co-feedstock needs further investigation to establish its benefits concerning biogas quality and quantity as a result of feeding ratio and clay composition.

The use of cow urine for feedstock dilution also acts as another additive to the AD process. Digesters using urine as a solvent had relatively lower H_2S concentration in the gas as compared to digesters that had water a solvent (Figure 16). This, therefore, indicate that the practice of using cow urine as solvent can reduce the H_2S content of the gas thereby making it more suitable for small-scale electricity generation. With an increased sulphur concentration in the influent (Figure 18), more H_2S content centration in the biogas would be expected for digesters with urine addition as compared to those with water as a solvent. On the contrary, the digesters, which had water as a solvent had higher H_2S content centration in the gas. Therefore, this indicates that the relatively high pH for digesters that had urine as a solvent apparently could have played a role in HS^- capturing in the liquid phase. These results can be well-explained by the circumneutral pKa value of 7.02 of H_2S/HS^-. The use of urine is currently encouraged to reduce water demand; however, urine also contains metal trace elements which can enhance the AD process efficiency [430]. The alkali metal and metal elements such as Na, K [430] need to be balanced for an efficient AD process. Therefore, the elemental composition of urine can have a positive effect on balancing the digester stability, meanwhile reducing on H_2S content in the biogas for electricity generation applications. Also, urine contains a significant amount of urea [431]. If urine is stored, urea is hydrolysed to ammonia and bicarbonate, which increases the pH of urine to values reaching as high as 9 [413]. Therefore, the usage of urine for feedstock dilution can affect the final pH in the system, hence stabilising or compromising the digestion process. As long as the pH does not reach values exceeding 8.0-8.5, the use of urine could be beneficial for the quality of biogas intended for electrical generation applications. Since urine adds additional sulphur and urea to the digester, excess ammonia can inhibit the AD process particularly at high pH values [432]. Also, additional sulphur can increase H_2S in the gas phase. Moreover, the use of urine is likely to affect the C/N ratio of the feedstock which can either positively or negatively impact the biogas quality and quantity. Therefore, the effect of urine for feedstock dilution needs to be carefully investigated in terms of its effect on the pH, C/N ratio, applicable loading and trace element dosage. The dilution of reactor content was recommended to mitigate the effect of excess ammonia and overloading of trace elements [432]. Consequently, the use of diluted urine instead of concentrated urine could have a more positive impact on the efficiency of the AD process. Further research is required to establish the optimal quantity of urine to achieve an efficient AD process.

Other operational practices, such as daily feeding and mixing, need to be encouraged among small-scale digester operators to improve the overall outcome of the AD process. Irregular feeding times, feedstock volume and mixing ratios will affect both the OLR and HRT of digesters, most likely affecting the quality and quantity of biogas. Such practices need to be standardised depending on the size of the digester and the nature of the used feedstock to guarantee optimal biogas generation for the envisaged electricity generation. This can lead to a more controlled OLR and HRT, as opposed to the current practice where feeding is done randomly and compromises the stability of AD. As a consequence of enhanced biogas production, more fuel will be available for biogas-electricity generation applications. Mixing is also likely to enhance the efficiency of AD but it is not currently embraced by off-grid digester operators. Mixing improves the contact between substrate and microorganisms [339]. Therefore, if such practice is embraced in small-scale digester operation, it is likely to enhance biogas quality and quantity. However, it was noted that according to the design of most digesters, stirring would be a tedious task. Consequently, it is highly recommended that a biogas digester for energy recovery is designed with a stirring mechanism. Also, solid materials and additive materials need to be encouraged to enhance the biogas production rate. Solid materials can act as co-digestion substrate, whereas additive materials such as ash contain metal elements such as Fe which can enhance the efficiency of the AD process [373].

Micro-aeration is an example of another practice, which should be embraced in small-scale biogas-electricity generation applications. This practice has been proven effective in small-scale digesters [361], but it is not commonly used in East Africa. An improved digester design for high-quality biogas recovery could include air dosage into the digester headspace to oxidise H_2S in the biogas. This practice could contribute to reducing the size of the additional cleaning unit, which in turn, will help to reduce the capital and operational cost for biogas-electricity generation system [299].

Thus far, pre-treatment is not commonly applied in small-scale biogas plants, which might be related to the use of animal manure as the main feedstock, which can be relatively easily digested without pre-treatment. There is an increasing interest in electrical power generation from biogas in off-grid communities which already count on other feedstock sources like plant-agricultural waste. An efficient pre-treatment for small-scle application needs to be re-considered in terms of its technical and economic feasibility. Moreover, it should be a versatile system, such that small-scale biogas plants already in existence, can be coupled with emerging small-scale SOFC technologies and the more conventional technologies such as ICEs. For a biogas-electricity generation system, thermal pre-treatment seems to be feasible if solar energy and the waste heat from conversion devices such as SOFCs is utilised as a source of heat for pre-treatment. Operational practices such as additive addition, mixing, among others need to be revived to enhance the AD process efficiency in small-scale digesters. Furthermore, irradiation from solar energy can also be used as a pre-treatment alternative, especially for countries with high solar irradiation.

4.6 | PROPOSAL FOR IMPROVED REACTOR DESIGN

A fixed dome design would be a good starting point for design modification to minimise daily temperature fluctuations during AD in the current settings. Construction materials that can insulate the digester during cold night conditions can be used during the construction. The enlargement of the inlet to avoid clogging (Figure 19b) and the incorporation of a mechanical stirring device are minor physical adjustments that could improve the digester performance.

There is potential to enhance the efficiency of biogas production employing locally available resources and straightforward modifications of the existing digesters. For instance, a simple mechanical mixer can be added to the existing fixed dome design to ensure proper mixing of the digestate to increase the conversion rates. Also, consistent daily feeding can enhance the mixing in the digester. Micro-aeration can be incorporated for in-situ H_2S reduction in biogas. For countries with abundant solar irradiation, solar-based pre-treatment, temperature enhancement of the AD process and post treatment of the digestate should be considered. However, further studies on the digestate quality in relation to application as fertilizer are recommended. As a summary of the revised literature and field observations of this study, a small-scale biogas-electricity generation system in Figure 21 is proposed.

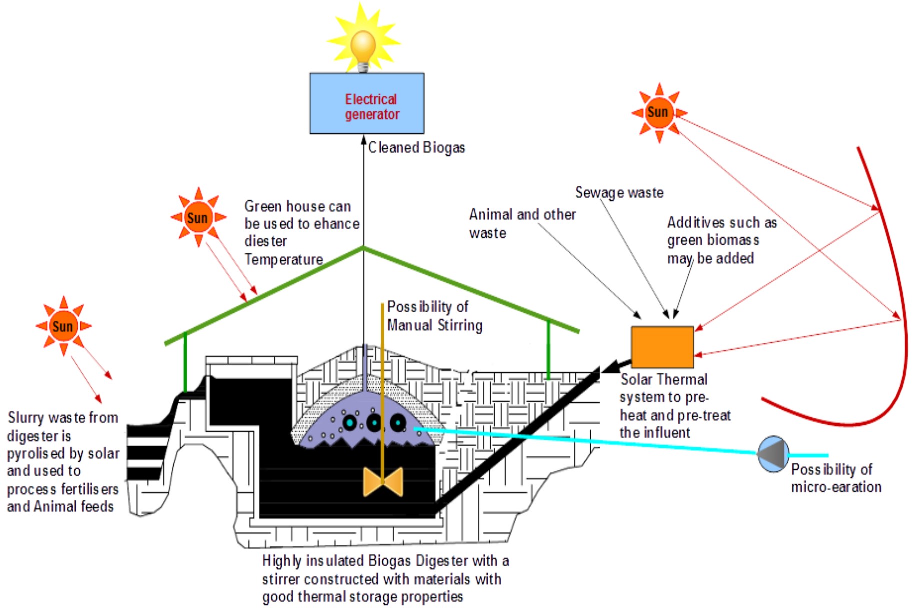


Figure 21. Model biogas-electricity generation system integrated with solar thermal system

4.7 | CONCLUSIONS

This study has shown that there is a potential to locally enhance biogas quality and quantity from small-scale digesters via available pre-treatment methods for feedstock, co-digestion, additives and operational practices. However, its implementation at small-scale in resource-constraint settings needs to be technically and economically evaluated. Furthermore, field observations have revealed that passive pre-treatments, additives and user practices can potentially impact biogas production. Specifically, the research has established that:

- There is a number of available co-digestion feedstocks in off-grid settings, such as banana leaves, which can be used apart from the usual animal and human waste. However, this needs additional practice such as milling and gridding to be effective.

- There is passive usage of co-feedstocks such as green leaves and additives such as soil. The usage of these locally available additives in off-grid community settings, could potentially enhance the AD process in small- scale digesters. However, there effect on process efficiency, needs to be more thoroughly evaluated.

- Urine is currently being used by some digester operators. However, urine could have several effects on the efficiency of the AD process and the quality of biogas in terms of impurities such as H_2S. Digesters using urine as solvent had lower H_2S content as compared to digesters that had water as solvent. Therefore, its use should be carefully evaluated to find out the extent of possible benefits, drawbacks and the optimal dilution ratio to enhance biogas production rate.

- Standard operation of the digesters was not always followed by off-grid digester operators. This has an effect on OLR, HRT among others. Therefore, good practices for digester operation such as agitation, daily feeding volume, dilution ratios need to be emphasized during user training to ensure stable operation and efficient biogas production in small-scale digesters.

Solar energy, though currently utilised passively, if embraced, can potentially enhance the digester temperature and also provide freely available thermal energy for pre-treatment of small-scale digester feedstocks. Solar irradiation can also be considered as a feasible alternative if mild temperature pre-treatment is applied in small-scale digesters. Also, solar energy can be a heat source to increase the digester temperature to an optimal range for the AD process. Its use can have a positive effect on biogas quality and quantity and thus can also enhance the economic feasibility of small-scale biogas-electricity generation systems. Despite the here mentioned advantages, further research and development is required to evaluate the economic and technical feasibility of solar integration with AD for small-scale biogas-electricity generation applications.

Biogas stoves

4

5

Laboratory and field-based study on the feasibility of In-situ H_2S reduction using cow urine as an envisaged operation cost reduction strategy

In-Situ H_2S reduction in biogas fuel for Solid Oxide Fuel Cell Applications by cow urine

ABSTRACT

Biogas, generated from small scale digesters, is a traditional energy source for satisfying the thermal energy demand in off-grid communities. Recent developments in small scale solid oxide fuel cells (SOFCs) technology and progress in research and development of dry reforming, opens perspectives to couple small scale SOFCs with already existing digesters to meet both thermal and electrical energy demand, enabling power access to off-grid communities.

However, one of the major challenges for SOFC integration to small scale digesters is the effect of biogas impurities, such as H_2S, on the performance of SOFCs. Previous work has shown that local operational practices could influence the biogas quality and particularly the H_2S content in the biogas. The here presented research expanded on the use of cow urine instead of water as solvent in manure digestion as a potential operational strategy that enables in-situ reduction of H_2S in the evolving biogas. This research investigated the following hypotheses: 1) urine addition results in a high pH that favours HS^- over H_2S, 2) given the presence of metal elements in the cow urine, insoluble metal sulphides are being formed, reducing the biogas H_2S content. The research was carried out by measuring cow urine composition of various samples, assessing the effects of different urine/water/manure mixtures on the evolving biogas-H_2S concentration, and verifying the experimental findings with phreeqC equilibrium speciation. Bio-kinetic modelling, using the anaerobic digestion model nr 1 (ADM1), was subsequently performed to explore the influence of different feed compositions on the H_2S content in the biogas.

It was observed that addition of cow urine in all experiments resulted in an elevated pH of the reactor compared to water dilution, yet both experiments I and II-2 showed an increased maximum H_2S content when urine dilution was applied, compared to water dilution. Cow urine and cow dung characterisation in terms of metals and S, showed that experiment II-1 had the highest Fe:S ratio of 1:0.3–1:0.9. Equilibrium modelling confirmed that despite the positive urine-induced pH effect, the measured Fe:S ratios could indeed be decisive, as with an Fe:S ratio of 1:6 and 1:0.5, the H_2S production at equilibrium was 61 and 10 mL/ kg of solution, respectively. Furthermore, it was predicted through bio-kinetic modelling that inconsistency in feedstock composition may result in temporary H_2S peaks exceeding 400 ppm. Overall, results showed that if a cow urine/manure mixture is characterised by a total metal:S ratio exceeding 1:0.5 and total S content of less than 0.5 mM, then hydrolysed cow urine addition presents an interesting in-situ H_2S cleaning strategy for biogas-SOFC applications.

5.1 | INTRODUCTION

Small–scale biogas plants are important to replace the common fossil fuel-based energy sources of off-grid communities, which are growing in number and size and are increasing the energy demand for rural agri-food systems [14]. The efficient use of renewable energy sources has the potential to decrease fossil-fuel based CO_2 emissions from agro-food systems, which consume 30% of the world's total energy [14].

Biogas from anaerobic digestion (AD) usually contains varying fractions of its main compounds CH_4 and CO_2, as well as varying fractions of trace compounds, such as H_2S and volatile organic compounds (VOCs), depending on the source [90]. The produced ratio CH_4:CO_2 in the biogas during AD is determined by the biochemical composition of the organic feedstock and the reactor operational conditions [433]. Therefore, several factors have been reported to influence the composition of biogas from AD, such as the type of fodder for the animals, the source and nature of the waste to be treated, and the design and operational practices of the digester [320][434]. Biogas from AD of sludge from waste water treatment plants (WWTPs) contains 55 to 65% of CH_4 and 35 to 45% of CO_2 [90]. From organic waste AD, biogas may contain 60 to 70% of CH_4 and 30 to 40% of CO_2, whereas for biogas from landfills, 45 to 55% of CH_4 and 30 to 40% of CO_2 with the rest being N_2 has been reported [90].

Biogas trace compounds, such as H_2S and volatile organic compounds (VOCs), are also present in varying quantities, depending on the feedstock composition and reactor operation. Biogas trace compounds are commonly referred to as impurities, because of their effects on both human health and energy process equipment. Their effects depend on their concentration in the biogas and the intended application of the biogas. Unlike other trace compounds like siloxanes, which are not common in high concentrations in biogas from small scale manure digesters, H_2S is one of the most common undesired compounds in the fuel for energy process equipment. H_2S also has been identified as one of the factors that contribute to biogas application failure in Africa [435], while it can also affect the efficiency of the AD process. For instance, high dissolved H_2S concentrations exceeding 0.15 gL^{-1} can affect methanogenesis, which can reduce the methane yield [436][437].

Metals have been reported to have a positive effect on the AD process in trace concentrations. The commonly required metals for a proper digestion process include Fe, Cu, Zn, Mn, Ni, Co, Mo, Se, and W [317]. If insufficiently present, then a balanced dosage can enhance the methane yield distinctly [243][337]. Dosing the digester with metals like Fe can also reduce the H_2S content in the biogas [336], which is due to the formation of metal sulphides. Apart from H_2S content reduction in the biogas, specifically Fe has been reported to enhance methane production and stabilize the AD process, as it was found to be required for cytochromes and ferroxin production in methanogens [337][338]. In addition, it has been reported that additives, such as $FeSO_4$, $FeCl_3$, Ca and Mg-salts and adsorbents, such as charcoal and silica gel, can potentially enhance the rate of biogas production [339]. However, it should be noted that inorganic additives also can become a source of secondary pollution to the environment [342]. Alternatively, some authors claim that organic additives, such as powdered legumes and leaves of some plants, may enhance the biogas yield by over 18% [339][345]. In addition to the increased organic load, this also could be due to the presence of trace elements, such as Fe, in green biomass [346]. Additives can also help to maintain favourable conditions in the digester, such as circumneutral pH, a pre-requisite for stabilized biogas production [339].

A biogas-SOFC energy system is being developed to cost-effectively meet the energy demands of rural off-grid communities in the developing world. Although, fuel cells costs have been reducing, costs reduction remains a serious challenge [438]. Possibly, overall costs can be further reduced using a trade-off with the biogas quality to be used as the fuel, provided long-term robust operation is not jeopardized. If successful, then a biogas-SOFC system could play an important complementary role in alternative off-grid energy supply systems. However, the presence of H_2S beyond threshold limit is still a challenge for biogas application as reported in Table 15, which is particularly true for biogas-SOFC systems [61]. Therefore, cleaning of the gas, regardless of the threshold of the equipment, is mostly preferred [121]. Although there are some SOFC materials that have exhibited high tolerance to H_2S, their cost is still a challenge [58]. On the other hand, it should be noted that cleaning of the biogas also would contribute to both capital and operation & maintenance costs of small-scale biogas-SOFC energy systems [299].

The use of urine as opposed to water for dilution of digester feed stock is one of the observed operational practices in Uganda. Urine contains cations like Na^+ and K^+ that may contribute to stabilise the pH as well as to dose specific metal elements such as Fe, which could act as co-factor in enzymes, enhancing AD efficiency, and precipitate sulphides as FeS [430][439]. In addition to this, urine contains urea [431], and when stored, urine is hydrolysed to ammonia and bicarbonate, which increases the pH of urine to > 9 [413][440]. Both trace metals and high pH can influence the AD process and hence biogas composition, including the H_2S content. Therefore, this research was aimed at investigating the effect of cow urine addition instead of water on H_2S concentration in the biogas. To the authors knowledge, so far, no studies have been conducted to investigate the feasibility of urine as a bio digester additive to enhance the AD process, as well as a possible in-situ H_2S cleaning method.

Table 15. Biogas impurity thresholds depending on the biogas application.

Gas application	Upgrading requirement	H_2S threshold	Siloxanes Threshold	Other VOCs threshold	Reference
Kitchen stove	Heating value comparable to natural gas	< 10 ppm	n.a.	n.a	[141]
Gas boiler	Upgrading may not be required.	< 250 ppm			[141]
CHP engines	> CH_4: 35% mol	545-1742 ppm*	9-44 ppm*	60-491(Cl) ppm*	[141][70]
Stirling engine	> CH_4: 35% mol	2800 ppm*	0.44 ppm*	232 ppm*$^{+}$	[70]
Natural gas grid injection	> CH_4: 95% vol CH_4: 70-98 % mol	< 5 mg/m^3 2-15 mg/m^3	n.a.	< 120 ppm**	[242][92] [141]
Vehicle fuel	> 96 % mol	5 mg/m^3	n.a	n.a.	[141]
Gas turbines	Upgrading may not be required	<10,000 ppm*	< 0.087 ppm*	< 1,500 ppm^{*+}	[70]
Micro turbines	Upgrading may not be required	25-70,000 ppm*	< 0.01 ppm*	200 ppm*$^{+}$	[70]
High temperature Fuel cells	Up grading may not be required due to possibilities of dry reforming [441]	< 1 ppm*	< 0.01 ppm*	< 5 ppm*$^{+}$	[70]

$^{+}$ halogens in biogas
*mg/m^3 of CH_4
** mg/m^3 of Sulphur
n.a. = not available

5.2 | MATERIALS AND METHODS

The study was carried out in five steps, which included: 1) characterisation of urine, 2) adaptation of the standardised biochemical methane potential (BMP) test towards a standardised biochemical gaseous H_2S potential (BSP) test using Dutch cow manure, 3) set-up and execution of two experimental BSP tests under field conditions of rural Uganda, 4) geochemical speciation modelling and 5) bio-kinetic modelling of H_2S production combined with geochemical speciation following the approach of Flores-Alsina et al. [442]. The BSP test is similar to the standardised BMP test [443], with the difference that the BSP test is focused on gaseous H_2S production potential as opposed to methane generation potential.

5.2.1 | Characterisation of urine

Fresh cow manure samples were collected from a farm in Delft (Hoeve Biesland), the Netherlands. Cow urine was collected from a farm in Enschede, the Netherlands. Samples were stored at 4°C. 1.5 mg of urine and cow dung samples were diluted to 50 mL with demineralised water and HNO_3 and used for further analysis to determine the element and S concentration. Sulphur and other elemental composition analysis of cow dung and urine samples were carried out by using ICP-OES 128 5300DV (Perkin Elmer Optima, Waltham, Massachusetts, USA) following the same procedure as described in Wasajja et al. [444].

5.2.2 | Experimental procedure for the measurement of gaseous H_2S in cow urine & manure digestion

5.2.2.1 Experiment I: BSP in laboratory environment

The BSP test was carried using an automated methane potential test system (AMPTS, Bioprocess Control, Sweden) with 15 cells [445]. The test was performed in triplicate. In the setup, glass serum bottles with a working volume of 400 ml and head space of 100 ml were used. The temperature of the bottles was maintained by a thermostatic water bath at 25°C for 40 days. The serum bottles were stirred at 120 rpm for 180 s after every 30 s of non-stirred conditions. Bottles were filled with 300 g of cow dung after applying a dilution in the ratio of 1:1. Each bottle was flushed with N_2. To achieve homogeneity, the inoculum was mixed by using a blender. K_2SO_4 solution was used to change the S/COD ratio. 0.5 ml of a 1 M K_2SO_4 solution was added to the cells 1-3, and 4-6, while the cells 7-9, 10-12 and 13-15 contained cow dung diluted with 50% urine and 50% water, cow dung diluted with urine, and cow dung diluted with water only, respectively. Cow manure functioned both as substrate and inoculum, to enable comparison to the field tests conducted in Uganda.

The next step was to adjust the BMP procedure to enable the prediction of the BSP. In the AMPTS, a water lock containing 3M NaOH solution is included, that is used to directly capture CO_2 from the biogas and enable the subsequent measurement of CH_4 only. Given the pKa of 7.2 of the H_2S/HS^- equilibrium [446], all produced H_2S is captured as well by the NaOH solution. Therefore, it is possible to use the same setup to analyse the BSP potential by analysing the total S concentration in the NaOH solution by ICP-OES, assuming that the redox state remains anaerobic until the end of the experiment. The metal element concentration in cow dung and urine that were used in the AMPTS experiments was also analysed using the ICP-OES, following the same sample destruction procedure as described by Wasajja et al. [447]. The captured sulphur in NaOH solution was used to calculate the H_2S produced per kg of manure.

Table 16. Inoculum composition in AMPTS cells

Cell No.	Inoculum
1-3	Cow dung + water + 0.5 ml of 1M K_2SO_4
4-6	Cow dung + urine + 0.5 ml of 1M K_2SO_4
7-9	cow dung + 50% urine + 50% water
10-12	cow dung + urine
13-15	cow dung + water

5.2.2.2 Experiment II: field-based BSP

The two field-based experiments II-1 and II-2 were carried out to further investigate the effects of urine on H_2S formation from cow dung. Fresh urine was collected from a Ugandan farm. It was left to hydrolyse for 30 days under atmospheric conditions. Fresh cow dung was also collected on the day of the start of each experiment from the same farm. Water was collected from a tap supplied by pumped water from an underground borehole.

In both the field-based experiments II-1 and II-2, nine 10 litre reactors were constructed out of plastic spray bottles (Appendix 1). They were equipped with a manometer pressure gauge (Festo, Germany) with a range of 0-1 bar to monitor the biogas pressure. The H_2S gas was sampled through the outlet of the bottle using a hand sampling pump (Dräger accuri, Luebeck, Germany). The H_2S content in the biogas was measured during sampling using the same hand sampling pump equipped with H_2S measurement tubes (Dräger, Luebeck, Germany) with ranges of 0 – 2,000 ppm and 0 – 7% (v/v).

In both experiment II-1 and II-2, reactors 1-3 were fed with 2 kg of cow dung diluted with 2 litres of water, reactors 4-6 with 2 kg of cow dung diluted with 2 litres of hydrolysed urine and reactors 7-9 with 2 kg of cow dung diluted with 1 litre of hydrolysed urine and 1 litre of water. It is highly important for the interpretation of the results to note that both experiments were conducted at a different time point with different cow dung and urine composition, albeit manure samples were collected from the same farm.

The second difference was that in experiment II-1, biogas pressure was left to accumulate, while biogas samples were taken. Consequently, in subsequent mass balance calculations, pre- and post-sampling pressure had to be corrected for. However, in experiment II-2, biogas pressure was left to accumulate until sampling, after which all accumulated gas was released to equilibrate to atmospheric pressure. Then biogas pressure was again allowed to accumulate until the next sampling point. This cycle was repeated until pressure no longer accumulated.

5.3 | THEORETICAL GEOCHEMICAL SULPHUR SPECIATION IN COW URINE/MANURE DIGESTION AT EQUILIBRIUM CONDITIONS

The aim of geochemical speciation modelling was to calculate and quantitatively determine the influence of urine mineral composition and total input sulphur on the theoretical gaseous H_2S equilibrium content. Based on the urine and manure composition in each of the three experiments, PhreeqC software was used to model sulphur speciation at equilibrium under the prevailing conditions in the gas, liquid, and solid phase [448]. As input parameters, the calculated total mass concentrations in cow manure and urine based on ICP-OES analysis were used (Table 17). As output, the equilibrium metal concentrations, pH, and H_2S content in the biogas were calculated and compared with the measured gaseous H_2S content in the three experiments. The applied 4 scenarios were: 1. Using water as a solvent, considering element concentrations of cow dung only; 2. Using urine as a solvent, considering element concentrations of both cow dung and urine; 3. Effect of increasing SO_4^{2-} concentration in the influent, considering high sulphate content in the feedstock; and 4. Effect of increasing Fe concentration in the influent, considering high Fe content in the feedstock. For the calculations, it was assumed that under anaerobic conditions all sulphate would be converted to H_2S/HS^- by sulphate reducing bacteria (SRB). Details of the used codes are presented in appendix 2.

5.3.1 | Prediction of dynamics in gaseous H_2S biogas content in continuous cow urine/ manure digestion

The bio-kinetic anaerobic digestion model nr. 1 (ADM1) was used to simulate the effects of using urine instead of water as a solvent during AD of cow manure to predict biogas and H_2S production over time. The model was adapted from Flores-Alsina et al. [442] and contained a metal speciation module, similar to the phreeqC approach as introduced in section 2.4. The model was adapted to the calibrated parameters for cow manure digestion as reported by Wichern et al. [449] in appendix 3, concerning the parameters: disintegration constant (k_{Dis}), acetate uptake rate ($k_{m,ac}$), upper pH limit for acidogens ($pH_{UL,acid}$), lower pH limit for acidogens ($pH_{LL,acid}$), propionate uptake rate ($k_{m,pro}$), half saturation coefficient for propionate uptake ($K_{S.pro}$), half saturation coefficient for hydrogen uptake ($K_{S.H2}$) and nitrogen content of composite and inert material ($N_{xc,I}$). The influent parameters were adjusted as shown in appendix 4. Four scenarios were modelled, which included: i) cow dung with water as solvent, ii) cow dung with urine as solvent, iii) cow dung with diluted urine as solvent, iv) increased sulphur concentration in cow dung with diluted urine as solvent. For the urine scenarios, inorganic nitrogen concentration was increased from 2.31×10^{-3} to 7.68×10^{-3} – 10.02×10^{-3} mg $L^{-1.}$ Since urine contains sulphur as sulphate [431], the sulphate concentration was doubled for concentrated urine and increased by 1.5 times for diluted urine. In addition, the concentrations of trace elements of urine + cow manure were used according to results of elemental analysis (Table 17).

5.4 | RESULTS

5.4.1 | Cow urine and manure composition

The composition of cow urine and cow manure used in experiments I, II-1 and II-2 regarding sulphur and the different elements is shown in Table 17, which gives an overview of the molar elemental composition measured by the ICP-OES. The raw elemental data has been converted into mM and has been clustered into trace metals, which, based on their literature reported K_{sp} values, are prone to form precipitates with sulphide. The sum of the macro cations Na^+, K^+, Ca^{2+}, and Mg^{2+} as well as the macro-anions PO_4^{3-} (TP) and S^{2-} (TS) is reported in meq/L, to facilitate evaluating their potential role in reactor alkalinity and potential influence on reactor pH. Even without NH_4^+ having been measured, the urine adds a significant cationic concentration to the substrate mixture.

Table 17. Element concentration in urine and cow dung used in experiments I, II-1 and II-2.

Exp	Solvent	Substrate	Trace metals (mM)				Macro cations (mM)				Macro anions (mM)		Sum (meq/L)	Sum (meq/L)
			Fe	Mn	Pb	Zn	Na	K	Ca	Mg	TP	TS	cat	an
I	Urine		0.0	0.0	0.0	0.0	0.1	1.4	0.2	0.1	0.1	0.1	10.0	0.4
	Urine		0.1	0.0	0.0	0.0	0.1	1.4	0.2	0.1	0.1	0.1	9.8	0.4
	Urine		0.1	0.0	0.0	0.0	0.1	1.4	0.2	0.1	0.1	0.1	9.7	0.4
	Water	Cow manure	0.1	0.0	0.0	0.0	0.1	1.2	1.6	0.6	0.9	0.4	9.6	3.6
	Water	Cow manure	0.1	0.0	0.0	0.0	0.1	0.8	1.5	0.7	0.9	0.4	8.2	3.7
	Water	Cow manure	0.1	0.0	0.0	0.0	0.1	1.7	1.6	0.6	0.9	0.5	13.3	3.8
II-1	Water	Cow manure	0.9	0.1	0.0	0.0	0.1	0.8	1.8	0.5	0.5	0.3	11.0	2.1
	Water	Cow manure	0.8	0.1	0.0	0.0	0.1	0.6	2.0	0.5	0.6	0.3	10.3	2.2
-	Urine		0.0	0.0	0.0	0.0	0.0	5.9	0.0	0.1	0.0	0.2	8.4	0.3
	Urine		0.1	0.0	0.0	0.0	0.0	5.7	0.1	0.2	0.1	0.2	8.1	0.5
	Urine	Cow manure	0.6	0.1	0.0	0.0	0.2	2.9	1.0	0.5	0.3	0.2	15.0	1.4
	Urine	Cow manure	0.9	0.1	0.0	0.0	0.2	3.5	2.4	0.7	0.6	0.4	20.7	2.6
	Water	Cow manure	0.4	0.1	0.0	0.0	0.1	0.6	1.0	0.4	0.3	0.1	10.4	1.0

	Water	Cow manure	1.0	0.1	0.0	0.0	0.2	0.9	1.7	0.5	0.4	0.3	14.9	1.8
II-2	Urine		0.0	0.0	0.0	0.0	0.0	7.1	0.0	0.2	0.0	0.2	9.2	0.4
	Urine		0.0	0.0	0.0	0.0	0.0	6.9	0.0	0.2	0.0	0.2	9.0	0.4
		Cow manure	0.4	0.1	0.0	0.0	0.1	1.1	3.5	0.6	0.9	0.4	14.0	3.5
	Water	Cow manure	0.0	0.0	0.0	0.0	0.1	0.5	0.1	0.1	0.0	0.0	4.9	0.1
	Water	Cow manure	0.3	0.0	0.0	0.0	0.0	0.6	1.2	0.3	0.3	0.1	5.9	1.3
	Water	Cow manure	0.3	0.0	0.0	0.0	0.0	0.6	1.2	0.3	0.3	0.1	6.0	1.3
	Urine	Cow manure	0.5	0.1	0.0	0.0	0.1	3.8	2.5	0.7	0.7	0.4	14.5	3.0
	Urine	Cow manure	0.5	0.1	0.0	0.0	0.1	3.7	2.3	0.7	0.7	0.4	13.7	3.0

* Concentration in 1.5 mg of sample diluted to 50 ml demineralised water and HNO

5.4.2 | Gaseous H_2S production in cow urine and manure digestion

5.4.2.1 Experimental results

Table 18 presents the total biogas production and the calculated total amount of H_2S produced, as well as the assessed Fe:S ratio, total S in the feed and pH in experiment I, experiment II-1 and II-2. Results showed that urine as solvent affected the H_2S content in the biogas both positively and negatively.

Through the positive controls, bottles 1-6, it was indicated that the method of capturing the H_2S, in the 3M NaOH solutions gave a reasonable accuracy in recovering the spiked 0.5M K_2SO_4. Unfortunately, the general performance of biogas production could not be considered as a sound positive control, likely because no adapted inoculum was added, the lag phase exceeded the experimental time of 30 days. Therefore, further analysis has been limited to a general comparison between H_2S produced in either the urine or water diluted Dutch cow manure. Results obtained from laboratory BSP experiments (experiment I) showed that the addition of urine, despite the increase in alkalinity, resulted in an increased H_2S-production of 51 mL/kg cow manure compared to 41 mL/kg cow manure for the water diluted bottles. In experiment II-1 less H_2S was produced in the urine diluted triplicate experiment, but also in this experiment, the biogas production was below expectation, likely because of the visually observed gas leakages. The latter experiment produced biogas between ~6.5 and 9.0 L/kg of manure, but showed a higher H_2S content when urine was utilized. It is noteworthy from the experimental results that urine also affects the biogas production quantity; results of Experiment II-2 showed a pronounced negative effect (Table 18).

If only the pH increase, induced by the increased alkalinity of the urine, was of importance, all the three urine diluted experiments should have produced less gaseous H_2S compared to their water counterparts. However, this was not observed. As such, also the total S concentration and Fe:S ratio are presented in Table 18. Due to the low concentrations of all other trace metals and iron being the most dominant one, the Fe:S ratio was determined and not the sum of all trace metals. It was anticipated that in case of a high Fe:S ratio, i.e., excess iron, the BSP would decrease and with a lower Fe:S ratio, the BSP should increase compared to experiments in the same pH range.

Results from experiment I showed that despite the relatively low pH and an unfavourable Fe:S ratio, the H_2S production per kg of manure is still very low. This low production is likely due to the low concentration of both iron and sulphur and the low stripping effect, since there was only very little biogas produced. For experiment II-1, the favourable Fe:S ratio, seems to be reflected in a low BSP. Experiment II-2 on the other hand, shows a relatively high H_2S production, despite the favourable Fe:S ratio and the high pH. Nevertheless, because of the tenfold higher biogas production, the resulting H_2S concentration is still very low in experiment II-2.

Table 18. Total biogas and total H2S production and relevant parameters influencing the H2S content in biogas in the BSP experiments.

Parameters influencing biogas H_2S content	Solvent	Experiment I	Experiment II-1	Experiment II-2	Description
Total Biogas Production (L/kg of manure)	H_2O	0.88±0.10	8.8±4.7	92.5±4.8	
	Urine	0.74±0.07	9.4±7.7	76.8±9.6	
Total H_2S Production (mL/kg of manure)	H_2O	41.1±0.1	4.4±0.1	18.1±4.6	H_2S content in biogas depends on absolute production of both H_2S and CH_4/CO_2
	Urine	51.1±0.2	3.1±1.8	40.9±7.3	
Total molar S (mM)**	H_2O	0.4	0.3	0.4	
	Urine	0.5	0.5	0.6	
pH	H_2O	6.0 – 6.1	7.1 – 7.2	6.5 – 6.6	Increased urea and ammonium, will have a pH increasing effect resulting in increased HS^- speciation
	Urine	7.0 – 7.6	8.3 – 8.4	8.4 – 8.5	
Fe:S (molar ratio)	H_2O	1:4 – 1:9	1:0.3 -1:0.9	1:0.6 – 1:1.8	Increased metal content will decrease concentrations HS^- and H_2S through metal-sulphide precipitation
	Urine	1:2.5- 1:6.3	1:0.5 – 1:0.7	1:1.5 – 1:2.0	

* The biogas and H2S production from all the experiments I, II-1 and II-2 is presented in appendix 1.

** in 50 ml diluted samples

5.4.2.2 Chemical speciation of sulphur in cow urine & manure digestion

To acquire more in-depth insight in the multiple parameter interaction on the speciation of S, the measured results were compared with the outcomes of equilibrium modelling using PhreeqC for the 3 urine dilution experiments. The assessed liquid matrix concentrations (Table 17) and pH (Table 18) were used as input parameters. The results are plotted in Figure 22 and the relevant experimental pH range is indicated with dotted lines.

PhreeqC results showed that pH had a great effect on the H_2S partial pressure in the biogas (Figure 22a) and that an increase in pH exceeding 7.0 sharply reduced the H_2S partial pressure. Results clearly showed that differences in influent composition affected the pH and the resulting H_2S partial pressure in the biogas. Modelling results agreed with the BSP experiments, in which reactors with urine showed a different resulting H_2S content and pH. Experiment II-1 with highest Fe:S had the highest proportion of HS^- as compared to experiment I and II-2 with lower Fe:S ratios. It should be kept in mind that also the cation species Na^+, K^+, Ca^{2+}, Mg^{2+} contribute to S speciation (Table 17). From Figure 22C, it can be seen that the liquid is highly saturated with respect to FeS_2 (pyrite) and this indicates that in all three experiments, any available iron will precipitate S in the stoichiometric ratio of the precipitate. It is noteworthy that also the saturation index of mackinawite, having a 1:1 molar Fe:S ratio, indicated super saturation (data not shown). In addition, also other trace metals appeared supersaturated for S precipitate formation, such as, MnS, PbS and ZnS (data not shown).

Modelling experiment I, II-1 and II-2, considering the same Fe:S ratios as measured in the experiments diluted with urine, showed that an increase in Fe:S ratio resulted in a decrease in the H_2S content in the gas phase. Using the scenario of experiment I, with an Fe:S ratio of 1:6, the resulting H_2S production was 90 mL/kg of feedstock at a pH of 7.0 (data not presented here). For experiment II-1 and II-2, with an Fe:S ratio of 1:0.5 and 1:1.8, the H_2S production was 16.7 mL/kg of feedstock and 49.5 mL/kg of feed stock, respectively. Apparently, by decreasing the Fe:S ratio from 1:0.5 to 1:1.8, the increase in H_2S production is more than doubled. Therefore, doubling the S concentration in the substrate can potentially double the H_2S concentration in the biogas if pH remains constant.

The PhreeqC speciation model, with urine and manure composition as input parameters, also confirmed that CO_2 speciation followed, according to expectations, the same trend as H_2S under these conditions. The higher the pH, the lower the CO_2 content in the gas. Therefore, for technologies that aim at biogas cleaning and upgrading, CO_2 and H_2S removal compete for cation availability. Overall, a higher pH than circumneutral would be preferred from the perspective of gas composition, though too high pH (typically > 8.5) may hinder the biological process [434]. Also, the free NH_3 content in the liquid and biogas is expected to be higher at a high pH, potentially reaching inhibitory levels for the methanogenic biomass.

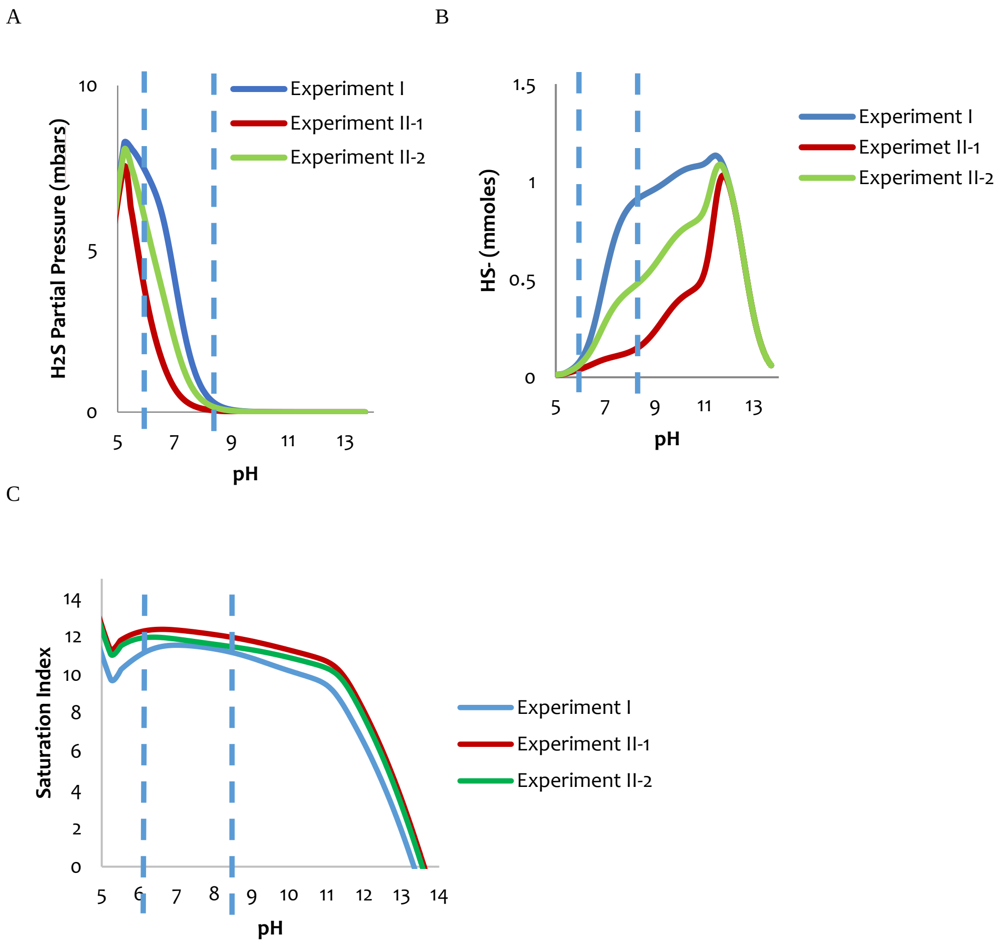
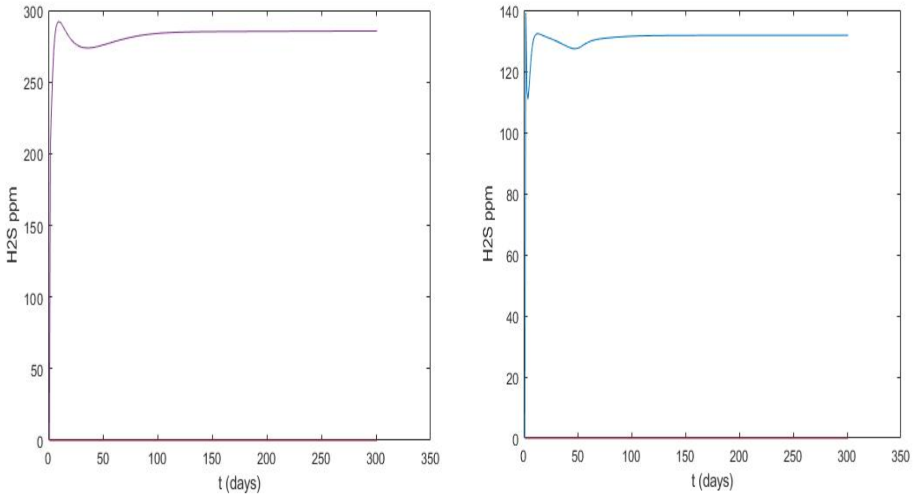


Figure 22. Effects of pH and Fe on S speciation in Experiment I, II-1 and II-2 with 100% urine dilution. 22A shows the effect of pH on H_2S partial pressure in the biogas, 22B shows the effect of pH on the HS^- concentration in the liquid phase, and 22C depicts the Fe-S saturation index in all experiments.

5.4.3 | Prediction of dynamics in the biogas gaseous H_2S content during continuous cow urine/ manure digestion

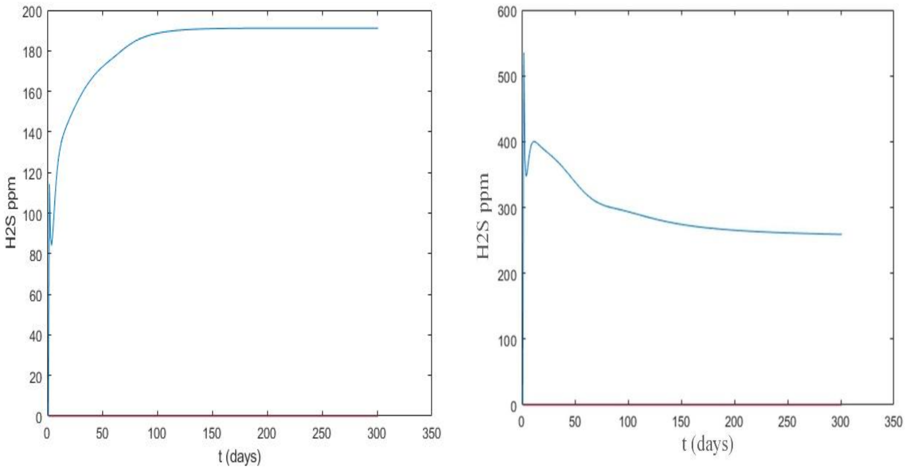
Under field conditions, rural digesters are often intermittently fed. The biokinetic model ADM1 was used to simulate the biogas H_2S content of a continuous flow reactor, while incorporating a chemical S speciation model, similar to the phreeqC model, following the approach and code developed by Flores-Alsina et al [442]. Figure 23 shows the ADM1 results for the biogas H_2S concentration using water (Figure 23a), urine (Figure 23b), and diluted urine

(Figure 23c) as the solvent. The parameters for the model input are shown in appendix 3 and they were based on literature data [431] and the metal element analysis presented in Table 17. The flow rate of the digester was left at the default value of 188 m³/d and the temperature was set to 25°C mimicking the average ambient temperature in Uganda. A final H_2S content of 280 ppm in the biogas was obtained for water as the solvent and a digester pH of 7.0. For urine as the solvent the H_2S content was 130 ppm at a pH of 7.4, despite the doubling of the total S concentration. Comparing the experiments with diluted urine (1:1) and diluted urine with increased SO_4^{2-} concentrations, results showed that an increased SO_4^{2-} content resulted in an increased biogas H_2S concentration (Figure 23d). The increased biogas H_2S concentration applying diluted urine as solvent indicated that if urine is to be used as an in-situ H_2S reduction mechanism, care should be taken to determine its sulphur concentration in advance. Urine with high SO_4^{2-} concentrations may require a higher degree of dilution to keep the digester sulphur loads to an appropriate level. It must be noted that more dilution also would concomitantly reduce the ammonia concentration, resulting in a lower pH.



A

B



C D

Figure 23. Dynamic profile of H_2S content in the biogas with the use of different solvents. 23A H_2S concentration with H_2O as solvent, 23B H_2S concentration with urine as solvent, 23C H_2S concentration with diluted urine (1:1) as solvent and 23D H_2S concentration for diluted urine with increase in SO_4 concentration from 1.49 x 10^{-4} mg S/L to 4.7 x 10^{-4} mg/L

Common operational practices of small-scale biogas digesters result in varying feed quantities, depending on the availability of feedstock [447]. Also, there is no standard feeding timetable [447]. This non-continuous feeding scenario and inconsistency in feedstock composition, based on results presented in this chapter, will most likely lead to a variable biogas H_2S content in ranges that could be detrimental to SOFC operation.

5.5 | DISCUSSION

5.5.1 | Comparison of experimental and theoretical biogas H_2S concentrations using cow urine/water as dilution of cow manure.

Previous work [444] had shown that Ugandan manure digesters are characterised by large fluctuations in the biogas H_2S content which appeared related to the addition of cow urine as solvent. Results obtained from experiments in our current work showed that using urine as the solvent indeed affected the H_2S content in the biogas, albeit both positively and negatively. It was hypothesized that the difference in H_2S content would be attributable to the urine and cow dung mixture composition and more specifically to the Fe:S ratio, the pH, and the total sulphur content of the feed stock. To verify this hypothesis, the experimentally determined composition of cow dung diluted with 100% urine was used to calculate the sulphur speciation and a comparison was made between the calculated and measured soluble iron and total sulphur concentration, as well as the produced gaseous H_2S (Figure 24).

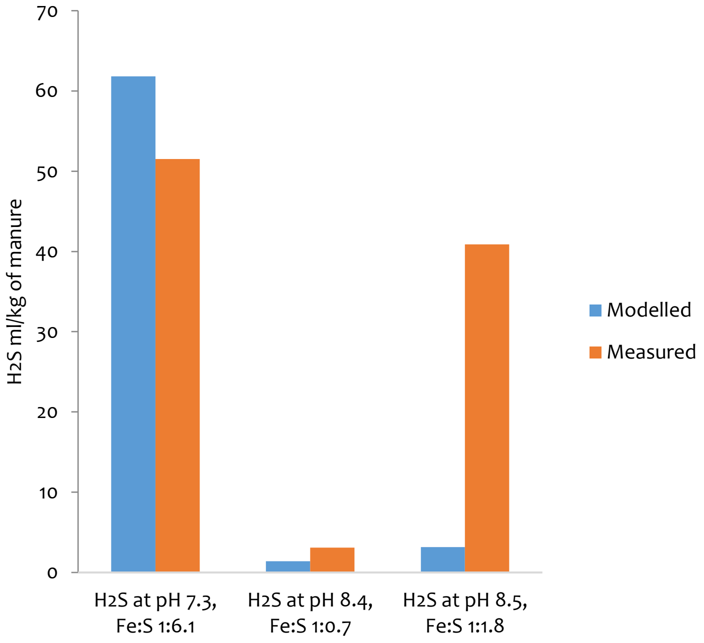


Figure 24. Comparison of the total amount of produced gaseous H_2S between experimental and modelled values using 100% urine dilution.

Evaluating both the measured and modelled results indicated that at an Fe:S ratio of 1:6.1 and pH 7.3 (Experiment I), the model can predict a relative rapid rise in H_2S to 50-60 mL/ kg of cow manure. A high Fe:S ratio combined with a high pH (8.4), both experimentally assessed as well as in the model, resulted in an accurate and low production of gaseous H_2S (Experiment II-1). Experiment II-2 is characterized by a low model prediction of 3.2 mL/ kg of cow dung, but a high actual measured value of 40 mL/ kg of cow dung.

Results listed in Table 18 showed that experiment I, experiment II-1, and II-2 had different Fe:S ratios, which were also dependent on the used solvent (urine or water). The average Fe:S ratio for reactors diluted with urine from experiment I, experiment II-1, and experiment II-2 was 1:6.1,1:0.7, 1:1.8, respectively.

Modelling with PhreeqC using the measured Fe:S ratios with reactors diluted with 100% urine from all experiments clearly showed that the prevailing Fe:S ratio influenced the resultant H_2S in the gas, which clearly was also pH dependent. Our results corroborate with Schmidt et al [14], who reported that metal elements are reported to not only enhance the anaerobic digestion process but also to reduce the H_2S content in the gas phase, since they react with HS^- / S^{2-} to form metal sulphides which remain in the liquid phase [336]. The Fe:S ratio-depending modelled resultant H_2S production agreed well with the measured results (Figure 24). PhreeqC model results showed that the lower the Fe:S ratio in the feedstock diluted with urine, the higher the resultant H_2S in the gas. Experiment I, which had the lowest Fe:S ratio, had the highest resultant H_2S production of 62 mL/kg of feedstock, whereas experiment I-1 with the highest Fe:S ratio had the lowest resultant H_2S production of 1.4 mL/kg of feedstock. The strikingly observed inconsistency between the modelled values and the experimental values in experiment II-2 was attributed to error propagation of the H_2S measurements, following the chosen experimental set-up. During the experiment, the gas was released after every measurement resulting in a pressure drop. According to Henry's law, H_2S has the highest Henry's constant of 1.15 mol L^{-1} MPa^{-1} as compared to that of CO_2 and CH_4, which are 0.318 mol L^{-1} MPa^{-1} and 0.016 mol L^{-1} MPa^{-1} [450]. This implies that dissolved H_2S already produced migrates preferentially to the gas phase compared to CH_4 and CO_2. Therefore, H_2S in subsequent measurements could be accounted for multiple times leading to an over estimation of the cumulative experimental H_2S production. On the other hand, the measured pH was 8.5 which was relatively high for bicarbonate-controlled alkalinity. Measurement errors in the pH, if propagated as model input, would lead to a 3-times under estimation of the modelled predicted H_2S if the actual reactor pH was 8, instead of the recorded value of 8.5.

A similar trend was also observed comparing the measured results of urine and water dilution. When applying urine as diluent the resultant H_2S production from experiment 1, experiment II-1 and experiment II-2 was on average 51, 3 and 41 mL kg^{-1} of feedstock. Applying water as diluent resulted in an average Fe:S ratio in experiment I, experiment II-1 and experiment II-2 of 1:7.5, 1:0.6, 1:1.2 respectively. The Fe:S ratio was lowest in experiment I, having the highest average H_2S production of 41 mL kg^{-1} of manure followed by 4.4 mL kg^{-1} of manure and 18 mL kg^{-1} of manure in experiment II-1 and experiment II-2, respectively. It was further noted that reactors from experiment II-1 diluted with urine had relatively lower H_2S production than those diluted with water. This could be attributed to the higher pH of reactors diluted with urine as compared to those diluted with water. Contrary to this observation, reactors from experiment I and II-2 diluted with urine had higher H_2S production than reactors diluted with water. This, therefore, suggested that at a given pH, the metal elements:S ratio of the feed stock had a determining effect on the resultant H_2S in the biogas.

From Table 17, it follows that urine contains metal elements and sulphur. This implies that the use of urine instead of water as solvent adds extra sulphur and metal elements in the feedstock of the digester. However, if the metal element and sulphur content in feedstock diluted with urine has the ratio of metal element:S to less than 1:1, the use of urine as solvent instead of water is likely to increase the resultant H_2S content in the biogas.

The results of the present work show that the use of urine can greatly affect the equilibrium H_2S content in the biogas, influencing the composition of the biogas. Reduced H_2S content in the biogas could be attributed to the presence of metal elements in urine, such as Na, Fe, Mg etc. [430] and its relative high pH when it is hydrolysed. It is noteworthy that the chemical composition of urine could vary depending on the storage time, which can be attributed to hydrolysis of urea and other biochemical reactions, depending on conditions of storage [431]. Notably, the NH_4^+ concentration will be higher leading to an increased pH if hydrolysed urine is used for dilution. The sulphate concentration in urine may exceed values of 250 mg S L^{-1} [431], which can increase the sulphur concentration in the feedstock and hence will increase the H_2S content in the biogas. However, in some cases, the S concentration in urine is less than 100 mg S L^{-1}. The variation in the urine S content is attributed to dietary intake [451]. If urine with low sulphate concentration is used for dilution, while the metal content is high within cow dung and urine itself, a low H_2S content in the biogas is expected. Data presented in Table 18 show that experiments with a higher Fe:S ratio in the medium had a lower H_2S content in biogas, referring to reactors with urine dilution as compared to those with water dilution.

It is worth to note that urine may contain variable amounts of ammonia, sulphur and metals. At constant pH, high concentrations of sulphur will consequently increase the H_2S content in the biogas and high concentration of ammonia, and metal concentration in the feedstock can potentially inhibit the anaerobic digestion process. Therefore, if urine is to be used as an in-situ H_2S reduction method in the biogas, a proper balance between the additional sulphur load, and metal loads and the potential increase in pH is needed. It is also noteworthy that PhreeqC results are given under equilibrium conditions, which was, however, not the case for the batch-wise performed BSP experiments; for instance, in experiment I, a very low biogas production rate was observed indicating a non-stable digestion process. Therefore, further research under dynamic conditions is recommended.

In addition to the biogas H_2S content, urine also had a clear effect on the generated biogas quantity. In all experiments using 50% urine and 50% water dilution (urine:water 1:1), the biogas production was enhanced, which even exceeded the biogas production when 100% urine dilution was applied (Appendix 5, 7 and 9). Apparently, a proper urine to water dilution needs to be determined prior to use in anaerobic digestion.

5.5.2 | The importance of predicting gaseous H_2S biogas content dynamics in continuous cow urine/ manure digestion

Modelling results using ADM1 to simulate the concentration of H_2S in the biogas using varying feedstock composition confirmed experimental results. While working at a comparable pH, a decreasing Fe:S ratio increased the resultant H_2S in the biogas. From field results in our previous research [444], it was observed that the frequency of feeding varies widely from one digester to the other. Such practices could result into varying biogas production rates and H_2S content. ADM1 modelling results in our present research indeed showed that inconsistency in feedstock composition and pattern resulted into a varying H_2S content. Although in practice, the H_2S pattern may not exactly follow the feedstock composition and pattern due to complexity of the AD process and physical properties such as mixing conditions in the reactor, ADM1 results showed that variable H_2S concentrations in the biogas can be expected. Therefore, when designing a cleaning system for H_2S, such variations should be considered. The kinetics of both H_2S and CH_4 production rates are likely to be feedstock dependent. Results showed that fluctuation in H_2S content in the biogas ranged between 100 ppm – 400 ppm, depending on the time of sampling. It is worth noting that specific cow urine and manure composition in terms of N and S-binding metal content needs to be determined to enable realistic predictions of field digester performance.

5.6 | CONCLUSION

Experimental results showed that pH and trace metal elements influenced the H_2S content in the biogas of a manure digester. Results from experiments and modelling indicated that if urine is used with a high Fe:S ratio, i.e., greater than 1:0.5, the H_2S content in the biogas will be relatively low. Experimental data showed that cow urine contained metal elements and was characterised by a relatively high pH exceeding 7.7 when hydrolysed. A relatively high pH influenced the H_2S content by sulphur speciation, whereas metal elements reacted with S^{2-}/HS^- to form metal sulphides. Therefore, the H_2S content in the biogas is determined by the total S content, the pH, and the Fe:S ratio. Results clearly showed that if urine is used as a solvent in biogas digester feed stock preparation, the biogas H_2S content is greatly affected. The overall effect of urine depends on the exact mineral urine composition and the composition of the used cow dung. If diluted feedstock with urine has a high Fe:S ratio, in-situ H_2S reduction in the evolving biogas is expected.

Therefore, if urine with low sulphur content and high metal content is used for dilution of digester feedstock, such that the overall Fe:S ratio is greater than 1:1, then the pH of feedstock will increase and in-situ H_2S reduction in biogas will be enhanced. Hence, in such case, urine dilution will be attractive for application in biogas-SOFC energy systems. However, if high-sulphur content urine is used, such that Fe:S ratio is less than 1:1, the usability of urine for in-situ H_2S biogas cleaning becomes less attractive.

Crashed char

6

Laboratory and field-based study on the use of locally available biochar as H_2S adsorbent

The effect of metal elements, pH and other impurities on adsorption of H2S

ABSTRACT

Biochar is readily available in off grid areas where the envisaged biogas-SOFC energy system will be applied. This can be a good cheaper source of cleaning adsorbent as compared to commercial adsorbents. Preliminary experiments show that biochar can clean biogas to the required level of H_2S for SOFC application. However, detailed study in terms of the influence of metal content in biogas and pH on the adsorption capacity needs further research and development.

Note: The preliminary results included in this chapter have been included in this thesis, as they indicate the feasibility of using biochar to remove H_2S to the required levels, but more extensive studies are recommended.

6.1 | INTRODUCTION

Biogas from waste is an envisaged technology to meet both energy and sanitation needs of off-grid communities. On small scale, biogas has been utilised more to meet thermal energy needs than electrical needs. With this back ground, cleaning of the gas has not been of interest. However, due to the increasing interest of generating electricity from small scale digesters [19], the gas is required to be cleaned from impurities such as H_2S which have an effect to the operation and durability of electricity generation system. Among the impurities, H_2S is considered to be the highest impurity content in off-grid farm biogas digesters which majorly use animal manure as the feed stock [81]. Other impurities such as siloxanes and other VOCs are considered to be very low for biogas from farm digesters [452]. Different biogas electricity generators have different impurity tolerance limits [124]. If SOFC is envisaged as one of the generators, very low H_2S content in biogas of less than 2 ppm(v) is required [62].

Small scale SOFC system of capacity less than 5 kW are being promoted by a number of companies [47][49][50][55]. This provides an opportunity to integrate SOFCs with small scale digesters. Hence, there is potential for off-grid electricity supply from small scale biogas-SOFC energy system. However, one of the major challenges of SOFCs is the effect of H_2S on the operations efficiency and reforming process if dry reforming is envisaged. Therefore, for safe operation of SOFCs, H_2S within the biogas has to be cleaned. The conventional cleaning of the gas has been by use of adsorbents such as activated carbon, ZnO among others [299]. However, these adsorbents are not readily available in off-grid setting and therefore may increase the operation cost of a biogas-SOFC energy system [299]. Hence, readily available adsorbent needs to be considered for successful operation of gas cleaning unit of a biogas-SOFC system in off-grid setting.

Bio-char is readily available adsorbent in off-grid settings. It can be produced from conventional biomass from agricultural waste. Bio-char can be environmentally friendly replacement of the use of activated carbon [453]. The advantage of biochar as compared to other sorbents such as activated carbon and ZnO is its adsorption capacity increases in the presence of moisture [454]. Biochar moisture content of upto 85% has been reported to enhance H_2S adsorption [455]. It should be note that biogas contains up to 6% of moisture [456], therefore this is an added advantage to use biochar in biogas-SOFC cleaning unit. Another characteristic which makes biochar more suitable for H_2S adsorption is its relatively higher pH as compared to other sorbents such as AC

[454]. High pH of the adsorbent has been reported to enhance the adsorption capacity of biochar [457].The same authors [457] also reported that the production of biochar at lower temperature has been reported to use less energy and also cost effective. It should be noted that the characteristics of biochar depend on the both the pyrolysis temperature and the original source of biochar [457]. This also reported by Chak and Park et al that characteristic of biochar depends on the source and the carbonisation temperature [453].

Although the adsorption of biochar has been studied by a number researchers, to author's knowledge, the effect of pH and together with elemental composition of biochar on the adsorption capacity has not been reported before.

6.2 | MATERIALS AND METHODS

Biomass materials were carbonised using a locally made carboniser in Uganda. The carbonisation temperature was above 400°C as measured by the thermal camera (Figure 25) and infra-red thermal gun (colemeter, HongKong, China). In addition, commercial activated carbon was used. Jackfruit tree branches were cut from a single tree. Leaves were separated from branches and left to semi dry under a shade. Fresh cow dung was also collected from a farm and left to semi dry under a shade. Leaves, branches and cow dung were carbonised as shown in figure 26. Samples of biochar from leaves, tree branches, cow dung and activated carbon were prepared following the same procedure as described by Wasajja et al. [444]. Element composition of the sample analysis was carried out using ICP-OES 128 5300DV (Perkin Elmer Optima, Waltham, Massachusetts, USA) following the procedure described by Wasajja et al. [444]. pH was measured using a pH meter (Greisinger G 1500 series, Regenstauf, Germany with pH resolution of 0.01 and temperature of 1°C). The surface porous structure of carbonised biochar was characterised by nitrogen sorption at 77 K using the NOVATouch gas sorption analyser from Quantachrome (Quantachrome Instruments, Boynton Beach, Florida, USA). Prior to the measurements, the samples were degassed at the degas station of the same instrument, using either 60 or 130°C under vacuum for 16 hours. The specific Brunauer Emmet Teller (BET) theory was used for the determination of the BET surface area of biochar, was determined based on the adsorption isotherm input data. This calculation is standardized within the TouchWin software of Quantachrome, and provided a linear fit with a correlation coefficient of 0.99.

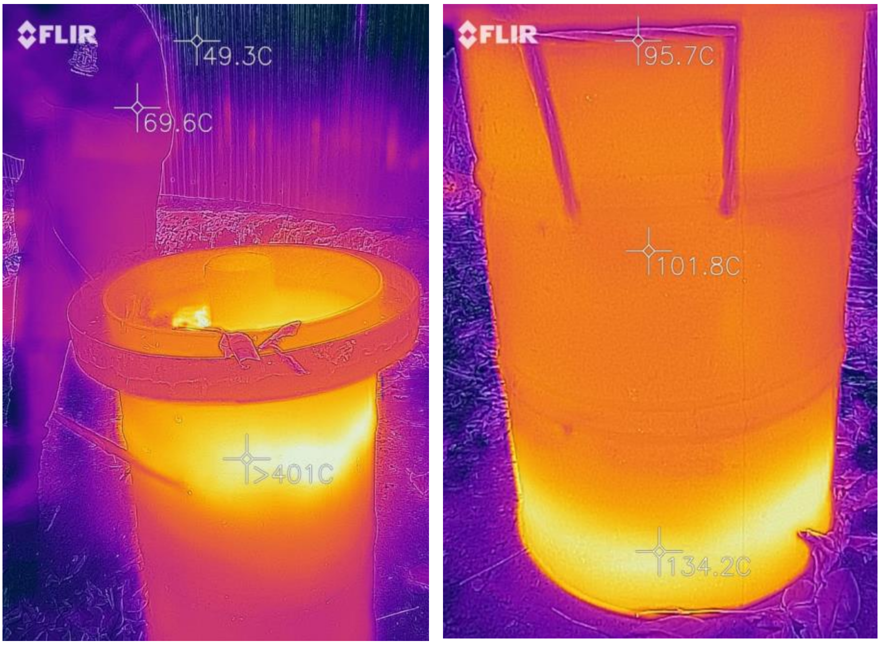


Figure 25. Temperature profile of bio-char carbonization taken by the thermal camera (taken at different time)

Figure 26. Photo of biochar carbonization

6.2.1 | Pre-Laboratory Based Experiment

To test the effective of the biochar in the laboratory, Biogas generated by continuous reactor fed by synthetic waste water connected to a cleaning column. The cleaned gas was collected in the gas bags. H_2S before the column and the cleaned gas was measured by Dräger tubes. H_2S was sampled and measured by using a gas hand sampling pump (Dräger accuri, Luebeck, Germany) fixed with a Dräger tube (Dräger, Luebeck, Germany). Dräger tubes of different ranges 0-5 ppm and 0 – 150 ppm were used.

6.2.2 | Field based experiment

The field-based experiment was set up as shown in figure 27. A glass column of height 0.50 m and internal diameter of 0.03 m was used. 5.5 g of glass beads and 5.5 g of adsorbent were used for each type of biochar. The inlet gas tube was connected to the outlet of gas meter with a nominal flow rate of 500 ml h^{-1} (Ritter, Germany) which was in turn connected to the main gas pipe. The out let of the column was fixed with the outlet gas pipe with a valve which was used to sample the outlet gas measured. H_2S was sampled and measured by using a gas hand sampling pump (Dräger accuri, Luebeck, Germany) fixed with a Dräger tube (Dräger, Luebeck, Germany). Dräger tubes of different ranges 0-5 ppm, 0-150 ppm and 0-2,000 ppm. H_2S random measurements were done to determine the input H_2S in the column and H_2S content in the outlet gas of the column.

Identical biochar was used to carry out the field-based experiment. The experiment was carried out as shown in Figure 27. Four experiments were conducted using three different type of biochar's and activated carbon. Biochar of Jack fruit leaves, Jack fruit tree branches, cow dung and activated carbon was used. 5.5 g of biochar were loaded in the glass column with 5.5 g of glass beads. For each set of the experiment, the type of biochar was changed respectively. Constant biogas flow was run through the column to determine the break through time of each biochar and activated carbon. The flow was regulated by the valve and measured by the flow meter.

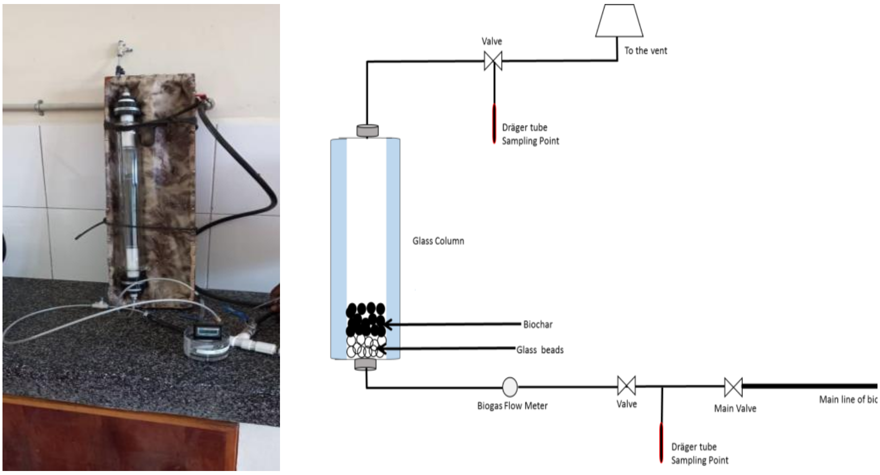
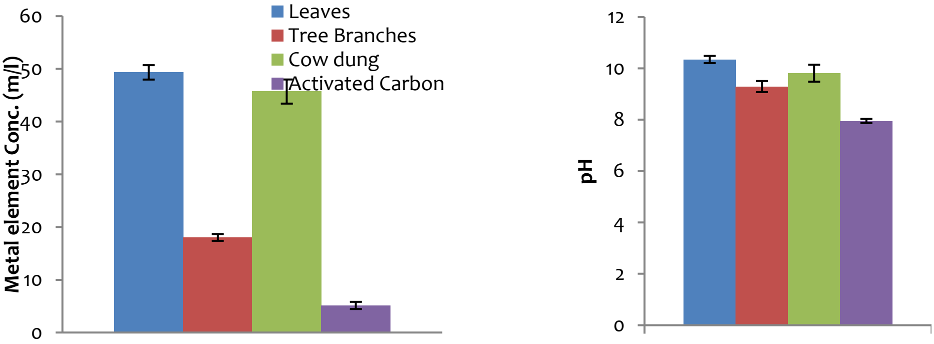


Figure 27. Experimental setup

6.3 | RESULTS

The elemental analysis of biochar is as shown in the appendix 11 below. Figure 28 shows that biochar from leaves had the highest amount of metal element content whereas biochar from tree branches had the least metal content. It is observed that generally biochar had more metal content as compared to activated carbon. Also, the BET analysis of biochar from cow dung, tree leaves and tree branches are also as shown in Figure 29. Results from BET analysis show that activated carbon has a very big surface area of over 1100 $m^2 g^{-1}$ surface area as compared to biochar of which the highest among the three categories was of that cow dung which is 27 $m^2 g^{-1}$.



(a) (b)

Figure 28. 28(a) Metal element content in biochar from leaves, tree branches, cow dung and activated carbon (1.5 mg of sample diluted up to 50 ml). 28(b) corresponding pH.

Figure 29. BET surface area biochar from leaves, tree branches, cow dung and activated carbon.

It was observed that biochar can effectively clean the gas to 0 ppm. From the pre-liminary lab experiments, the H_2S content in biogas was 20 ppm and the H_2S content of cleaning was 0 ppm before the breakthrough time. Also, from the field-based experiments, the H_2S in the biogas was varying from 50 ppm to 120 ppm but still biochar could clean the gas to 0 ppm of H_2S before the breakthrough (Figure 30). Preliminary results clearly shows that biochar can be used as cleaning adsorbent for H_2S. However, its effective in terms varying field operation needs to be investigated further.

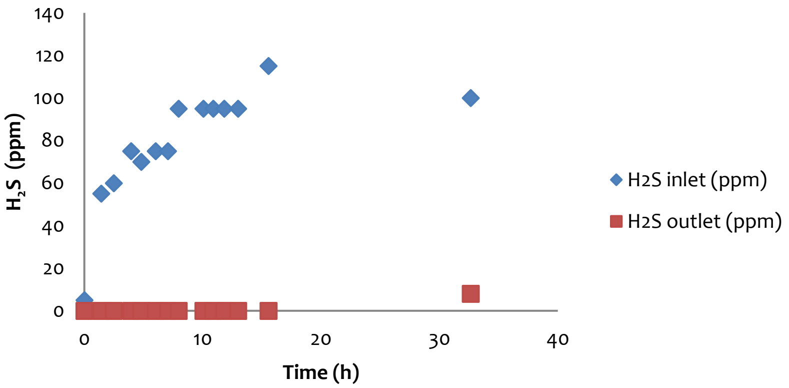


Figure 30. Measured H_2S inlet and outlet for leaves biochar

6.4 | DISCUSSION AND CONCLUSION

It has been observed that biochar contains metal elements which are essential for H_2S adsorption. This coupled with high pH of biochar can be an added advantage to use locally available biochar as an adsorbent H_2S. It has been reported that the surface area of leaf biochar plays an important role in the adsorption capacity of H_2S together with other factor such as pH, carbonisation temperature and mineral elements present on biochar [458][459]. However, from the field experiments, it was observed that there was varying pressure hence varying flow rate since the biogas was being used for cooking through the day. Therefore, the effectiveness biochar needs further investigation in the laboratory and controlled conditions. Detailed analysis is still required to investigated the effectiveness of biochar as adsorbent under varying physical and operating conditions.

Since the surface area of biochar plays a critical role on adsorption capacity [459], the influence of metal element content and pH on the different types of biochar with varying surface areas needs further studies under controlled conditions. The results will help to set the optimal conditions in terms of space gas velocity, contact time, pressure and other operating parameters for optimal absorption of H_2S. Carbonisation temperature has also been reported as one of the factors which can influence the adsorption capacity of biochar [459], therefore for different available biochar, the optimal carbonisation temperature for carbonisation needs to be further investigated. Aeration has been reported as one of the methods used to enhance H_2S removal from the gas [460], therefore the effect of aeration of biochar on adsorption capacity needs to be investigated. Since biogas, is composed of other impurities such as mercaptans and siloxanes [80], it is anticipated that the higher the composition of such impurities in biogas, the higher the competition for adsorption on biochar pores. Therefore, the effect of other impurities such as mercaptans and siloxane need to be investigated too.

Pre-paid electrical energy meter

7

Economic Study of biogas-SOFC energy system

Improving the economic feasibility of small-scale biogas-solid oxide fuel cell energy systems

ABSTRACT

A small scale (up to 5 kWe) biogas-Solid Oxide Fuel Cell (SOFC) energy system is an envisioned system, which can be used to meet both electrical and thermal energy demand of off-grid settlements. SOFC systems are reported to be more efficient than alternatives like internal combustion engines (ICE). In addition to energy recovery, implementation of biogas-SOFC energy systems can enhance sanitation among these settlements.

However, the capital investment costs and the operation and maintenance costs of a biogas-SOFC energy system is currently higher than the existing alternatives. This research, therefore, focused on economic analysis of investment and operation costs of the biogas-SOFC energy system. This analysis was done with view on identifying the possible system component alternatives, which may lower the overall system costs to improve its economic feasibility. For purifying the biogas prior to SOFC use, results revealed that the use of biochar instead of activated carbon might distinctly reduce the overall system cost and greatly increase its chances of economic feasibility. Results showed that the use of biochar instead of readily manufactured activated carbon as an adsorbent in biogas-SOFC cleaning units can reduce the operation and maintenance cost of biogas-SOFC energy system by over 80%. Also, the use of internal reforming as opposed to external reforming can greatly reduce the system capital cost by over 25% and hence further increase the chances of system economic feasibility.

By applying the proposed cost reduction strategies coupled with subsidies such as tax reduction or exemption, the biogas-SOFC energy system can become economically competitive with already existing technologies for off-grid electricity generation, like solar photovoltaic systems.

7.1 | INTRODUCTION

Electricity generation from biogas plants is of growing interest to meet the energy needs of off-grid communities. A number of pilot projects with this objective have been carried out by different organizations, like the German Corporation for International Cooperation (GIZ) and the Netherlands Development Organization (SNV) in East Africa [461][462][463]. Some countries, like South Africa, consider electricity generation from biogas as a low hanging fruit [464]. According to the same source, a potential of 93 MWe is feasible in medium term to be generated from wastewater treatment plants (WWTPs), contributing to cover 20 % of the total electricity generation potential from biogas in South Africa. Solid oxide fuel cells (SOFCs) are energy converters which can use biogas as a fuel to generate both thermal and electrical energy. A biogas-SOFC energy system is an envisioned system targeting to meet both thermal and electrical energy needs for the rural and off-grid population in a more efficient and sustainable way. The added advantage of the proposed system to other alternatives is the capability of waste utilization hence reducing sanitation related diseases which is becoming an increasing problem to rural people [5]

In contrast to the conventional gas and diesel engines, SOFC would not require high methane and low water content in biogas, since both water and carbon dioxide are required if reforming is envisaged [463]. However, SOFCs require highly cleaned gas from impurities. And apart from these impurities, currently, the major challenge of SOFCs is the high investment and operational costs. Recently, a few companies have started manufacturing small scale SOFC systems with capacities up to 5 kWe on commercial scale [49][50]. Such a small scale SOFC system can perfectly match with a small-scale biogas system hence forming a biogas-SOFC energy system for rural energy supply. SOFCs are more efficient compared to the convectional technologies like internal combustion engines, since they are not limited by the Carnot efficiency [12].

Biogas from anaerobic digestion (AD) is an attractive source of fuel to utilise in a biogas-SOFC energy system since it involves the use of already existing wastes to recover energy. Furthermore, the anticipated waste heat from such energy system can be utilised to optimise the AD process and/or sterilise the digestate. Moreover, thermal energy in excess may be used for drinking water production, which may contribute to improved health conditions, while also increasing the economic returns of SOFCs. Biogas-SOFC energy systems are considered attractive since they also contribute to controlled organic waste stabilisation, which would otherwise result in sanitation related diseases and at the same time produce fertilisers for agricultural applications [3][4]. Another advantage of SOFCs is that they can work in modulation ranges of 50-100%. This ability enables SOFCs to work on variable gas flows, which is typical for small scale systems that are often installed without gas storage [52]. However, the costs of a biogas-SOFC is high with SOFC currently being the most expensive part. Nonetheless, cost reduction is required to make biogas-SOFC systems competitive to alternative technologies such as solar cells and other systems.

Staffell et al. [65], reported that fuel cells have been "*fore ever five years away from commercialization*" hence lagging behind as compared to other domestic technologies. They further reported that although cost predictions for SOFC was \$500 per kWe with an additional \$500 – 1,000 for a complete micro-combined heat and power (CHP) system, the actual costs of SOFC have not met this target yet and goals have been changed to realistic values. It is assumed that mass production of small-scale systems for domestic applications could accelerate their move from laboratory to commercialisation. In fact, it is reported that production volumes are a dominant factor in determining early SOFC manufacturing costs and hence, it highly influences the overall SOFC costs [465]. For instance, production costs of fuel cells can potentially drop from \$500/kWe to less than \$100/kWe if production can be increased from 100 to 50,000 systems per year [466]. The same authors [65] also reported that over 10,000 domestic micro-CHP units were already operating in Japan in 2011 and annual sales were expected to double by 2012. And as of 2021, 300,000 CHP units and back up-power systems have been installed in Japan, and the target is to install 5 million systems by 2050 [467].

It has been reported that small scale biogas plants for direct gas use are economically viable in some sub-Sahara countries, like Uganda, with a payback period of approximately 1 year for a 16 m^3 digester volume of plant capacity [468]. In 2006, the international network for sustainability, reported the cost for 1-6 m^3 daily capacity of biogas production to cost \$1,800–3,900 [469]. This would imply that the installation cost per 1 m^3/day of biogas production capacity was about \$650–1,800 by then. The installation cost per 1 m^3/day of biogas production capacity would definitely be lower for plants of higher capacity. According to Lutaaya [403], fixed dome cost of a 6 m^3 digester volume ranged between \$1,000 – 1,200. Savings per annum for a family with a 10 m^3 digester volume as reported by the same author [403], was Ugandan shillings (UgShs.)

780,000 ($629[1]) due to reduced purchase of solid biomass (firewood and charcoal). When adjusting this amount with an average inflation rate of 6.4% since 1998 to date, the value is today equivalent to 1,119,000 ($320[2]) [470]. SNV reported biogas reactor investment costs in the order of UgSh.950,000 ($374[2]) for a 6 m^3 digester volume with a biogas production capacity of 2 m^3/day [471], which agrees with approximately $180 per cubic meter daily biogas production. It can be therefore deduced from literature that the average installation costs per m^3 of biogas production per day is between $180 - 1,800 whereas the cost per kWe is $100 - 500 for SOFC system. However, the cost of SOFC system per kWe is higher than this range when it comes to small systems of less than 5 kWe [53].

For the biogas–SOFC energy system, the costs will not only depend on the initial investment costs of a digester and a SOFC, but also on the operation and maintenance costs plus the additional costs required for fuel conditioning, like a biogas cleaning unit. It has been reported that the costs for gas purification can represent up to 20% of the electricity benefits for a biogas-SOFC plant of 300 kWe capacity [80]. The fixed operational costs, such as changing stacks in the SOFC, has been reported as the major barrier for integration of SOFCs in the energy mix. With the already mentioned advantages of a biogas-SOFC energy system, it is important to analyse the biogas-SOFC energy system costs and compare it with existing technologies such as biogas-internal combustion engine (ICE) system. This will help in making informed decisions from the economic point of view. Our present research, therefore, focuses on how the integration of local alternatives, such as using biochar as a cleaning adsorbent, as opposed to activated carbon, can affect the overall capital exploitation cost (CAPEX) and operational exploitation costs (OPEX), including maintenance, of the biogas-SOFC energy system. In addition, the effect of subsidies in terms of tax exemptions on both the CAPEX and OPEX is investigated, as well as the effects of system modifications, such as using internal reforming as opposed to external reforming. Biogas-SOFC energy system costs is compared with biogas-ICE energy systems and solar based energy systems.

---

[1] https://data.worldbank.org/indicator/PA.NUS.FCRF?locations=UG, Exchange rate in 1998 was 1 USD = UgShs 1240

[2] Exchange rate as per 21-01-2022, 1 USD = UgShs 3500

7.2 | MATERIAL AND METHODS

7.2.1 | Description of the studied site and system

The envisioned studied system is located in Kijonjo monastery, Kyotera district in Uganda. The monastery is currently having a 75 m^3 biogas digester. This biogas digester is fed with cow dung from a farm of over 130 cows. With the capacity of 9-15 kg of dung per day per cow [472], the gas capacity of this farm can go up to 35 m^3 of biogas per day putting the farm projected growth into consideration [473]. Also, the farm has 10 pigs and 100 chickens which can produce additional 1.5 m^3 of biogas per day. Additionally, sewage from the residents can also be used as co-feedstock to the digester and has a daily biogas production of 0.5 m^3. The power capacity requirement is estimated at 1 kW to power 40 rooms of the residents, security lights and phone charging. Based on the available gas and the power requirement, a 5 kWe capacity of a biogas-SOFC can be assumed for this site. If future growth is anticipated and extra gas is needed for the biogas-SOFC energy system, an additional digester can be installed.

7.2.2 | Economic analysis of the system

The economic analysis was carried out based on both the CAPEX and OPEX of the biogas-SOFC energy system. For comparison, a similar system of biogas-ICEs was designed, and its economic analysis was also carried out. Analysis of economic viability of systems was done, using the net present value (NPV) and payback period. NPV reflects the value of an investment throughout its life time depreciated to present value. NPV was calculated using equation 12.

$$NPV = \sum \frac{Cash\ flow}{(1+i)^t} - initial\ investiment$$

(Equation 12)

Where i is the depreciation rate and t is the time period in years. The payback period, which is the time required to recover the initial investment, was calculated using equation 13:

$$Payback\ period = \frac{Initial\ investiment}{Cash\ flow\ per\ year}$$

(Equation 13)

The future value of money was calculated using equation 14:

$$Future\ Value = \frac{Present\ Value}{(1+i)^n},$$

(Equation 14)

where i is the interest rate and n is the number of time periods (years).

Sensitivity analysis was carried out based on projected cost reduction, resulting from the use of locally available materials such as biochar as opposed to activated carbon for biogas cleaning. Also, system modifications such as the use of internal reforming as opposed to external reforming coupled with tax exemption are considered during the sensitivity analysis.

7.3 | ECONOMIC ANALYSIS OF BIOGAS-SOFC ENERGY SYSTEM

The economic analysis is based on the current economic conditions of Uganda, applying an interest rate of 17% [474] and an exchange rate of 3,500 Uganda Shillings (UgShs) for 1 US dollar (USD)[1]. Table 1 lists the assumptions for the conducted economic analysis. It is assumed that the already available cow dung will be used to generate biogas before it is used as fertilizer, hence the savings of fertilizer costs is also considered as an income. Digestate fertilisers are considered to be of higher quality as compared to undigested manure [475].

Table 19. Assumptions during economic analysis.

Item	Assumptions
Interest rate	17%
Dollar rate ($1)	UgShs 3,500
Project duration	20 years
Energy selling price	Assumed constant throughout the project duration
Source of income	Electricity and fertilizer purchase savings

7.3.1 | Capital costs and operations costs

From 2009 to 2017, fuel cell CAPEX costs have dropped by 70% and OPEX costs have dropped by approximately 57% [476]. For a fuel cell system, balance of plant (BoP) are auxiliary systems such as cleaning unit, power conditioning system, etc. BoP can be a dominant cost driver for the overall SOFC system costs and should not be overlooked especially for small scale SOFC systems of less than 5 kWe capacity [466]. Therefore, the future cost reduction should also focus on non-stack system components. The costs per kWe of manufacturing small SOFC systems like 10 kWe can be as high as three times as compared to the costs of manufacturing relatively big SOFC system of around 250 kWe, both at production capacity of 100 systems per year [466]. However, if the production capacity is increased to more than 50,000 systems per year, these costs could be almost comparable [466]. Photovoltaic (PV) inverters and SOFC inverters could share some key traits like DC voltage inversion to AC, anti-islanding protection, frequency synchronization and feed of sine wave current. However, their costs may not be necessarily similar. SOFC inverters are assumed to be cheaper to PV inverters, since some functionalities such as maximum power point tracking are not required [53].

The costs of a 1 kWe SOFC was between $21,000–31,000 in 2016 [53]. The price of a 5 kWe SOFC was between $6,000-8,500 per kWe installed (manufacturing costs and installed price analysis of stationary fuel cell systems), which in total amounts to $30,000-42,500 for a 5 kWe system. Considering the prevailing inflation rate, the costs of a 1 kWe and 5 kWe system amounts to $24,000-36,000 and 33,000-47,000 respectively[3] [27]. It should be noted that the SOFC labour installation cost per kWe is $12,000 and $2,500 for a 1 kWe and 5 kWe SOFC respectively [53]. For small SOFC systems of less than 5 kWe, the BoP hardware accounts for 60% of the total system cost [54]. It has been reported that 80% of the BoP plant cost is due to the required fuel processing, i.e., biogas cleaning and reforming [54]. Therefore, eliminating the fuel cleaning unit and the reformer could have a high impact on the overall SOFC CAPEX and OPEX [65]. For small scale system, the costs of installation take the biggest percentage of total installed system costs. However, this is likely to be different in developing countries where the cost of labour is low [53]. It is assumed that SOFC inverter cost will be comparable to the typical PV inverter cost [477]. The SOFC system costs summary is presented in Table 20.

---

[3] interest rate of i = 0.25 - 2.25 according to the interest bank rate of country of origin of this information [479]

Table 20. Indicative SOFC system costs summary

Sn.	Description	Cost per kWe for a 1 kWe ($)	Cost per kWe for a 5 kWe ($)	Total cost for a 5 kWe ($)	Ref
1	SOFC system	24,000–36,000	6,500–9,500	32,500-47,500	[53]
2	Installation cost of SOFC system	12,000	2,500	12,500	[53]
3	BoP cost of SOFC System @60% of total system cost	14,000–21,500	3,900–5,600	19,500–28,000	[54]
4	Fuel Processing of SOFC system @80% of BoP	11,500 – 17,500	3,000 – 4,500	15,000 – 22,500	[65]

OPEX for SOFC include payment for the workers, cost of changing the absorber, costs for changing fuel cell stacks, amongst others. The operational fixed cost, such as changing stacks, has been reported as the major barrier for integration of SOFCs in the energy mix [478]. Therefore, a distinct reduction in OPEX is a key factor for having an economic breakthrough of small-scale biogas-SOFC energy systems. Table 21 presents the envisaged OPEX of a biogas-SOFC energy system.

7.3.2 | System Cost analysis

For assessing the overall cost analysis, the current economic conditions of Uganda were considered. The envisaged biogas-SOFC energy system is considered to have a total installed power level of 1-5 kWe and a life span of 20 years. The interest rate in Uganda is estimated at 17–20% [474], whereas this is 0.25-2.25% in USA [479]. The current cost of the fuel cell is taken to be $24,000 to 36,000 for a 1 kWe and $33,000 to 47,000 for a 5 kWe SOFC system (installed costs) [53]. Although, it is expected that the costs will decrease to about $21,500 for a 1 kWe and $30,000 for a 5 kWe with mass production of 10,000 to 50,000 units per year [53]. These costs include the installation costs and the BoP costs, which account for over 60% of the SOFC system cost [53]. The costs of the biogas cleaning system is part of the BoP and is considered to be $100–250. The costs of the biogas cleaning system is part of the BoP and is considered to be $100-250. The cost of biochar adsorbents is assumed to be lower than that of commercial adsorbents such as activated carbon which costs more than $4.8 per kg of H_2S adsorbed [299]. Therefore, the cost biochar is expected to be below

\$4.8 per kg of H_2S adsorbed. The consumption of adsorbents can be minimized if in-situ cleaning techniques are used, such as the use of urine for cattle dung dilution to increase the digester pH for enhanced H_2S solubilisation and to induce H_2S precipitation as metal-sulphides during AD [447]. It is assumed that the cells are replaced after every 5 years, and the costs are assumed as \$1,900–6,000 for a 1 kWe and 4,000–7,500 for a 5 kWe SOFC system. Table 21 summarises the CAPEX and OPEX parameters considered.

The costs of installation of the digester per m^3 of biogas produced per day is assumed to be between \$180-1,800 based on literature and price quotations from selected biogas plant installers (appendix 12). The observed costs varied distinctly between private companies, which can be partly attributed to the fact that some suppliers promote biogas plants on subsidised basis from international donors. Nonetheless, the typical commercial costs without any subsidy would lie within the range based on price quotations from private companies in Uganda.

OPEX would ideally include the salaries of the operators. It is assumed that one employee could be enough to operate the envisaged system on part time basis. The costs for this labour according to the Uganda scale is assumed to be UgShs 300,000 (\$86[1]). Other running cost would be changing of adsorbents and the changing of the cell stacks which are listed in Table 21. Other expenses such as the annual maintenance cost and annual spare parts are estimated to be 6% of the annual OPEX [53], whereas annual miscellaneous expenses is 12% of the annual OPEX [53]. Since most of the required spare parts are imported from abroad, it is assumed that they will be taxed on importation. Taxes are assumed to be 34.5% [480][481][482]. Taxes include value added tax, levy and withholding tax according to the Uganda tax laws.

With the above parameters, the NPV is less than - \$50,000 for an operational period of 20 years and therefore the system is not economically feasible.

Table 21. CAPEX and OPEX of a biogas-SOFC energy System.

No.	Item	Description (USD)	Comment
1	Fuel cell (5 kW)*	33,000	
2	Inverter	2,000	
3	Other electrical accessories	500	
2	Biogas digester	10,500	
3	Gas Supply system and storage	1,000	
4	Gas cleaning equipment	3,000	

Table 21 continued…

No.	Item	Description (USD)	Comment
5	Design and installation	0	included in SOFC cost
	Sub-Total 1	**50,000**	
6	Miscellaneous cost (5% of the investment))	25,00	
8	Taxes	12,000	
	Total installation costs	**64,500**	
	Annual Running costs		
7	Labours costs	1,000	
8	**Cost of adsorbent**	5,000	With activated carbon used as adsorbent
10	**Annual miscellaneous**		
	Total running costs per year	6,000	
	Other fixed costs		
11	**Spare parts/cost of changing the cells**	**6,000**	changed every after three years
	Annual miscellaneous cost		
12	Income from fertilisers	1,000	
13	Income from electricity using assumed cost of electricity@ $ 0.21/kWh	8,300	
	Total income per year	**9,300**	

*The approximate minimum cost of a 5kWe is considered with assumption that the cost is decreasing with time

However, it is assumed that the costs of the SOFC system would drop with mass production. A cost reduction analysis (Figure 31), showed that the envisaged biogas-SOFC system would become economically feasible at a price of approximately $10,000 for the entire system. However, Table 21 indicated that the costs of other equipment, such as the biogas cleaning equipment, is about 60% of the total costs of a biogas-SOFC energy system. Therefore, for attaining economic feasibility of the envisaged biogas-SOFC energy system, other cost components, such as the digester itself, should be reduced as well. It should be noted that the cost target for a small scale SOFCs is $1,000–1,700/kWe [466]. This implies that the target price for a 5 kWe biogas-SOFC system is around $5,000 and thus, a cost reduction of other equipment, such as cleaning unit and biogas digester of $5,000 is required.

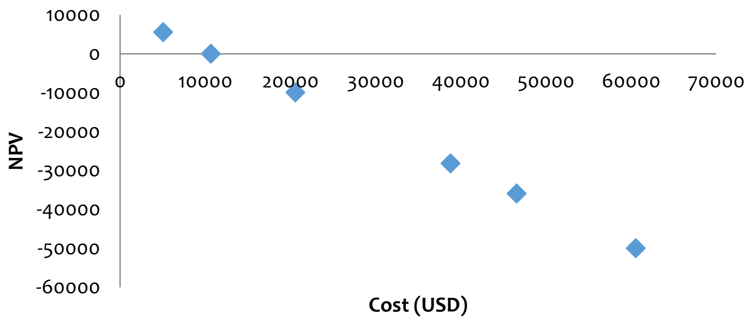


Figure 31. Sensitivity analysis of SOFC system cost (USD) on net present value (NPV)

7.3.3 | Effect of locally available materials on the economic feasibility of a biogas-SOFC energy system

With activated carbon as adsorbent, the operation cost per year is estimated to be over $6,000 based on the cost of adsorbent per kg of H_2S adsorbed [299]. However, using biochar as adsorbent, the operational costs are reduced to approximately $1,000 per year since biochar can be carbonised on site from the already existing biomass. It is assumed that the cost of carbonisation of biochar is insignificant and can be incorporated in labour cost and in miscellaneous costs. The estimated current CAPEX of the proposed system is approximately $65,000 (Table 21). When activated carbon is used as adsorbent, the negative NPV value becomes zero, indicating economic feasibility, when the costs are reduced to $12,500 (cost of the entire biogas-SOFC system). When biochar is used, the operational costs will be reduced to $1,000 and thus, the NPV value would increase. In the latter case, the negative NPV value becomes zero when the costs of the biogas-SOFC system is reduced to $40,500 (Figure 32). This implies that if biochar is used as adsorbent, higher future costs of the biogas-SOFC are allowed, i.e., up to $40,000, to become economically feasible. Whereas, if activated carbon is used, the future costs of a biogas-SOFC energy system needs to drop to at least $12,000 to become economically feasible (Figure 32). The latter value seems unrealistic since the costs of solely the digester is about $10,000 (Table 21) and it is unlikely that these costs will further decrease, since AD is a mature technology. Moreover, if also other cost reduction strategies are considered, such as utilisation of internal reforming as opposed to external reforming, subsidies & tax exemption, and mass production, the proposed use of biochar as alternative adsorbent can realistically accelerate the economic feasibility of the proposed biogas-SOFC energy system.

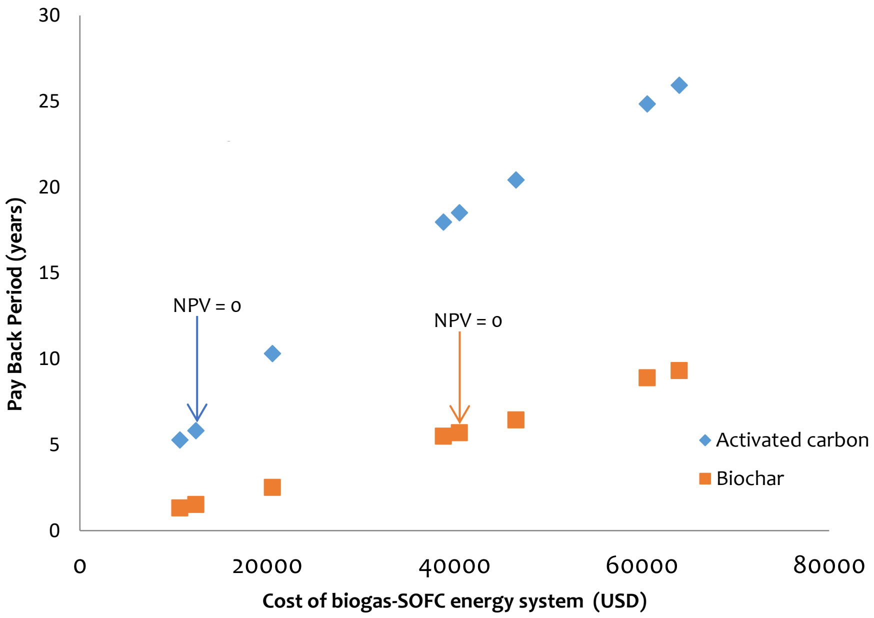


Figure 32. Foreseen payback period as a function of biogas-SOFC energy system costs, using either activated carbon or biochar as gas cleaning adsorbent. Arrows indicate at what system costs the NPV reaches zero, using either of the two adsorbents.

From Figure 32, it is observed that for the same capital investment cost, the biochar payback period is distinctly shorter because of the lower operating cost for using biochar as adsorbent instead of activated carbon. The calculated differences in yearly operational costs provide opportunities to invest in a more expensive SOFC system.

When using activated carbon as an adsorbent, even if the cost of the SOFC system only (without the cost of biogas digester) is reduced to $1,000, the NPV is - $15,500 (scenario B in Figure 33). It is assumed that cost of other parts, like the biogas system in Table 21, may not reduce with time and are assumed to be constant. This implies that despite a drastic reduction in the SOFC costs, the biogas-SOFC system won't be economically viable, at least in the nearby future. However, if biochar is considered as an adsorbent, the biogas-SOFC starts to be economically viable when the cost of the whole biogas-SOFC system can be reduced to $7,000, indicated by a positive NPV in Figure 33 (scenarios E and F).

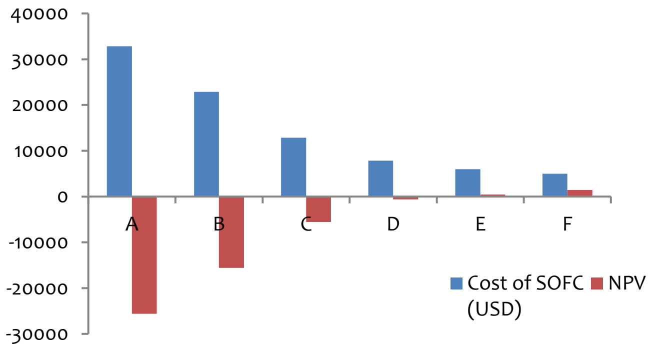


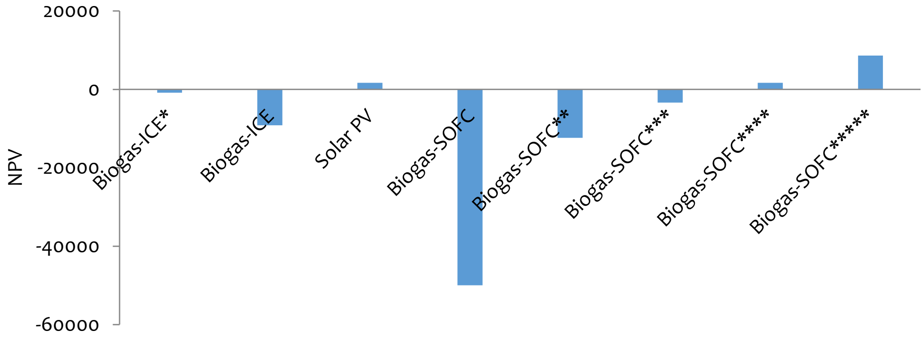
Figure 33. Predicted cost reduction of SOFC system with corresponding NPV values using locally produced biochar as adsorbent. NPV is negative from A to D and positive from E to F

7.3.4 | Internal Vs External reformer

Francesco [483] analysed the exergy and energy efficiency of internal and external dry reforming of a small scale SOFC of 5 kWe capacity using cycle tempo simulation software tool. Results showed that both types of reforming have comparable efficiencies. Apparently, internal reforming does not negatively affect the exergy and thermal efficiency of a SOFC. As indicated in Table 20, for a small scale SOFC, BoP accounts for 60% of the costs of a SOFC system [54]. Although, this may not be the case with the projected fuel cell costs reduction. Of these 60%, the fuel processing system accounts for 80%. The fuel processing system can be eliminated if dry reforming is envisaged. From Table 21, it follows that a 5 kWe SOFC system costs about $33,000. This implies that the fuel processing system costs approximately $16,000. With this reduction, the NPV is - $38,400 and for the system which uses biochar as an adsorbent, the NPV will further increase to - $10,300. With subsidies in terms of tax exemption, the NPV with activated carbon and with the use of biochar is - $26,400 and $1,600 respectively (Figure 33, scenario F). These calculations showed that a 5 kWe biogas-SOFC system is currently economically feasible if internal reforming is applied, biochar is used as adsorbent, and subsidies are applicable.

7.3.5 | Comparison of a similar system of 5 kWe PV and ICE systems

An economic comparison was made between the biogas-SOFC energy system, a biogas-ICE system and a solar PV system. The CAPEX cost for the biogas-ICE is $13,500 and that of a solar PV system is $37,000 based on quotations from private companies in Uganda. It is also assumed that the ICE will be replaced every three years at a cost of $2,000 [484], which increases the CAPEX cost of the biogas-ICE energy system. All three energy systems were designed for a power capacity of 5 kWe and identical full load hours. For the purpose of comparison, both real and full load operation hours were included in Figure 34, although this may not be very practical, especially for the biogas-ICE engine. Results revealed that biogas-ICE and biogas-SOFC have a negative NPV value and hence are currently not economically feasible at least for the Uganda situation. However, as reported before, the biogas-SOFC energy system starts to be economically feasible at a system capital cost of less than $40,000 if a cheap adsorbent for biogas cleaning such as locally produced biochar is used. From Figure 34, it can be deduced that with subsides in terms of tax exemption and using biochar, the biogas-SOFC energy system is economically competitive with already existing biogas-ICE systems. Figure 34 illustrates that a small-scale biogas–SOFC energy system might become economically feasible if operation costs are reduced, e.g., by using biochar for gas cleaning purposes. Also, it is noted that tax exemption can contribute to more than 30% of the SOFC system costs, since most of the parts are imported. It is further noted that if subsidies are applied, biochar is used and fuel processing is eliminated by applying dry reforming, the biogas-SOFC energy system has a positive NPV value and becomes economically feasible (Figure 34). Under the mentioned conditions the NPV is approximately equivalent to that of currently applied solar PV systems. With further costs reduction in SOFC manufacturing, the NPV further increases. It can be observed that biochar can potentially accelerate the economic breakthrough of a biogas-SOFC energy system. However, future research should properly investigate the biochar characteristics in terms of element composition and surface area to guarantee adsorption capacity of a given quantity as it is the case for activated carbon.



* Biogas - ICE operated at full load for 24 hrs
** Biogas - SOFC system with subsidies and using biochar
*** Biogas - SOFC system without subsidies, using biochar and with SOFC projected cost of $1,000/kWe
**** Biogas - SOFC system with subsidies, without fuel processing and uses biochar
***** Biogas - SOFC system with subsidies, using biochar and with SOFC projected cost of $1,000/kWe

Figure 34. NPV of Biogas-ICE and Solar PV energy systems and that of Biogas-SOFC at different scenarios

7.3.6 | **Sensitivity Analysis**

In the sensitivity analysis, two scenarios were considered, i.e., scenario 1 and 2, of which scenario 1 does not consider the inflation rate. For scenario 2, the average inflation rate for Uganda for the past ten years of 6.25% was considered [479]. The interest rate was chosen as the sensitive parameter in the sensitivity analysis for the two scenarios since it varies with time, and it is country dependent. It should be noted that the interest rate of 17% in Uganda was relatively high as compared to the interest rate of 3% in the USA, where the SOFC was produced. The current costs of a biogas-SOFC energy system of $64,000 was considered.

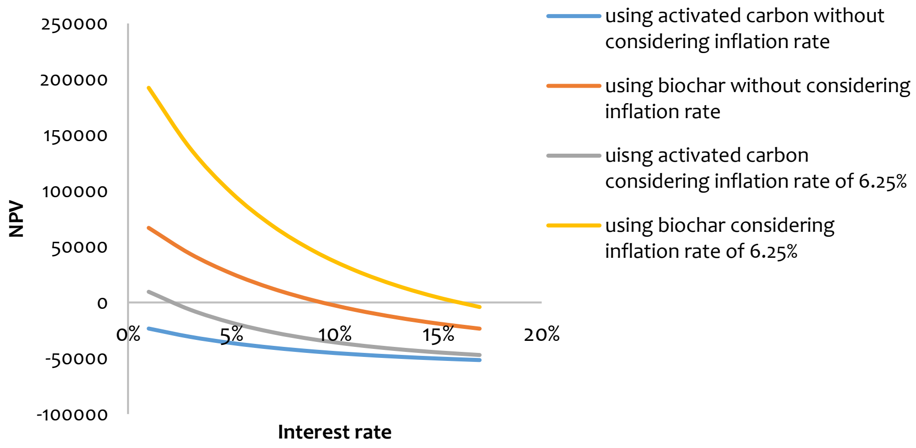


Figure 35. NPV as a function of interest rate, with and without inflation rate of 6.25%.

The lowest NPV values were observed with scenario 1, using activated carbon as the gas cleaning adsorbent without considering inflation rate. The corresponding NPV values started at - $51,600 at 17% interest rate with a payback period based on energy and fertiliser income of approximately 26 years. When using biochar as adsorbent, a payback period of approximately 9 years and NPV value of - $23,400 is realised**.** This trend is similar to scenario 2 when an inflation rate of 6.25% was considered using activated carbon as the gas cleaning adsorbent and the NPV values started from -$47,000 at 17% interest rate and payback period of approximately 19 years. For biochar, the NPV value started from - $4,000 with the payback period of approximately 7 years. It is observed that in both scenarios, the use of biochar will accelerate the economic feasibility of the biogas-SOFC energy system.

7.4 | CONCLUSION

Predictive calculations showed that locally available materials such as biochar may have a distinct positive effect on the economic feasibility of the biogas-SOFC energy system. Materials like biochar adsorbent can be used to reduce the operation cost by over 80%. This can significantly bring down the overall system cost and hence accelerate the economic feasibility of a biogas-SOFC energy system. Considering the Uganda interest rate of 17%, the current economic status of the proposed biogas-SOFC energy system is very high, as compared to other alternatives like solar PV. However, with forecasted costs of $1,000/kWe, the biogas-SOFC energy system is economically feasible when subsidies and/or tax exemption is applied, the costs of fuel processing is reduced (utilizing a cheap adsorbent), and internal reforming is used as opposed to external reforming. It is specifically observed that when biochar as a gas cleaning adsorbent is used, the economic feasibility of a biogas-SOFC energy system will be considerably accelerated.

8

General discussion, conclusion and outlook

8.1 | GENERAL DISCUSSION AND CONCLUSION

This chapter highlights the most important results of the research and discusses the findings in the broader context of technology implementation. Section 8.1 summarizes the main findings per chapter and reflects on these in relation to latest literature. In section 8.2 this then culminates in the outlook, i.e., in which steps are described by which biogas-SOFC energy systems could be brought closer to market.

8.1.1 | Gas cleaning as potential cost reduction strategy for biogas-SOFC System operation

Chapter 1 describes that despite many small-scale biogas plants having been donor funded by NGOs all over the African continent, and particularly in sub-Saharan Africa [485], very few of them have been successfully operated [3]. For example, in Kenya, out of 300 units which were installed between 1980 and 1990, only 25% were still in operation by 2008 [3]. The development of large-scale anaerobic digestion is still low despite the big potential [485]. A number of relatively big systems for electricity generations have been set up in Sub-Saharan Africa. For example, the Kigali Institute of Science and Technology installed two large biogas systems of 830 m^3 volume capacity in 2003 and of 1,430 m^3 capacity in 2005 aiming at treating toilet waste while producing biogas mainly for cooking [3]. The government of Botswana installed a biogas plant for water pumping in mid 1980s, which failed shortly after as a consequence of misunderstandings with the target community [485]. Another initiative reported in the literature is the $2.5 million investment, funded by Global Environment Facility (GEF), which was designed to generate 23,000 m^3 of methane per day, by anaerobic digestion of landfill waste in Dar-es-salaam in Tanzania but the project never kicked off, due to cost escalation and institutional constraints [3]. It was estimated that if this project was successful and replicated in Tanzania, 10% of the total electricity demand in Tanzania could be generated with biogas [3].

Although there have been a number of setbacks hindering successful implementation of anaerobic digestion for biogas in developing countries, chapter 1 also emphasises that there is a lot of untapped potential for this technology. Added advantage of including biogas in the rural energy mix is that both energy and sanitation challenges of rural communities can be solved simultaneously. Due to technological revolution, it is noted that there is a growing interest in electrical energy generation from biogas as opposed to the current practice of thermal energy generation for cooking purposes.

At present, small scale SOFCs are seen as potential energy converters to be coupled to already existing biogas digesters in developing countries [49][50][55]. Therefore, a small-scale biogas-SOFC energy system is the envisioned technology which is considered as potential technology to bridge the gap between rural electricity need and electrical energy production from biogas digesters. A biogas–SOFC energy system is introduced as alternative source of energy for rural electrification. Such a system can simultaneously address both energy and sanitation challenges of off-grid communities. Unlike typically available renewable energy solutions like solar, biogas production can be a side product of enhanced sanitation, since waste has to be disposed in a proper way. By using AD as treatment technique energy can be generated from it. Therefore, biogas-SOFC energy system can potentially solve both the energy and sanitation problems in the rural community sector. This thesis aims to demonstrate that such a system is both technically and economically feasible to replace or complement the existing rural energy supply system such as solar PV.

The thesis also describes how several technical challenges remain, such as internal dry reforming at stack level, that could have major financial implications for successful implementation of a biogas-SOFC energy system in off-grid energy mix. In the chapters 2-7, various technical and financial challenges are being studied in depth. The biggest envisaged drawbacks is the current high capital cost of SOFCs and the high sensitivity of the anode to impurities such as H_2S in biogas. If these drawbacks are overcome, the biogas-SOFC energy system can both technically and economically compete with existing off-grid energy supply systems such as solar-PV based system. For the biogas-SOFC energy system to be economically feasible, local materials needs to be incorporated in the value chain of the entire system (chapter 7). These local materials include using urine as solvent to enhance biogas production, as described in chapter 4, but also for In-situ H_2S capture to reduce on upstream gas cleaning costs (chapter 5) and biochar for upstream cleaning of the gas (chapter 6).

8.1.2 | Boundary limit of H_2S internal dry reforming

In chapter 2, different gas cleaning technologies were analysed with a view of identifying the most technical and economical effective one for a small-scale biogas-SOFC energy system. There are number of gas cleaning technologies reported in literature which include physio-chemical technologies and biological technologies. Cleaning of gas can increase the system operation cost by over 40% [240]. Sorbent for gas cleaning contribute distinctly to the operation costs of the biogas-SOFC energy system. The cost of the gas cleaning can vary from as low as less than 1 EUR per kg of H_2S adsorbed to as high as 140 EUR per kg of

H_2S adsorbed. In-situ cleaning technologies are identified as the cheapest of biogas cleaning. However, they may not reduce the H_2S content to the required level of less than 2 ppmv required for SOFCs [62]. It should be noted that biogas may contain H_2S as high as 4,000 ppm [452]. Therefore, such technologies need to be coupled with other downstream cleaning technologies such as sorbents adsorption for quality and cost-effective gas cleaning.

8.1.3 | Biogas digester operation practices for in-situ H_2S reduction in biogas.

In chapter 3, H_2S boundary limit for biogas internal reforming was experimentally studied. Since biogas contains majorly CH_4 and CO_2, to produce CO and H_2 fuel for SOFCs, reforming or partial oxidation is required. For small scale SOFCs, usually partial oxidation is applied. However, as this consumes a part of the biogas, it decreases the overall efficiency of the system. In biogas-SOFC energy systems, dry reforming would be preferred as opposed to steam reforming. This is because biogas already consist of CO_2 required for dry reforming and no extra energy would be required to generate steam required for steam reforming. For small scale SOFCs, internal reforming would be preferred since it reduces system complexity of integrating an external reformer. This would reduce on the system's CAPEX and, hence, enhance on the system economic feasibility. However, H_2S within biogas has a detrimental effect on gas dry reforming. Hence, the boundary limit of H_2S needs to be determined prior to the system application.

Experimental research using Ni-ScSZ and Ni-GDC anodes showed that H_2S concentrations in the biogas as low as 0.125 ppm affects internal dry reforming. This therefore, implies that for the biogas-SOFC energy system application, a rigorous and robust gas cleaning system is required. This is likely to have an effect on both CAPEX and OPEX of the proposed biogas-SOFC energy system.

8.1.4 | In-situ H_2S reduction using cow urine as an envisaged operational costs reduction strategy

In chapter 4, a theoretical study was carried out on the existing operational practices, which can positively reduce the resultant H_2S content in the biogas. At present, a number of feedstocks from agricultural fields of off-grid communities are currently not utilised. Such feed stock includes banana leaves and other agricultural plant wastes, which are available depending on the season. The current feedstock observed during the conducted field study is majorly animal waste (cow and pig dung) and to a small extent human waste (toilet linked). Physical pre-treatment such as milling, chipping and grinding would open up diversity of feedstocks for small scale digesters. If physical pre-treatment is embraced, this would enhance co-digestion, which would not only increase the efficiency of anaerobic digestion, but also dilute H_2S in the biogas as a consequence of a higher methane production rate [321][326]. Hence, acting as in-situ H_2S cleaning strategy thus reducing the resultant operation costs of gas cleaning.

However, it was observed during the field study that the current operational practices of small-scale digesters could result in passive feedstock pre-treatment and co-digestion. A number of operational practices observed in the field include; storage of the feedstock under direct sun irradiation, mixture of the feedstock with green plant materials such as leaves, dilution of feedstock with urine and passive micro-aeration. Such practices might have an influence on the efficiency of the anaerobic digestion process and resulting H_2S content in the gas. However, their potential positive effects require further detailed studies.

From the field study, a model digester (Figure 21) is proposed. This would incorporate field observed operational practices with envisaged positive effect to both efficiency of digestion process and reduction of H_2S in biogas.

8.1.5 | In-situ H_2S reduction using cow urine as an envisaged operation cost reduction strategy

Chapter 5 examined an experimental and modelling study on the boundary conditions within which cow urine addition could effectively act as in-situ biogas cleaning strategy. During the field visit, it was observed that some biogas operators used urine for dilution of feedstock as opposed to water. Urine contains metal elements such as Fe [451] which would have a positive effect on H_2S reduction in biogas, through FeS precipitation [486]. In addition, urine can increase the pH of anaerobic digestion process resulting from urea hydrolysis, which would also reduce the H_2S content in the biogas [413]. However, the increased NH_3/NH_4^+ concentrations at higher pH can negatively affect the efficiency of the anaerobic digestion process [487].

From experimental and modelling investigations, the effect of urine on H_2S content in the biogas has been further investigated. It was experimentally observed that urine can either increase or decrease H_2S in the gas depending on the metal and sulphur concentration and the used ratio of urine/water for dilution.

Since ammonia, sulphur and metal composition vary depending on the urine used, care should be taken before application. It was also confirmed through experiments and mechanistic modelling that the use of diluted urine as opposed to concentrated urine can indeed result in relatively higher biogas production and at the same time lower H_2S content in the gas.

Therefore, if urine is to be used as an in-situ H_2S reduction strategy, constant monitoring of its composition is required, such that the released ammonia increases the pH, but ammonia does not reach inhibitory concentrations. Moreover, also the presence of metal elements relative to sulphur loading requires proper optimisation. From Figure 23, it can be concluded that urine can reduce H_2S from 290 ppm to 130 ppm in the biogas. Successful application of using urine as in-situ H_2S reduction strategy would distinctly reduce the gas cleaning cost; gas cleaning is regarded indispensable for successful operation of the biogas-SOFC energy system. It is noteworthy that detailed experimental investigations are required to find optimal dilution ratios of urine which can result in both enhanced quality and quantity of biogas.

8.1.6 | Biochar as H_2S adsorbent to meet H_2S boundary limit for internal SOFC dry reforming

Biochar has been reported as an adsorbent for H_2S in biogas. In off-grid settings, such materials are freely available and could greatly reduce the recurring gas cleaning cost. It is hypothesised that metal composition and high pH of biochar contribute to H_2S adsorption.

In chapter 6, preliminary field experiments were carried out to investigate the effectiveness of biochar as locally available adsorbents for biogas cleaning. From experimental investigations, locally produced biochar of different sources that is to say, cow dung, jack fruit tree branches, and leaves, were investigated. Their effectiveness of H_2S adsorption depend on the initial H_2S concentration, the biochar metal content and pH was compared to that of activated carbon. Pre-liminary results reveal that biochar treating biogas with a maximum of 120 ppmv H_2S, is effective in adsorption of H_2S to the required level of SOFCs impurity intake, i.e., 0.125 ppmv.

8.1.7 | Effect of using urine and biochar as on economic feasibility of small-scale Biogas-SOFC energy system

In chapter 7, an economic analysis was performed in which the impact of the investigated H_2S removal technologies on the reduction of both CAPEX and OPEX of the biogas-SOFC energy system was confirmed. It is often stated that the current drawback of SOFCs is the high capital cost, which for a 5 kW SOFC can cost over \$30,000. In comparison, the capital investment for a 5 kWp solar-PV system would roughly only require 50% of this investment which approximates \$15,000 according to quotations from solar companies in Uganda. Although it was projected before that by now, SOFCs costs would be considerably lower, this has not yet been achieved [438]. At the same time, the system costs for a 100% renewable solar-PV system that would be able to produce 24/7 and be as functional as a biogas SOFC system, should also include battery storage capacity or a diesel generator. Under these conditions, and assumed battery capacity of 288 kWh (full time equivalent of 5 kW) at a cost of about \$28,000, the total system capital expenditure would amount to \$30,000-35,000. The latter value is in the same order of magnitude, despite both solar-PV and batteries having reached a stage of mass production. The comparison in terms of operational costs, would be more favourable for the solar-PV battery system, as fuel should be supplied to an SOFC. However, if it concerns waste processing, these costs should not be solely attributed to the energy system, but also to the functionality of the waste treatment or fertilizer production, depending on the situation. It should be further noted that alternatives like solar-PV systems could have challenges in supply chain such as availability of lithium batteries. All this needs to be considered when making cost trajectories of alternative technologies.

It is, however, anticipated that with integration of SOFCs in the rural energy mix, production would increase and, hence, bring down the system initial costs. The use of locally available materials like urine for in-situ H_2S reduction and biochar for downstream H_2S reduction can significantly reduce on both the CAPEX and OPEX of a biogas-SOFC energy system. However, for further enhancement of the economic feasibility of the biogas-SOFC energy system, other cost reduction strategies such as favourable government policies, like a waiver in terms of tax holidays or a special energy loan with low interest rate, need to be explored too.

Low H_2S levels in biogas can further enhance the feasibility of internal dry reforming. This implies that a robust cleaning system is required for the technical breakthrough of internal dry reforming. Using internal dry reforming can reduce the system CAPEX by more than 48% (chapter 7). Calculations in chapter 7 show that with cost projection reductions, the use of internal dry reforming can increase the NPV and hence increases chances of economic breakthrough of a biogas-SOFC energy system.

Moreover, when biochar is used instead of activated carbon, an economic breakthrough with a positive NPV can be expected on the short term (Figure

32). This, therefore, implies that as cost reduction projection of SOFCs is envisaged, back casting needs to be done to realise economic feasibility of the proposed biogas-SOFC energy system. Frugal innovation is required in terms of redesigning the entire SOFC system and embedding it in a local socio-economic context, while using cost-effective “local” materials during operation.

8.2 | OUTLOOK

8.2.1 | In-situ H_2S reduction

As previously described in section 8.1.6, the use of local materials such as biochar for in-situ H_2S reduction in biogas can accelerate the economic feasibility of a biogas-SOFC energy system. However, when deciding to use urine for in-situ H_2S reduction, the elemental content such as Fe and S, as well as NH_3 in the digester and the resulting pH needs to be regularly checked. The mentioned parameters play a crucial role for biogas generation enhancement and in-situ H_2S capture. Depending on the operational strategy, either manual sampling and monitoring or real time monitoring of H_2S and metal:S ratio is required if urine is to be used as an in-situ H_2S reduction strategy. There are some technologies for real time monitoring of biogas parameters, which are proposed by number of researchers[488][489]. However, this would again increase the operation of the system. Therefore, a trade-off between such technologies and the current practice needs to be considered. Next to the biogas monitoring, other interventions might be used that could actuate on the monitored values, for example the addition of other substrates high in iron and low in sulphur. Overall, for off-grid application, research should be directed towards analysis of cost implication and commercialisation of such technologies in small-scale power plant industry. Biochar, depending on the mineral content, can also play a crucial role in in-situ and upstream H_2S capture. Recent research has shown that locally produced biochar is effective in removing sulphur in aqueous solutions as well as H_2S in gas mixture [490]. However, the quality of locally produced biochar cannot be guaranteed and may have a lower adsorption capacity compared to the already existing commercially available adsorbents like activated carbon. This calls for standardisation of specific biochar parameters like, porosity, ash content, and surface area, which determine the functionality of the biochar. Based on the adsorption capacity, the total quantity of biochar needs to be carefully aligned with the in-situ H_2S removal performance. Biochar efficacy is also affected by operating parameters of the gas cleaning unit such as biogas production rate and fluctuations herein, as well as the moisture content. Nevertheless, biochar can be an interesting pre-treatment mechanism to reduce the feedstock H_2S content and resultant H_2S in the biogas. However, research and development are still required to determine the optimal performance of biochar under full-scale field operating conditions [491].

8.2.2 | Use of local materials for biogas in-situ and downstream cleaning

This work has evaluated the use of local materials for biogas in-situ cleaning and downstream cleaning. The focus has been on H_2S reduction only and evaluation of other impurities such as mercaptans and other VOCs requires further research. However, since urine affects H_2S in the biogas, it is most likely that it will have an effect to all sulphur containing compounds. The volatile organic sulphur compounds are considered to be the most critical compound to affect the SOFC operation [299]. Although other VOCs are less harmful to the SOFCs, it has been reported that they can still have an effect on the general operation efficiency of the SOFCs by affecting the reforming reaction and increasing mass transfer resistance [76][77]. However, some researchers urge that the VOCs content is highly affected by the operational parameters of the AD process such as, temperature and the nature of the feedstock [492]. Since urine affects the anaerobic digestion process, the extent to which urine affect the content of these compounds needs to be evaluated.

The effect of urine on H_2S has been carried out based on batch experiments performed under mesophilic conditions. However, process operation strategy and temperature directly affect the dynamics of the AD process and hence the biogas H_2S content [492]. Therefore, the effect of urine on H_2S needs to be studied under varying operating conditions, including temperature.

Biochar adsorption offers an alternative option for biogas downstream cleaning. The research note focused on H_2S cleaning and preliminary results showed that biochar can clean the biogas to the required level of H_2S. However, biogas contains other impurities such as mercaptans and other VOCs. The presence of larger molecules than H_2S have been reported to affect the effectiveness of H_2S absorption by biochar [493]. Therefore, the presence of VOCs in biogas needs further research, including the effects of VOCs on the effectiveness of biochar H_2S adsorption. Also, since biochar has a high pH and contains mineral elements such as Fe, which can react with S^{2-}/HS^- reducing the H_2S content in the biogas, research is recommended to explore how the dosing of biochar to the digester can affect both the biogas quality and quantity.

Lastly, H_2S content was shown to have a direct effect on biogas internal dry reforming. Results show that H_2S as low as 0.125 ppm can affect the performance of internal dry reforming. Research is being carried out to develop more H_2S tolerant anode materials [494][495]. Nevertheless, the limit of such materials is still at the threshold levels of a few ppm, while the biogas H_2S content can be as high as 4,000 ppm. Therefore, research into a robust in-situ and downstream cleaning technology to reduce the H_2S as low as possible is equally required. Thus far, the effect of H_2S on dry reforming has been studied at cell level, but an upscaled fuel cell stack, containing multiple cell pairs, could be affected differently, due to internal flow divisions and kinetic profiles. Therefore, studies on stack level are required to validate the cell results. This creates an interested research option to further explore.

8.2.3 | Towards implementation of a Biogas-SOFC energy system in rural energy mix.

The biogas-SOFC energy system is an attractive energy generation system as it enhances both sanitation and energy access to remote areas. However, the major drawback of such a system is high initial capital expenditures. If this system is to be realised, there should be a frugal evaluation of the entire system to substitute some parts with the less expensive one, but which can serve the same purpose. Operational materials such as the adsorbents need to be critically evaluated and substituted with the less expensive locally available one. To further reduce on the capital cost, in-situ dry reforming as opposed to external dry reforming need to be considered. Less expensive material for biogas digester also needs to be considered. Furthermore, cost reduction strategies for auxiliary parts such as inverters also need to be researched. If all this is coupled with mass production, then the implementation of the biogas-SOFC energy system in the rural energy mix can be accelerated.

In-situ dry reforming can be used to reduce on the system complexity and hence the overall capital investment costs of the whole system. In-situ dry reforming seems to be a feasible approach, since Ni in SOFCs is the catalyst for the dry reforming process and SOFC operating temperature is above 700°C. In addition, cleaning of the biogas to the required H_2S levels needed for the SOFC can increase the operational costs of the biogas-SOFC energy system. Therefore, in-situ H_2S reduction can further reduce the upstream cleaning cost of the biogas prior to fuelling the SOFC. Furthermore, locally available materials can be used in the downstream cleaning which further reduces the operational costs.

Therefore, for implementation of small-scale biogas-SOFC energy systems with competitive energy costs compared to alternatives, in-situ dry reforming, in-situ gas cleaning and usage of locally available biochar for downstream gas cleaning needs to be considered. Especially for small scale systems (< 5kWe), this is very critical since the cost per kWe is relatively high as compared to big scale systems, with power capacities exceeding 10 kWe. It is noteworthy that penetration of such technologies in the rural energy mix will enhance mass production, which can further contribute to overall system initial capital and operational costs reduction.

Bibliography

[1] P.R. Shukla, Biomass Energy In India : Transition From Traditional To Modern, The Social Engineer. 6 (2014) 23–43.

[2] A. Chaurey, M. Ranganathan, P. Mohanty, Electricity access for geographically disadvantaged rural communities-technology and policy insights, Energy Policy. 32 (2004) 1693–1705. https://doi.org/10.1016/S0301-4215(03)00160-5.

[3] B. Amigun, R. Sigamoney, H. von Blottnitz, Commercialisation of biofuel industry in Africa: A review, Renewable and Sustainable Energy Reviews. 12 (2008) 690–711. https://doi.org/10.1016/j.rser.2006.10.019.

[4] A. Daisy, The Impact and Treatment of Night Soil in Anaerobic Digester: A Review, J Microb Biochem Technol. 03 (2011) 43–50. https://doi.org/10.4172/1948-5948.1000050.

[5] Schistosomiasis, (n.d.). http://www.who.int/news-room/fact-sheets/detail/schistosomiasis (accessed June 14, 2018).

[6] SNV Rwanda Annual Report: Community Hygiene Clubs Catalyse Hygiene Behaviour Change. The Heague, the Netherlands: SNV Netherlands Development Organsation;, 2014.

[7] B. Road, Annual Report- 2013, 2013.

[8] SNV Annual Report; Renewable Energy: Over View of the sector Development Results, WASH achievements. The Heague, the Netherlands: SNV Netherlands Development Organisation;, 2016.

[9] S.R. Smith, N.L. Lang, K.H.M. Cheung, K. Spanoudaki, Factors controlling pathogen destruction during anaerobic digestion of biowastes, 25 (2005) 417–425. https://doi.org/10.1016/j.wasman.2005.02.010.

[10] O. Ellabban, H. Abu-Rub, F. Blaabjerg, Renewable energy resources: Current status, future prospects and their enabling technology, Renewable and Sustainable Energy Reviews. 39 (2014) 748–764. https://doi.org/10.1016/j.rser.2014.07.113.

[11] S. Mac, P. Llabr, Anaerobic digestion of organic solid wastes . An overview of research achievements and perspectives, 74 (2000).

[12] Inc. EG&G Technical Services, Fuel Cell Handbook, U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 2004. https://doi.org/10.1002/zaac.200300050.

[13] M. Carriquiry, A.D. Cu, Cow power : the energy and emissions benefits of converting manure to biogas, (2008). https://doi.org/10.1088/1748-9326/3/3/034002.

[14] I. Renewable, E. Agency, A.O. Fao, Renewable energy for agri-food systems, n.d.

[15] J.-F.K. Akinbami, M.O. Ilori, T.O. Oyebisi, I.O. Akinwumi, O. Adeoti, Biogas energy use in Nigeria: current status, future prospects and policy implications, Renewable and Sustainable Energy Reviews. 5 (2001) 97–112. https://doi.org/10.1016/S1364-0321(00)00005-8.

[16] P.C. Ghimire, SNV supported domestic biogas programmes in Asia and Africa, Renew Energy. 49 (2013) 90–94. https://doi.org/10.1016/j.renene.2012.01.058.

[17] K.C. Surendra, D. Takara, A.G. Hashimoto, S.K. Khanal, Biogas as a sustainable energy source for developing countries: Opportunities and challenges, Renewable and Sustainable Energy Reviews. 31 (2014) 846–859. https://doi.org/10.1016/j.rser.2013.12.015.

[18] Y. Chisti, Biodiesel from microalgae beats bioethanol, Trends Biotechnol. 26 (2008) 126–131. https://doi.org/10.1016/j.tibtech.2007.12.002.

[19] SNV Biogas News Letter 7: Production rate of biogas plants in 2011 and first half of 2012. The Heague, the Netherlands; SNV Netherlands Development Organisation;, 2012.

[20] T. Bond, M.R. Templeton, History and future of domestic biogas plants in the developing world, Energy for Sustainable Development. 15 (2011) 347–354. https://doi.org/10.1016/j.esd.2011.09.003.

[21] Ministry of Energy and Mineral Development, The Renewable Energy Policy for Uganda, 2007.

[22] Uganda : Biofuels Digest, (n.d.). https://www.biofuelsdigest.com/bdigest/tag/uganda/ (accessed December 28, 2018).

[23] M. Gao, D. Wang, Y. Wang, X. Wang, Y. Feng, Opportunities and Challenges for Biogas Development : a Review in 2013 – 2018, (2019) 25–35.

[24] A.I. Rugumayo, Renewable Energy Policy Issues in Africa, 2008.

[25] Ministry of Energy and Mineral Development, The Energy Policy for Uganda, 2002.

[26] Government of Ethiopia; National Energy and Petroleum Policy, 1973.

[27] Ministry of Energy and Minerals; National Energy Policy; Tanzania, 2015.

[28] Burkina Faso (2012) - Policy and Regulatory Overviews - Clean Energy Information Portal - reegle, (n.d.). http://www.reegle.info/policy-and-regulatory-overviews/BF (accessed April 3, 2018).

[29] Burundi (2012) - Policy and Regulatory Overviews - Clean Energy Information Portal - reegle, (n.d.). http://www.reegle.info/policy-and-regulatory-overviews/BI (accessed June 12, 2018).

[30] South Sudan (2012) - Policy and Regulatory Overviews - Clean Energy Information Portal - reegle, (n.d.). http://www.reegle.info/policy-and-regulatory-overviews/SS (accessed June 12, 2018).

[31] Government of Ethiopia; National Energy and Petroleum Policy, (2015) 1–130.

[32] Benin (2012) - Policy and Regulatory Overviews - Clean Energy Information Portal - reegle, (n.d.). http://www.reegle.info/policy-and-regulatory-overviews/BJ (accessed June 12, 2018).

[33] Senegal (2014) - Policy and Regulatory Overviews - Clean Energy Information Portal - reegle, (n.d.). http://www.reegle.info/policy-and-regulatory-overviews/SN (accessed June 12, 2018).

[34] SNV Domestic Biogas News letter 5: Production rate of biogas plants in 2010 and first half of 2011. The Heague, the Netherlands: SNV Netherlands Development Organisation;, 2011.

[35] SNV Annual Report; Renewable Energy: Over View of the sector Development Results, WASH achievements. The Heague, the Netherlands: SNV Netherlands Development Organisation;, 2014. https://doi.org/10.1016/j.parkreldis.2015.02.017.

[36] SNV Annual Report; Renewable Energy: Over View of the sector Development Results, WASH results overview. The Heague, the Netherlands: SNV Netherlands Development Organisation;, 2015.

[37] L. Carrette, K.A. Friedrich, U. Stimming, Fuel Cells - Fundamentals and Applications, Fuel Cells. 1 (2001) 5–39. https://doi.org/10.1002/1615-6854(200105)1:1<5::AID-FUCE5>3.0.CO;2-G.

[38] C.J. Greiner, M. KorpÅs, A.T. Holen, A Norwegian case study on the production of hydrogen from wind power, Int J Hydrogen Energy. 32 (2007) 1500–1507. https://doi.org/10.1016/j.ijhydene.2006.10.030.

[39] C. Song, Fuel processing for low-temperature and high-temperature fuel cells: Challenges, and opportunities for sustainable development in the 21st century, Catal Today. 77 (2002) 17–49. https://doi.org/10.1016/S0920-5861(02)00231-6.

[40] M. Della Pietra, S.J. McPhail, S. Prabhakar, U. Desideri, S.W. Nam, V. Cigolotti, Accelerated test for MCFC button cells: First findings, Int J Hydrogen Energy. 41 (2016) 18807–18814. https://doi.org/10.1016/j.ijhydene.2016.07.021.

[41] D.A. Osinkin, Degradation of Ni-Zr0.9Sc0.1O1.95anode in H2+ H2O at low temperature: Influence of nickel surface charge, Int J Hydrogen Energy. 43 (2018) 943–950. https://doi.org/10.1016/j.ijhydene.2017.11.071.

[42] M.W. Ellis, M.R. Von Spakovsky, D.J. Nelson, Fuel cell systems: efficient, flexible energy conversion for the 21st century, Proceedings of the IEEE. 89 (2001) 1808–1818. https://doi.org/10.1109/5.975914.

[43] L. Zhang, S.P. Jiang, H.Q. He, X. Chen, J. Ma, X.C. Song, A comparative study of H2S poisoning on electrode behavior of Ni/YSZ and Ni/GDC anodes of solid oxide fuel cells, Int J Hydrogen Energy. 35 (2010) 12359–12368. https://doi.org/10.1016/j.ijhydene.2010.08.067.

[44] M. Cimenti, J.M. Hill, Thermodynamic analysis of solid oxide fuel cells operated with methanol and ethanol under direct utilization, steam reforming, dry reforming or partial oxidation conditions, J Power Sources. 186 (2009) 377–384. https://doi.org/10.1016/j.jpowsour.2008.10.043.

[45] C. Guerra, A. Lanzini, P. Leone, M. Santarelli, N.P. Brandon, Optimization of dry reforming of methane over Ni/YSZ anodes for solid oxide fuel cells, J Power Sources. 245 (2014) 154–163. https://doi.org/10.1016/j.jpowsour.2013.06.088.

[46] M. Usman, W.M.A. Wan Daud, H.F. Abbas, Dry reforming of methane: Influence of process parameters - A review, Renewable and Sustainable Energy Reviews. 45 (2015) 710–744. https://doi.org/10.1016/j.rser.2015.02.026.

[47] SolidPower, Compact solutions for highly efficient energy, (n.d.). https://www.solidpower.com/en/about-us/ (accessed July 12, 2019).

[48] BOSCH, (n.d.). https://www.bosch-hydrogen-energy.com/sofc/ (accessed May 11, 2023).

[49] WATT Imperium™ - Watt Fuel Cell, (n.d.). https://www.wattfuelcell.com/portable-power/watt-imperium/ (accessed July 2, 2018).

[50] Kyocera News Releases 2017, (n.d.). https://global.kyocera.com/news/2017/0702_bnfo.html (accessed July 3, 2018).

[51] M. Badami, M. Mura, P. Campanile, F. Anzioso, Design and performance evaluation of an innovative small scale combined cycle cogeneration system, 33 (2008) 1264–1276. https://doi.org/10.1016/j.energy.2008.03.001.

[52] M. Gandiglio, D. Drago, M. Santarelli, Techno-economic Analysis of a Solid Oxide Fuel Cell Installation in a Biogas Plant Fed by Agricultural Residues and Comparison with Alternative Biogas Exploitation Paths, Energy Procedia. 101 (2016) 1002–1009. https://doi.org/10.1016/j.egypro.2016.11.127.

[53] B.D. James, A.B. Spisak, W.G. Colella, Manufacturing Cost Analysis of Stationary Fuel Cell Systems, 2015.

[54] Battelle Memorial Institute; MANUFACTURING COST ANALYSIS OF 1 KW AND 5 KW SOLID OXIDE FUEL CELL (SOFC) FOR AUXILLIARY POWER APPLICATIONS, Columbus, in: 2014. https://doi.org/10.1063/1.4980713.

[55] Elcogen, Solid Oxide Fuel Cell Stacks, (n.d.). https://elcogen.com/products/solid-oxide-cell-stacks/ (accessed July 9, 2019).

[56] Y. Matsuzaki, The poisoning effect of sulfur-containing impurity gas on a SOFC anode: Part I. Dependence on temperature, time, and impurity concentration, Solid State Ion. 132 (2000) 261–269. https://doi.org/10.1016/S0167-2738(00)00653-6.

[57] S. Wongchanapai, H. Iwai, M. Saito, H. Yoshida, Performance evaluation of a direct-biogas solid oxide fuel cell-micro gas turbine (SOFC-MGT) hybrid combined heat and power (CHP) system, J Power Sources. 223 (2013) 9–17. https://doi.org/10.1016/j.jpowsour.2012.09.037.

[58] S.A. Saadabadi, A. Thallam Thattai, L. Fan, R.E.F. Lindeboom, H. Spanjers, P. V. Aravind, Solid Oxide Fuel Cells fuelled with biogas: Potential and constraints, Renew Energy. 134 (2019) 194–214. https://doi.org/10.1016/j.renene.2018.11.028.

[59] J. Larminie, A. Dicks, Fuel Cell Systems Explained, 2nd ed., John Wiley & Sons, 2003. https://doi.org/10.1002/9781118878330.

[60] O.A. Marina, L.R. Pederson, M.C. Williams, G.W. Coffey, K.D. Meinhardt, C.D. Nguyen, E.C. Thomsen, Electrode Performance in Reversible Solid Oxide Fuel Cells, J Electrochem Soc. 154 (2007) B452. https://doi.org/10.1149/1.2710209.

[61] P. V. Aravind, W. De Jong, Evaluation of high temperature gas cleaning options for biomass gasification product gas for Solid Oxide Fuel Cells, Prog Energy Combust Sci. 38 (2012) 737–764. https://doi.org/10.1016/j.pecs.2012.03.006.

[62] D. Papurello, A. Lanzini, SOFC single cells fed by biogas : Experimental tests with trace contaminants, Waste Management. 72 (2018) 306–312. https://doi.org/10.1016/j.wasman.2017.11.030.

[63] M. Ippommatsu, H. Sasaki, S. Otoshi, Evaluation of the cost performance of the SOFC cell in the market, Int J Hydrogen Energy. 21 (1996) 129–135. https://doi.org/10.1016/0360-3199(95)00037-2.

[64] Y. Wang, K.S. Chen, J. Mishler, S.C. Cho, X.C. Adroher, A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research, Appl Energy. 88 (2011) 981–1007. https://doi.org/10.1016/j.apenergy.2010.09.030.

[65] I. Staffell, R. Green, The cost of domestic fuel cell micro-CHP systems, Int J Hydrogen Energy. 38 (2013) 1088–1102. https://doi.org/10.1016/j.ijhydene.2012.10.090.

[66] X. Xu, X. Cao, L. Zhao, T. Sun, Comparison of sewage sludge- and pig manure-derived biochars for hydrogen sulfide removal, Chemosphere. 111 (2014) 296–303. https://doi.org/10.1016/j.chemosphere.2014.04.014.

[67] P.W. Abrahams, Geophagy (soil consumption) and iron supplementation in Uganda, Tropical Medicine and International Health. 2 (1997) 617–623. https://doi.org/10.1046/j.1365-3156.1997.d01-348.x.

[68] G.B. Johnson, P. Hjalmarsson, K. Norrman, U.S. Ozkan, A. Hagen, Biogas Catalytic Reforming Studies on Nickel-Based Solid Oxide Fuel Cell Anodes, Fuel Cells. 16 (2016) 219–234. https://doi.org/10.1002/fuce.201500179.

[69] A. Lanzini, P. Leone, Experimental investigation of direct internal reforming of biogas in solid oxide fuel cells, Int J Hydrogen Energy. 35 (2010) 2463–2476. https://doi.org/10.1016/j.ijhydene.2009.12.146.

[70] M. Arnold, Reduction and monitoring of biogas trace compounds; VVT Research Research Notes 2496: VVT Technical Research Centre of Finland;Espoo Finland, 2009. https://doi.org/978-951-38-7314-1.

[71] L. Axelsson, M. Franzén, M. Ostwald, G. Berndes, G. Lakshmi, N.H. Ravindranath, A review of biogas purifi cation processes, Biofuels, Bioproducts and Biorefining. 6 (2012) 246–256. https://doi.org/10.1002/bbb.

[72] P. Ranalli, Microbiology of methane formation, in: Improvement of Crop Plants for Industrial End Uses, Springer, 2007: pp. 340–368. https://doi.org/10.1007/978-1-4020-5486-0.

[73] M. Yu, H. Gong, Z. Chen, M. Zhang, Adsorption characteristics of activated carbon for siloxanes, J Environ Chem Eng. 1 (2013) 1182–1187. https://doi.org/10.1016/j.jece.2013.09.003.

[74] T.L. Guidotti, Occupational exposure to hydrogen sulfide in the sour gas industry: some unresolved issues, Int Arch Occup Environ Health. 66 (1994) 153–160. https://doi.org/10.1007/BF00380773.

[75] D. Papurello, S. Silvestri, L. Tomasi, I. Belcari, F. Biasioli, M. Santarelli, Biowaste for SOFCs, Energy Procedia. 101 (2016) 424–431. https://doi.org/10.1016/j.egypro.2016.11.054.

[76] D. Papurello, A. Lanzini, D. Drago, P. Leone, M. Santarelli, Limiting factors for planar solid oxide fuel cells under different trace compound concentrations, Energy. 95 (2016) 67–78. https://doi.org/10.1016/j.energy.2015.11.070.

[77] M. Santarelli, L. Briesemeister, M. Gandiglio, S. Herrmann, P. Kuczynski, J. Kupecki, A. Lanzini, F. Llovell, D. Papurello, H. Spliethoff, B. Swiatkowski, J. Torres-sanglas, L.F. Vega, Carbon recovery and re-utilization (CRR) from the exhaust of a solid oxide fuel cell (SOFC): Analysis through a proof-of-concept, Biochem Pharmacol. 18 (2017) 206–221. https://doi.org/10.1016/j.jcou.2017.01.014.

[78] W. Urban, H. Lohmann, J.I.S. Gómez, Catalytically upgraded landfill gas as a cost-effective alternative for fuel cells, J Power Sources. 193 (2009) 359–366. https://doi.org/10.1016/j.jpowsour.2008.12.029.

[79] M.C.M. van Loosdrecht, P.H. Nielsen, C.M. Lopez-Vazquez, D. Brdjanovic, Biological Sulphate-Reduction, in: Experimental Methods in Wastewater Treatment, IWA Pub, 2016: pp. 54–72.

[80] D.D. Papadias, S. Ahmed, R. Kumar, Fuel quality issues with biogas energy - An economic analysis for a stationary fuel cell system, Energy. 44 (2012) 257–277. https://doi.org/10.1016/j.energy.2012.06.031.

[81] S. Rasi, A. Veijanen, J. Rintala, Trace compounds of biogas from different biogas production plants, Energy. 32 (2007) 1375–1380. https://doi.org/10.1016/j.energy.2006.10.018.

[82] E.A. McBean, Siloxanes in biogases from landfills and wastewater digesters, Canadian Journal of Civil Engineering. 35 (2008) 431–436. https://doi.org/10.1139/L07-144.

[83] N. De Arespacochaga, C. Valderrama, J. Raich-Montiu, M. Crest, S. Mehta, J.L. Cortina, Understanding the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas-A review, Renewable and Sustainable Energy Reviews. 52 (2015) 366–381. https://doi.org/10.1016/j.rser.2015.07.106.

[84] M. Arnold, T. Kajolinna, Development of on-line measurement techniques for siloxanes and other trace compounds in biogas, Waste Management. 30 (2010) 1011–1017. https://doi.org/10.1016/j.wasman.2009.11.030.

[85] R. Dewil, L. Appels, J. Baeyens, Energy use of biogas hampered by the presence of siloxanes, Energy Convers Manag. 47 (2006) 1711–1722. https://doi.org/10.1016/j.enconman.2005.10.016.

[86] G. Soreanu, M. Béland, P. Falletta, K. Edmonson, L. Svoboda, M. Al-Jamal, P. Seto, Approaches concerning siloxane removal from biogas - A review, Canadian Biosystems Engineering / Le Genie Des Biosystems Au Canada. 53 (2011).

[87] D. Papurello, C. Soukoulis, E. Schuhfried, L. Cappellin, F. Gasperi, S. Silvestri, M. Santarelli, F. Biasioli, Monitoring of volatile compound emissions during dry anaerobic digestion of the Organic Fraction of Municipal Solid Waste by Proton Transfer Reaction Time-of-Flight Mass Spectrometry, Bioresour Technol. 126 (2012) 254–265. https://doi.org/10.1016/j.biortech.2012.09.033.

[88] Home - PubChem Compound - NCBI, (n.d.). https://www.ncbi.nlm.nih.gov/pccompound (accessed June 13, 2018).

[89] P. V. Aravind, J.P. Ouweltjes, N. Woudstra, G. Rietveld, Impact of Biomass-Derived Contaminants on SOFCs with Ni/Gadolinia-Doped Ceria Anodes, Electrochemical and Solid-State Letters. 11 (2007) B24. https://doi.org/10.1149/1.2820452.

[90] S. Rasi, Biogas Composition and Upgrading to Biomethane Saija Rasi Biogas Composition and Upgrading to Biomethane, 2009. https://doi.org/978-951-39-3607-5.

[91] J.F.B. Rasmussen, A. Hagen, The effect of H2S on the performance of Ni-YSZ anodes in solid oxide fuel cells, J Power Sources. 191 (2009) 534–541. https://doi.org/10.1016/j.jpowsour.2009.02.001.

[92] A. Lanzini, H. Madi, V. Chiodo, D. Papurello, S. Maisano, M. Santarelli, J. Van herle, Dealing with fuel contaminants in biogas-fed solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) plants: Degradation of catalytic and electro-catalytic active surfaces and related gas purification methods, Prog Energy Combust Sci. 61 (2017) 150–188. https://doi.org/10.1016/j.pecs.2017.04.002.

[93] A. Norheim, I. Wærnhus, M. Broström, J.E. Hustad, A. Vik, Experimental Studies on the Influence of H_2S on Solid Oxide Fuel Cell Performance at 800 °C, Energy & Fuels. 21 (2007) 1098–1101. https://doi.org/10.1021/ef060532m.

[94] Veyo S.E., EVALUATION OF FUEL IMPURITY EFFECTS ON SOLID OXIDE FUEL CELL PERFORMANCE Final Technical Report, Pittsburgh, 1998.

[95] J.N. Kuhn, N. Lakshminarayanan, U.S. Ozkan, Effect of hydrogen sulfide on the catalytic activity of Ni-YSZ cermets, J Mol Catal A Chem. 282 (2008) 9–21. https://doi.org/10.1016/j.molcata.2007.11.032.

[96] C.M. Grgicak, M.M. Pakulska, J.S. O'Brien, J.B. Giorgi, Synergistic effects of Ni1-xCox-YSZ and Ni1-xCux-YSZ alloyed cermet SOFC anodes for oxidation of hydrogen and methane fuels containing H2S, J Power Sources. 183 (2008) 26–33. https://doi.org/10.1016/j.jpowsour.2008.05.002.

[97] J.P. Trembly, A.I. Marquez, T.R. Ohrn, D.J. Bayless, Effects of coal syngas and H2S on the performance of solid oxide fuel cells: Single-cell tests, J Power Sources. 158 (2006) 263–273. https://doi.org/10.1016/j.jpowsour.2005.09.055.

[98] A.I. Marquez, T.R. Ohrn, J.P. Trembly, D.C. Ingram, D.J. Bayless, Effects of coal syngas and H2S on the performance of solid oxide fuel cells. Part 2. Stack tests, J Power Sources. 164 (2007) 659–667. https://doi.org/10.1016/j.jpowsour.2006.10.102.

[99] Z. Cheng, M. Liu, Characterization of sulfur poisoning of Ni-YSZ anodes for solid oxide fuel cells using in situ Raman microspectroscopy, Solid State Ion. 178 (2007) 925–935. https://doi.org/10.1016/j.ssi.2007.04.004.

[100] A. Lussier, S. Sofie, J. Dvorak, Y.U. Idzerda, Mechanism for SOFC anode degradation from hydrogen sulfide exposure, Int J Hydrogen Energy. 33 (2008) 3945–3951. https://doi.org/10.1016/j.ijhydene.2007.11.033.

[101] M. Drimal, K. Koppová, Z. Klöslová, E. Fabiánová, Environmental exposure to hydrogen sulfide in central Slovakia (Ruzomberok area) in context of health risk assessment., Cent Eur J Public Health. 18 (2010) 224–229.

[102] H. Madi, A. Lanzini, S. Diethelm, D. Papurello, J. Van Herle, M. Lualdi, J. Gutzon Larsen, M. Santarelli, Solid oxide fuel cell anode degradation by the effect of siloxanes, J Power Sources. 279 (2015) 460–471. https://doi.org/10.1016/j.jpowsour.2015.01.053.

[103] F. Accettola, G.M. Guebitz, R. Schoeftner, Siloxane removal from biogas by biofiltration: Biodegradation studies, Clean Technol Environ Policy. 10 (2008) 211–218. https://doi.org/10.1007/s10098-007-0141-4.

[104] H. Madi, S. Diethelm, S. Poitel, C. Ludwig, J. Van herle, Damage of siloxanes on Ni-YSZ anode supported SOFC operated on hydrogen and bio-syngas, Fuel Cells. 15 (2015) 718–727. https://doi.org/10.1002/fuce.201400185.

[105] K. Haga, S. Adachi, Y. Shiratori, K. Itoh, K. Sasaki, Poisoning of SOFC anodes by various fuel impurities, Solid State Ion. 179 (2008) 1427–1431. https://doi.org/10.1016/j.ssi.2008.02.062.

[106] H. Madi, S. Diethelm, C. Ludwig, J. Van Herle, Organic-sulfur poisoning of solid oxide fuel cell operated on bio-syngas, Int J Hydrogen Energy. 41 (2016) 12231–12241. https://doi.org/10.1016/j.ijhydene.2016.06.014.

[107] P. Hofmann, K.D. Panopoulos, L.E. Fryda, A. Schweiger, J.P. Ouweltjes, J. Karl, Integrating biomass gasification with solid oxide fuel cells: Effect of real product gas tars, fluctuations and particulates on Ni-GDC anode, Int J Hydrogen Energy. 33 (2008) 2834–2844. https://doi.org/10.1016/j.ijhydene.2008.03.020.

[108] P. Hofmann, K.D. Panopoulos, P. V. Aravind, M. Siedlecki, A. Schweiger, J. Karl, J.P. Ouweltjes, E. Kakaras, Operation of solid oxide fuel cell on biomass product gas with tar levels >10 g Nm-3, Int J Hydrogen Energy. 34 (2009) 9203–9212. https://doi.org/10.1016/j.ijhydene.2009.07.040.

[109] W. Mojtahedi, J. Abbasian, Catalytic decomposition of ammonia in a fuel gas at high temperature and pressure, Fuel. 74 (1995) 1698–1703. https://doi.org/10.1016/0016-2361(95)00152-U.

[110] A. Wojcik, H. Middleton, I. Damopoulos, J. Van Herle, Ammonia as a fuel in solid oxide fuel cells, J Power Sources. 118 (2003) 342–348. https://doi.org/10.1016/S0378-7753(03)00083-1.

[111] Q. Ma, R. Peng, Y. Lin, J. Gao, G. Meng, A high-performance ammonia-fueled solid oxide fuel cell, J Power Sources. 161 (2006) 95–98. https://doi.org/10.1016/j.jpowsour.2006.04.099.

[112] G. Meng, C. Jiang, J. Ma, Q. Ma, X. Liu, Comparative study on the performance of a SDC-based SOFC fueled by ammonia and hydrogen, J Power Sources. 173 (2007) 189–193. https://doi.org/10.1016/j.jpowsour.2007.05.002.

[113] A. Fuerte, R.X. Valenzuela, M.J. Escudero, L. Daza, Ammonia as efficient fuel for SOFC, J Power Sources. 192 (2009) 170–174. https://doi.org/10.1016/j.jpowsour.2008.11.037.

[114] R. Francis, British Corrosion Journal Effect of pollutants on corrosion of copper alloys in sea water: Part 1: Ammonia and chlorine Effect of pollutants on corrosion of copper alloys in sea water Part 1: Ammonia and chlorine, British Cororsion Journal. 20 (1985) 167–174. https://doi.org/10.1179/000705985798272650.

[115] Ammonia corrosion of copper tubes in air removal section in condenser for power plant, 2018.

[116] R.B. Williams, S.R. Kaffka, R. Oglesby, DRAFT INTERIM PROJECT REPORT; DRAFT Comparative Assessment of Technology Options for Biogas Clean-up, Davis, 2014.

[117] N. Abatzoglou, S. Boivin, A review of biogas purification processes, Biofuels, Bioproducts and Biorefining. 6 (2012) 246–256. https://doi.org/10.1002/bbb.

[118] D. Mescia, S.P. Hernández, A. Conoci, N. Russo, MSW landfill biogas desulfurization, Int J Hydrogen Energy. 36 (2011) 7884–7890. https://doi.org/10.1016/j.ijhydene.2011.01.057.

[119] M. Mueller, Air Quality Issues Related to Using Biogas from Anaerobic, Fullerton, 2015.

[120] M. Błesznowski, J. Jewulski, A. Zieleniak, Determination of H2S and HCl concentration limits in the fuel for anode supported SOFC operation, Central European Journal of Chemistry. 11 (2013) 960–967. https://doi.org/10.2478/s11532-013-0228-1.

[121] S.L. Malone Rubright, L.L. Pearce, J. Peterson, Environmental toxicology of hydrogen sulfide, Nitric Oxide. 71 (2017) 1–13. https://doi.org/10.1016/j.niox.2017.09.011.

[122] S.H. Roth, Toxicological and Environmental Impacts of Hydrogen Sulfide, Signal Transduction and the Gasotransmitters. (2004) 293–313. https://doi.org/10.1007/978-1-59259-806-9_17.

[123] E. Lim, O. Mbowe, A.S.W. Lee, J. Davis, Effect of environmental exposure to hydrogen sulfide on central nervous system and respiratory function: a systematic review of human studies., Int J Occup Environ Health. 22 (2016) 80–90. https://doi.org/10.1080/10773525.2016.1145881.

[124] J. Tang, Y. Shao, J. Guo, T. Zhang, G. Meng, F. Wang, The effect of H2S concentration on the corrosion behavior of carbon steel at 90 °C, Corros Sci. 52 (2010) 2050–2058. https://doi.org/10.1016/j.corsci.2010.02.004.

[125] A. Hagen, G.B. Johnson, P. Hjalmarsson, Electrochemical evaluation of sulfur poisoning in a methane-fuelled solid oxide fuel cell: Effect of current density and sulfur concentration, J Power Sources. 272 (2014) 776–785. https://doi.org/10.1016/j.jpowsour.2014.08.125.

[126] M. Javadi, F. Golkhou, N. Sheikhy, M. Moghiman, Carbon disulfide production via hydrogen sulfide methane reformation, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering. 4 (2010) 198–201.

[127] J.O.L. Wendt, C. V. Sternling, Effect of Ammonia in Gaseous Fuels On Nitrogen Oxide Emissions, J Air Pollut Control Assoc. 24 (1974) 1055–1058. https://doi.org/10.1080/00022470.1974.10470013.

[128] D. Graiver, K.W. Farminer, R. Narayan, A Review of the Fate and Effects of Silicones in the Environment, J Polym Environ. 11 (2003) 129–136. https://doi.org/10.1023/A:1026056129717.

[129] T.S. Li, W.G. Wang, Sulfur-poisoned Ni-based solid oxide fuel cell anode characterization by varying water content, J Power Sources. 196 (2011) 2066–2069. https://doi.org/10.1016/j.jpowsour.2010.10.015.

[130] O. Marttila, J.J.K. Jaakkola, V. Vilkka, P. Jäppinen, T. Haahtela, The south karelia air pollution study: The effects of malodorous sulfur compounds from pulp mills on respiratory and other symptoms in children, Environ Res. 66 (1994) 152–159. https://doi.org/10.1006/enrs.1994.1051.

[131] W. Sand, Importance of Hydrogen Sulfide , Thiosulfate , and Methylmercaptan for Growth of Thiobacilli during Simulation of Concrete Corrosion, Appl Environ Microbiol. 53 (1987) 1645–1648.

[132] M.G. Narotsky, R.A. Pegram, R.J. Kavlock, Effect of dosing vehicle on the developmental toxicity of bromodichloromethane and carbon tetrachloride in rats, Fundamental and Applied Toxicology. 40 (1997) 30–36. https://doi.org/10.1006/faat.1997.2376.

[133] K.H. Kim, S.A. Jahan, E. Kabir, R.J.C. Brown, A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects, Environ Int. 60 (2013) 71–80. https://doi.org/10.1016/j.envint.2013.07.019.

[134] Y. Kidoguchi, C. Yang, R. Kato, K. Miwa, Effects of fuel cetane number and aromatics on combustion process and emissions of a direct-injection diesel engine, JSAE Review. 21 (2000) 469–475. https://doi.org/10.1016/S0389-4304(00)00075-8.

[135] K. Arve, H. Backman, F. Klingstedt, K. Eränen, D.Y. Murzin, Hydrogen as a remedy for the detrimental effect of aromatic and cyclic compounds on the HC-SCR over Ag/alumina, Appl Catal B. 70 (2007) 65–72. https://doi.org/10.1016/j.apcatb.2005.10.036.

[136] E. Buysman, BIOGAS AND HOUSEHOLD AIR QUALITY Household Air Quality Impact of biogas stoves versus wood-fired stoves in Rural Cambodia Biogas and Household Air Quality; Climate Neutral Report., 2015.

[137] C.L. Joppert, D. Perecin, M.M. Santos, S.T. Coelho, J.L.P. Camacho, A short-cut model for predicting biomethane availability after biogas upgrading, J Clean Prod. 200 (2020) 148–160. https://doi.org/10.1016/j.jclepro.2018.07.269.

[138] J. Staniforth, R.M. Ormerod, Implications for using biogas as a fuel source for solid oxide fuel cells: Internal dry reforming in a small tubular solid oxide fuel cell, Catal Letters. 81 (2002) 19–23. https://doi.org/10.1023/A:1016000519280.

[139] D.J. Moon, J.W. Ryu, Electrocatalytic reforming of carbon dioxide by methane in SOFC system, Catal Today. 87 (2003) 255–264. https://doi.org/10.1016/j.cattod.2003.10.017.

[140] Y. Shiratori, T. Ijichi, T. Oshima, K. Sasaki, Internal reforming SOFC running on biogas, Int J Hydrogen Energy. 35 (2010) 7905–7912. https://doi.org/10.1016/j.ijhydene.2010.05.064.

[141] Q. Sun, H. Li, J. Yan, L. Liu, Z. Yu, X. Yu, Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation, Renewable and Sustainable Energy Reviews. 51 (2015) 521–532. https://doi.org/10.1016/j.rser.2015.06.029.

[142] N. de Arespacochaga, C. Valderrama, C. Mesa, L. Bouchy, J.L. Cortina, Biogas deep clean-up based on adsorption technologies for Solid Oxide Fuel Cell applications, Chemical Engineering Journal. 255 (2014) 593–603. https://doi.org/10.1016/j.cej.2014.06.072.

[143] M. Schweigkofler, R. Niessner, Removal of siloxanes in biogases, J Hazard Mater. 83 (2001) 183–196. https://doi.org/10.1016/S0304-3894(00)00318-6.

[144] S. Pipatmanomai, S. Kaewluan, T. Vitidsant, Economic assessment of biogas-to-electricity generation system with H2S removal by activated carbon in small pig farm, Appl Energy. 86 (2009) 669–674. https://doi.org/10.1016/j.apenergy.2008.07.007.

[145] N.S. Siefert, S. Litster, Exergy & economic analysis of biogas fueled solid oxide fuel cell systems, J Power Sources. 272 (2014) 386–397. https://doi.org/10.1016/j.jpowsour.2014.08.044.

[146] K. Kim, S.K. Jeon, C. Vo, C.S. Park, J.M. Norbeck, Removal of Hydrogen Sulfide from a Steam-Hydrogasifier Product Gas by Zinc Oxide Sorbent, (2007) 5848–5854. https://doi.org/10.1021/ie0614531.

[147] I.I. Novochinskii, C. Song, X. Ma, X. Liu, L. Shore, J. Lampert, R.J. Farrauto, Low-temperature H2S removal from steam-containing gas mixtures with ZnO for fuel cell application. 1. ZnO particles and extrudates, Energy and Fuels. 18 (2004) 576–583. https://doi.org/10.1021/ef030137l.

[148] C. Zuber, M. Husmann, H. Schroettner, C. Hochenauer, T. Kienberger, Investigation of sulfidation and regeneration of a ZnO-adsorbent used in a biomass tar removal process based on catalytic steam reforming, Fuel. 153 (2015) 143–153. https://doi.org/10.1016/j.fuel.2015.02.110.

[149] E. Sasaoka, S. Hirano, S. Kasaoka, Y. Sakata, Characterization of Reaction between Zinc Oxide and Hydrogen Sulfide, Energy & Fuels. 8 (1994) 1100–1105. https://doi.org/10.1021/ef00047a013.

[150] K. Kim, N. Park, Removal of hydrogen sulfide from a steam-hydrogasifier product gas by zinc oxide sorbent: Effect of non-steam gas components, Journal of Industrial and Engineering Chemistry. 16 (2010) 967–972. https://doi.org/10.1016/j.jiec.2010.04.003.

[151] A. Torkkeli, Droplet microfluidics on a planar surface, VTT Publications. 56 (2003) 3–194. https://doi.org/10.1002/aic.

[152] R. Slimane, J. Abbasian, Regenerable mixed metal oxide sorbents for coal gas desulfurization at moderate temperatures, Advances in Environmental Research. 4 (2000) 147–162. https://doi.org/10.1016/S1093-0191(00)00017-4.

[153] O. Karvan, H. Atakül, Investigation of CuO/mesoporous SBA-15 sorbents for hot gas desulfurization, Fuel Processing Technology. 89 (2008) 908–915. https://doi.org/10.1016/j.fuproc.2008.03.004.

[154] M. Hussain, N. Abbas, D. Fino, N. Russo, Novel mesoporous silica supported ZnO adsorbents for the desulphurization of biogas at low temperatures, Chemical Engineering Journal. 188 (2012) 222–232. https://doi.org/10.1016/j.cej.2012.02.034.

[155] H. Yang, Y. Lu, B.J. Tatarchuk, Glass fiber entrapped sorbent for reformates desulfurization for logistic PEM fuel cell power systems, J Power Sources. 174 (2007) 302–311. https://doi.org/10.1016/j.jpowsour.2007.08.031.

[156] H.T. Kim, S.M. Kim, K.W. Jun, Y.S. Yoon, J.H. Kim, Desulfurization of odorant-containing gas: Removal of t-butylmercaptan on Cu/ZnO/Al_2O_3, Int J Hydrogen Energy. 32 (2007) 3603–3608. https://doi.org/10.1016/j.ijhydene.2007.04.027.

[157] M. Balsamo, S. Cimino, G. de Falco, A. Erto, L. Lisi, ZnO-CuO supported on activated carbon for H_2S removal at room temperature, Chemical Engineering Journal. 304 (2016) 399–407. https://doi.org/10.1016/j.cej.2016.06.085.

[158] D. Liu, S. Chen, X. Fei, C. Huang, Y. Zhang, Regenerable CuO-based adsorbents for low temperature desulfurization application, Ind Eng Chem Res. 54 (2015) 3556–3562. https://doi.org/10.1021/acs.iecr.5b00180.

[159] A.S. Calbry-muzyka, A. Gantenbein, J. Schneebeli, A. Frei, A.J. Knorpp, T.J. Schildhauer, S.M.A. Biollaz, Deep removal of sulfur and trace organic compounds from biogas to protect a catalytic methanation reactor, Chemical Engineering Journal. 360 (2019) 577–590. https://doi.org/10.1016/j.cej.2018.12.012.

[160] C. Weinlaender, R. Neubauer, M. Hauth, C. Hochenauer, Removing H_2S from Biogas Using Sorbents for Solid Oxide Fuel Cell Applications, Chem Ing Tech. 89 (2017) 1247–1254. https://doi.org/10.1002/cite.201600167.

[161] W.J.W. Bakker, F. Kapteijn, J.A. Moulijn, A high capacity manganese-based sorbent for regenerative high temperature desulfurization with direct sulfur production Conceptual process application to coal gas cleaning, Chemical Engineering Journal. 96 (2003) 223–235. https://doi.org/10.1016/j.cej.2003.08.022.

[162] Vanadium Price - vanadium, vanadium price, vanadium pentoxide, ferro vanadium, (n.d.). https://www.vanadiumprice.com/ (accessed May 30, 2018).

[163] P. Wheeler, J.B. Holm-Nielsen, T. Jaatinen, A. Wellinger, A. Lindberg, A. Pettigrew, Biogas Upgrading and Utilisation;Task 24: Energy from biological conversion of organic waste, 1999.

[164] C. Lin, W. Qin, C. Dong, Applied Surface Science H_2S adsorption and decomposition on the gradually reduced ˛ -Fe_2O_3 (001) surface : A DFT study, Appl Surf Sci. 387 (2016) 720–731. https://doi.org/10.1016/j.apsusc.2016.06.104.

[165] H. Fan, T. Sun, Y. Zhao, J. Shangguan, J. Lin, Three-Dimensionally Ordered Macroporous Iron Oxide for Removal of H_2S at Medium Temperatures, (2013). https://doi.org/10.1021/es304791b.

[166] T. Ichio, S. Kasaoka, High-Temperature H_2S Removal from Coal-Derived Gas by Iron Ore Eiji, (1992) 603–608. https://doi.org/10.1021/ef00035a010.

[167] Y. Su, C. Huang, Y. Chyou, K. Svoboda, Journal of the Taiwan Institute of Chemical Engineers Sulfidation / regeneration multi-cyclic testing of Fe_2O_3 / Al_2O_3 sorbents for the high-temperature removal of hydrogen sulfide, J Taiwan Inst Chem Eng. 74 (2017) 89–95. https://doi.org/10.1016/j.jtice.2016.12.011.

[168] X. Wang, J. Jia, L. Zhao, T. Sun, Mesoporous SBA-15 supported iron oxide: A potent catalyst for hydrogen sulfide removal, Water Air Soil Pollut. 193 (2008) 247–257. https://doi.org/10.1007/s11270-008-9686-z.

[169] C. Cilleruelo, V. Ibarra, M. Pineda, Kinetic Study of High-Temperature Removal of H_2S by Novel Metal Oxide Sorbents, (1997) 846–853. https://doi.org/10.1021/ie960194k.

[170] D. Nguyen-thanh, K. Block, T.J. Bandosz, Adsorption of hydrogen sulfide on montmorillonites modified with iron, 59 (2005) 343–353. https://doi.org/10.1016/j.chemosphere.2004.10.022.

[171] K.J. Cantrell, S.B. Yabusaki, M.H. Engelhard, A. V Mitroshkov, E.C. Thornton, Oxidation of H 2 S by Iron Oxides in Unsaturated Conditions, 37 (2003) 2192–2199. https://doi.org/10.1021/es0209940.

[172] M. Yumura, E. Furlmsky, Comparison of CaO , ZnO , and Fe203 As H2S Adsorbents at High Temperatures, (1985) 1165–1168. https://doi.org/10.1021/i200031a045.

[173] J. Wang, Y. Zhang, L. Han, L. Chang, W. Bao, Simultaneous removal of hydrogen sulfide and mercury from simulated syngas by iron-based sorbents, 103 (2013) 73–79. https://doi.org/10.1016/j.fuel.2011.10.056.

[174] I. The, E.A. The, C. These, Sulphide in Sterically Hindered, 41 (1986) 405–408.

[175] B.E. Roberts, A.E. Mather, Solubility of C02 and H2S in a Mixed Solvent, Chem Eng Commun. 72 (1988) 201–211. https://doi.org/10.1080/00986448808940017.

[176] S. Wiechert, W.S. Ho, D.W. Savage, Sterically-Hindered amines for acid-gas absorption, 1987. https://doi.org/10.1080/03602548708058543.

[177] X. Wang, X. Ma, L. Sun, C. Song, A nanoporous polymeric sorbent for deep removal of H2S from gas mixtures for hydrogen purification, Green Chemistry. 9 (2007) 695. https://doi.org/10.1039/b614621j.

[178] Choosing an adsorption systemfor VOC: carbon, zeolite or polymers?U.S. Envi- ronmental protection Agency, Clean Air Technology Center, Technical Bulletin, Research Triangle Park, North Carolina, USA, 1999.

[179] S.J. Allen, L. Whitten, G. Mckay, The Production and Characterisation of Activated Carbons: A Review, Developments in Chemical Engineering and Mineral Processing. 6 (1998) 231–261. https://doi.org/10.1002/apj.5500060501.

[180] J. Yener, T. Kopac, G. Dogu, T. Dogu, Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon, Chemical Engineering Journal. 144 (2008) 400–406. https://doi.org/10.1016/j.cej.2008.02.009.

[181] P. Gislon, S. Galli, G. Monteleone, Siloxanes removal from biogas by high surface area adsorbents, Waste Management. 33 (2013) 2687–2693. https://doi.org/10.1016/j.wasman.2013.08.023.

[182] H.C. Shin, J.W. Park, K. Park, H.C. Song, Removal characteristics of trace compounds of landfill gas by activated carbon adsorption, Environmental Pollution. 119 (2002) 227–236. https://doi.org/10.1016/S0269-7491(01)00331-1.

[183] D. Papurello, S. Silvestri, A. Lanzini, Separation and Puri fi cation Technology Biogas cleaning : Trace compounds removal with model validation, Sep Purif Technol. 210 (2019) 80–92. https://doi.org/10.1016/j.seppur.2018.07.081.

[184] T.J. Bandosz, A. Bagreev, F. Adib, A. Turk, Unmodified versus caustics-impregnated carbons for control of hydrogen sulfide emissions from sewage treatment plants, Environ Sci Technol. 34 (2000) 1069–1074. https://doi.org/10.1021/es9813212.

[185] H.S. Choo, L.C. Lau, A.R. Mohamed, K.T. Lee, HYDROGEN SULFIDE ADSORPTION BY ALKALINE IMPREGNATED COCONUT SHELL ACTIVATED CARBON, Journal of Engineering Science and Technology. 8 (2013) 741–753.

[186] R. Sitthikhankaew, S. Predapitakkun, R. Wibulswas, Comparative Study of Hydrogen Sulfide Adsorption by using Alkaline Impregnated Activated Carbons for Hot Fuel Gas Purification, Energy Procedia. 9 (2011) 15–24. https://doi.org/10.1016/j.egypro.2011.09.003.

[187] F. Liu, J. Lu, C. Zhao, Study on the catalysts of sulfur-odor gas pollution treatment, (2014) 337–342. https://doi.org/10.1007/s13203-014-0069-7.

[188] N. Abu, S. Arabia, ACTIVATED CARBON ADSORPTION IN OXIDIZING ENVIRONMENTS, Water Res. 29 (1995) 653–660.

[189] I. Isik-Gulsac, Investigation of Impregnated Activated Carbon Properties Used in Hydrogen, Brazilian Journal of Chemical Engineering. 33 (2016) 1021–1030.

[190] D. Papurello, A. Lanzini, L. Tognana, S. Silvestri, M. Santarelli, Waste to energy: Exploitation of biogas from organic waste in a 500 Welsolid oxide fuel cell (SOFC) stack, Energy. 85 (2015) 145–158. https://doi.org/10.1016/j.energy.2015.03.093.

[191] T. Matsui, S. Imamura, Removal of siloxane from digestion gas of sewage sludge, Bioresour Technol. 101 (2010) S29–S32. https://doi.org/10.1016/j.biortech.2009.05.037.

[192] L. Sigot, G. Ducom, B. Benadda, C. Labouré, Adsorption of octamethylcyclotetrasiloxane on silica gel for biogas purification, Fuel. 135 (2014) 205–209. https://doi.org/10.1016/j.fuel.2014.06.058.

[193] A. Cabrera-Codony, M.A. Montes-Morán, M. Sánchez-Polo, M.J. Martín, R. Gonzalez-Olmos, Biogas upgrading: Optimal activated carbon properties for siloxane removal, Environ Sci Technol. 48 (2014) 7187–7195. https://doi.org/10.1021/es501274a.

[194] E. Finocchio, T. Montanari, G. Garuti, C. Pistarino, F. Federici, M. Cugino, G. Busca, Purification of biogases from siloxanes by adsorption: On the regenerability of activated carbon sorbents, Energy and Fuels. 23 (2009) 4156–4159. https://doi.org/10.1021/ef900356n.

[195] S. Nam, W. Namkoong, J.H. Kang, J.K. Park, N. Lee, Adsorption characteristics of siloxanes in landfill gas by the adsorption equilibrium test, Waste Management. 33 (2013) 2091–2098. https://doi.org/10.1016/j.wasman.2013.03.024.

[196] D. Papurello, L. Tomasi, S. Silvestri, I. Belcari, M. Santarelli, F. Smeacetto, F. Biasioli, Biogas trace compound removal with ashes using proton transfer reaction time-of- fl ight mass spectrometry as innovative detection tool, Fuel Processing Technology. 145 (2016) 62–75. https://doi.org/10.1016/j.fuproc.2016.01.028.

[197] T. Sun, K. Seff, Silver Clusters and Chemistry in Zeolites, Chem Rev. 94 (1994) 857–870. https://doi.org/10.1021/cr00028a001.

[198] S.M. Csicsery, Shape-selective catalysis inzeolites, 4 (1984) 116–126.

[199] P. Cosoli, M. Ferrone, S. Pricl, M. Fermeglia, Hydrogen sulphide removal from biogas by zeolite adsorption. Part I. GCMC molecular simulations, Chemical Engineering Journal. 145 (2008) 86–92. https://doi.org/10.1016/j.cej.2008.07.034.

[200] X. Xu, I. Novochinskii, C. Song, Low-temperature removal of H2S by nanoporous composite of polymer-mesoporous molecular sieve MCM-41 as adsorbent for fuel cell applications, Energy and Fuels. 19 (2005) 2214–2215. https://doi.org/10.1021/ef050061o.

[201] D. Papurello, R. Borchiellini, P. Bareschino, V. Chiodo, S. Freni, A. Lanzini, F. Pepe, G.A. Ortigoza, M. Santarelli, Performance of a Solid Oxide Fuel Cell short-stack with biogas feeding, Appl Energy. 125 (2014) 254–263. https://doi.org/10.1016/j.apenergy.2014.03.040.

[202] L.V.A. Truong, N. Abatzoglou, A H2S reactive adsorption process for the purification of biogas prior to its use as a bioenergy vector, Biomass Bioenergy. 29 (2005) 142–151. https://doi.org/10.1016/j.biombioe.2005.03.001.

[203] G. Israelson, Results of testing various natural gas desulfurization adsorbents, J Mater Eng Perform. 13 (2004) 282–286. https://doi.org/10.1361/10599490419199.

[204] S.P. Hernández, F. Scarpa, D. Fino, R. Conti, Biogas purification for MCFC application, Int J Hydrogen Energy. 36 (2011) 8112–8118. https://doi.org/10.1016/j.ijhydene.2011.01.055.

[205] H. Cui, S.Q. Turn, M.A. Reese, Removal of sulfur compounds from utility pipelined synthetic natural gas using modified activated carbons, Catal Today. 139 (2009) 274–279. https://doi.org/10.1016/j.cattod.2008.03.024.

[206] A.S. Calbry-Muzyka, A. Gantenbein, J. Schneebeli, A. Frei, A.J. Knorpp, T.J. Schildhauer, S.M.A. Biollaz, Deep removal of sulfur and trace organic compounds from biogas to protect a catalytic methanation reactor, Chemical Engineering Journal. 360 (2019) 577–590. https://doi.org/10.1016/j.cej.2018.12.012.

[207] G.Q. (Max) Lu, D.D. Lau, Characterisation of sewage sludge-derived adsorbents for H2S removal. Part 2: Surface and pore structural evolution in chemical activation, Gas Separation & Purification. 10 (1996) 103–111. https://doi.org/10.1016/0950-4214(96)00011-4.

[208] F. Bauer, C. Hulteberg, T. Persson, D. Tamm, Biogas upgrading – Review of commercial technologies, Malmö, 2013. https://doi.org/SGC Rapport 2013:270.

[209] P. Goyal, P. Baredar, A. Mittal, A.R. Siddiqui, Adsorption refrigeration technology - An overview of theory and its solar energy applications, Renewable and Sustainable Energy Reviews. 53 (2016) 1389–1410. https://doi.org/10.1016/j.rser.2015.09.027.

[210] I. Sarbu, C. Sebarchievici, General review of solar-powered closed sorption refrigeration systems, Energy Convers Manag. 105 (2015) 403–422. https://doi.org/10.1016/j.enconman.2015.07.084.

[211] G. Najeh, G. Slimane, M. Souad, B. Riad, E.G. Mohammed, Performance of silica gel-water solar adsorption cooling system, Case Studies in Thermal Engineering. 8 (2016) 337–345. https://doi.org/10.1016/j.csite.2016.07.002.

[212] D.C. Wang, Y.H. Li, D. Li, Y.Z. Xia, J.P. Zhang, A review on adsorption refrigeration technology and adsorption deterioration in physical adsorption systems, Renewable and Sustainable Energy Reviews. 14 (2010) 344–353. https://doi.org/10.1016/j.rser.2009.08.001.

[213] R.Z. Wang, T.S. Ge, C.J. Chen, Q. Ma, Z.Q. Xiong, Solar sorption cooling systems for residential applications: Options and guidelines, International Journal of Refrigeration. 32 (2009) 638–660. https://doi.org/10.1016/j.ijrefrig.2009.02.005.

[214] S. Rasi, J. Läntelä, A. Veijanen, J. Rintala, Landfill gas upgrading with countercurrent water wash, Waste Management. 28 (2008) 1528–1534. https://doi.org/10.1016/j.wasman.2007.03.032.

[215] M. Ajhar, Membrane-based Removal of Volatile Methylsiloxanes from Biogas, 2011.

[216] M. Ajhar, M. Travesset, S. Yüce, T. Melin, Siloxane removal from landfill and digester gas - A technology overview, Bioresour Technol. 101 (2010) 2913–2923. https://doi.org/10.1016/j.biortech.2009.12.018.

[217] H.H.J. Cox, M.A. Deshusses, Waste Gas Treatment in Biotrickling Filters, Curr Opin Biotechnol. 9 (2000) 256–262.

[218] H. Duan, L.C.C. Koe, R. Yan, Treatment of H2S using a horizontal biotrickling filter based on biological activated carbon: Reactor setup and performance evaluation, Appl Microbiol Biotechnol. 67 (2005) 143–149. https://doi.org/10.1007/s00253-004-1771-7.

[219] H.H.J. Cox, M.A. Deshusses, Co-treatment of H2S and toluene in a biotrickling filter, Chemical Engineering Journal. 87 (2002) 101–110. https://doi.org/10.1016/S1385-8947(01)00222-4.

[220] A.M. Montebello, M. Fernández, F. Almenglo, M. Ramírez, D. Cantero, M. Baeza, D. Gabriel, Simultaneous methylmercaptan and hydrogen sulfide removal in the desulfurization of biogas in aerobic and anoxic biotrickling filters, Chemical Engineering Journal. 200–202 (2012) 237–246. https://doi.org/10.1016/j.cej.2012.06.043.

[221] M. Ramírez, J.M. Gómez, G. Aroca, D. Cantero, Removal of hydrogen sulfide by immobilized Thiobacillus thioparus in a biotrickling filter packed with polyurethane foam, Bioresour Technol. 100 (2009) 4989–4995. https://doi.org/10.1016/j.biortech.2009.05.022.

[222] Y.C. Chung, C.P. Huang, J.R. Pan, C.P. Tseng, Comparison of autotrophic and mixotrophic biofilters for H2S removal, Journal of Environmental Engineering-Asce. 124 (1998) 362–367. https://doi.org/10.1061/(ASCE)0733-9372(1998)124:4(362).

[223] M. Fortuny, J.A. Baeza, X. Gamisans, C. Casas, J. Lafuente, M.A. Deshusses, D. Gabriel, Biological sweetening of energy gases mimics in biotrickling filters, Chemosphere. 71 (2008) 10–17. https://doi.org/10.1016/j.chemosphere.2007.10.072.

[224] H. Duan, R. Yan, L.C.C. Koe, Investigation on the mechanism of H2S removal by biological activated carbon in a horizontal biotrickling filter, Appl Microbiol Biotechnol. 69 (2005) 350–357. https://doi.org/10.1007/s00253-005-0057-z.

[225] H. Duan, R. Yan, L.C.C. Koe, X. Wang, Combined effect of adsorption and biodegradation of biological activated carbon on H2S biotrickling filtration, Chemosphere. 66 (2007) 1684–1691. https://doi.org/10.1016/j.chemosphere.2006.07.020.

[226] I. Omri, F. Aouidi, H. Bouallagui, J.J. Godon, M. Hamdi, Performance study of biofilter developed to treat H2S from wastewater odour, Saudi J Biol Sci. 20 (2013) 169–176. https://doi.org/10.1016/j.sjbs.2013.01.005.

[227] R.E.F. Lindeboom, F.G. Fermoso, J. Weijma, K. Zagt, J.B. Van Lier, Autogenerative high pressure digestion: Anaerobic digestion and biogas upgrading in a single step reactor system, 2011. https://doi.org/10.2166/wst.2011.664.

[228] R.E.F. Lindeboom, I. Ferrer, J. Weijma, J.B. van Lier, Effect of substrate and cation requirement on anaerobic volatile fatty acid conversion rates at elevated biogas pressure, Bioresour Technol. 150 (2013) 60–66. https://doi.org/10.1016/j.biortech.2013.09.100.

[229] F.A. Almomani, R.R. Bhosale, A. Kumar, C. Kennes, Removal of volatile sulfur compounds by solar advanced oxidation technologies and bioprocesses, Solar Energy. 135 (2016) 348–358. https://doi.org/10.1016/j.solener.2016.05.037.

[230] T. Baird, P.J. Denny, R. Hoyle, F. McMonagle, D. Stirling, J. Tweedy, Modified zinc oxide absorbents for low-temperature gas desulfurisation, Journal of the Chemical Society, Faraday Transactions. 88 (1992) 3375. https://doi.org/10.1039/ft9928803375.

[231] E. Sasaoka, S. Hirano, S. Kasaoka, Y. Sakata, Characterization of reaction between zinc oxide and hydrogen sulfide, Energy & Fuels. 8 (1994) 1100–1105. https://doi.org/10.1021/ef00047a013.

[232] M.P. Cal, M.J. Rood, S.M. Larson, Gas phase adsorption of volatile organic compounds and water vapor on activated carbon cloth, Energy and Fuels. 11 (1997) 311–315. https://doi.org/10.1021/ef960200p.

[233] R. Yan, D.T. Liang, L. Tsen, J.H. Tay, Kinetics and mechanisms of H2S adsorption by alkaline activated carbon, Environ Sci Technol. 36 (2002) 4460–4466. https://doi.org/10.1021/es0205840.

[234] R. Sitthikhankaew, D. Chadwick, S. Assabumrungrat, N. Laosiripojana, Effects of humidity, O2, and CO2on H2S adsorption onto upgraded and KOH impregnated activated carbons, Fuel Processing Technology. 124 (2014) 249–257. https://doi.org/10.1016/j.fuproc.2014.03.010.

[235] THIOPAQ O&G Process Description | Paqell, (n.d.). http://www.paqell.com/thiopaq/process-description/ (accessed July 3, 2018).

[236] Sulfothane: The easy way to utilise Biogas, (n.d.). http://technomaps.veoliawatertechnologies.com/processes/lib/2725,Leaflet_Sulfothane_LR.pdf (accessed July 3, 2018).

[237] L. Gil-Carrera, J.D. Browne, I. Kilgallon, J.D. Murphy, Feasibility study of an off-grid biomethane mobile solution for agri-waste, Appl Energy. 239 (2019) 471–481. https://doi.org/10.1016/j.apenergy.2019.01.141.

[238] K. Arrhenius, U. Johansson, Characterisation of contaminants in biogas before and after upgrading to vehicle gas, (2012).

[239] http://www.ecn.nl/docs/library/report/2011/l11122.pdf, (n.d.). https://www.youtube.com/watch?v=uV8LsfyCnSM (accessed August 23, 2018).

[240] P. Patel, S. Chuck, J. Kopasz, T. Benjamin, S. Ahmed, Gas Clean - Up for Fuel Cell APPLICATIONS WORKSHOP-Argonne National Laboratory, in: 2014: pp. 1–32.

[241] A.S. Mehr, M. Gandiglio, M. MosayebNezhad, A. Lanzini, S.M.S. Mahmoudi, M. Yari, M. Santarelli, Solar-assisted integrated biogas solid oxide fuel cell (SOFC) installation in wastewater treatment plant: Energy and economic analysis, Appl Energy. 191 (2017) 620–638. https://doi.org/10.1016/j.apenergy.2017.01.070.

[242] M. Hagen, E. Polman, Adding Gas from Biomass to the Gas Grid, 2001.

[243] S. Kato, K. Hashimoto, K. Watanabe, Methanogenesis facilitated by electric syntrophy via (semi) conductive iron-oxide minerals, 14 (2012) 1646–1654. https://doi.org/10.1111/j.1462-2920.2011.02611.x.

[244] S. Rasi, J. Läntelä, J. Rintala, Trace compounds affecting biogas energy utilisation – A review, Energy Convers Manag. 52 (2011) 3369–3375. https://doi.org/10.1016/j.enconman.2011.07.005.

[245] I. Díaz, I. Ramos, Bioresource Technology Economic analysis of microaerobic removal of H 2 S from biogas in full-scale sludge digesters, Bioresour Technol. 192 (2015) 280–286. https://doi.org/10.1016/j.biortech.2015.05.048.

[246] Q. Sun, H. Li, J. Yan, L. Liu, Z. Yu, X. Yu, Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation, Renewable and Sustainable Energy Reviews. 51 (2015) 521–532. https://doi.org/10.1016/j.rser.2015.06.029.

[247] R. Di Felice, P. Pagliai, ScienceDirect Prediction of the early breakthrough of a diluted H 2 S and dry gas mixture when treated by Sulfatreat commercial sorbent, Biomass Bioenergy. 74 (2015) 244–252. https://doi.org/10.1016/j.biombioe.2015.01.015.

[248] Odor Control Products and Equipments., LLC, (n.d.). https://ocpe.store/ (accessed July 20, 2019).

[249] Y. Xiao, S. Wang, D. Wu, Q. Yuan, Experimental and simulation study of hydrogen sulfide adsorption on impregnated activated carbon under anaerobic conditions, 153 (2008) 1193–1200. https://doi.org/10.1016/j.jhazmat.2007.09.081.

[250] R. Sitthikhankaew, S. Predapitakkun, R. Wibulswas, Comparative Study of Hydrogen Sulfide Adsorption by using Alkaline Impregnated Activated Carbons for Hot Fuel Gas Purification, Energy Procedia. 9 (2011) 15–24. https://doi.org/10.1016/j.egypro.2011.09.003.

[251] Quotation from supplier to TU Delft, 2018.

[252] United States Environmental Protection Agency, Drinking Water Treatment Technology Unit Cost Models and Overview of Technologies Drinking Water Treatment Technology Unit Cost Models, (n.d.). https://www.epa.gov/dwregdev/drinking-water-treatment-technology-unit-cost-models-and-overview-technologies (accessed July 20, 2019).

[253] Alibaba, Cost of Activated Carbon, (n.d.). https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=activated+carbon (accessed July 29, 2019).

[254] Alibaba, Cost of ZnO, (n.d.). https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=zinc+oxide&viewtype= (accessed July 29, 2019).

[255] P. Dhage, A. Samokhvalov, D. Repala, E.C. Duin, M. Bowman, B.J. Tatarchuk, Copper-promoted ZnO/SiO2 regenerable sorbents for the room temperature removal of H2S from reformate gas streams, Ind Eng Chem Res. 49 (2010) 8388–8396. https://doi.org/10.1021/ie100209a.

[256] Y. Wang, L. Yao, S. Wang, D. Mao, C. Hu, Low-temperature catalytic CO2 dry reforming of methane on Ni-based catalysts: A review, Fuel Processing Technology. 169 (2018) 199–206. https://doi.org/10.1016/j.fuproc.2017.10.007.

[257] T.R. Smith, A. Wood, V.I. Birss, Applied Catalysis A : General Effect of hydrogen sulfide on the direct internal reforming of methane in solid oxide fuel cells, Appl Catal A Gen. 354 (2009) 1–7. https://doi.org/10.1016/j.apcata.2008.10.055.

[258] D. Thiruselvi, P.S. Kumar, M.A. Kumar, C.H. Lay, S. Aathika, Y. Mani, D. Jagadiswary, A. Dhanasekaran, P. Shanmugam, S. Sivanesan, P.L. Show, A critical review on global trends in biogas scenario with its up-gradation techniques for fuel cell and future perspectives, Int J Hydrogen Energy. 46 (2021) 16734–16750. https://doi.org/10.1016/j.ijhydene.2020.10.023.

[259] Q. Lu, Y. Hou, S.R. Laraib, O. Khalifa, K. Li, W. luan Xie, M. shu Cui, Y. ping Yang, Electro-catalytic steam reforming of methane over Ni-CeO2/Γ-Al2O3-MgO catalyst, Fuel Processing Technology. 192 (2019) 57–64. https://doi.org/10.1016/j.fuproc.2019.04.021.

[260] G. Goula, V. Kiousis, L. Nalbandian, I. V. Yentekakis, Catalytic and electrocatalytic behavior of Ni-based cermet anodes under internal dry reforming of CH4 + CO2 mixtures in SOFCs, Solid State Ion. 177 (2006) 2119–2123. https://doi.org/10.1016/j.ssi.2006.03.040.

[261] A. Lanzini, P. Leone, C. Guerra, F. Smeacetto, N.P. Brandon, M. Santarelli, Durability of anode supported Solid Oxides Fuel Cells (SOFC) under direct dry-reforming of methane, Chemical Engineering Journal. 220 (2013) 254–263. https://doi.org/10.1016/j.cej.2013.01.003.

[262] A.A. Trendewicz, R.J. Braun, Techno-economic analysis of solid oxide fuel cell-based combined heat and power systems for biogas utilization at wastewater treatment facilities, J Power Sources. 233 (2013) 380–393. https://doi.org/10.1016/j.jpowsour.2013.01.017.

[263] S.K. Schubert, M. Kusnezoff, Sulphur Poisoning of Sofc Anodes, 2nd International Workshop on Degradation Issues on Fuel Cells ,Thessaloniki. (2011).

[264] A. Hagen, J.F.B. Rasmussen, K. Thydén, Durability of solid oxide fuel cells using sulfur containing fuels, J Power Sources. 196 (2011) 7271–7276. https://doi.org/10.1016/j.jpowsour.2011.02.053.

[265] J.F.B. Rasmussen, A. Hagen, The effect of H_2S on the performance of SOFCs using methane containing fuel, Fuel Cells. 10 (2010) 1135–1142. https://doi.org/10.1002/fuce.201000012.

[266] D.K. Niakolas, Sulfur poisoning of Ni-based anodes for Solid Oxide Fuel Cells in H/C-based fuels, Appl Catal A Gen. 486 (2014) 123–142. https://doi.org/10.1016/j.apcata.2014.08.015.

[267] C. Guerra, A. Lanzini, P. Leone, M. Santarelli, N.P. Brandon, Optimization of dry reforming of methane over Ni / YSZ anodes for solid oxide fuel cells, J Power Sources. 245 (2014) 154–163. https://doi.org/10.1016/j.jpowsour.2013.06.088.

[268] J.F.B. Rasmussen, A. Hagen, The Effect of H_2S on the Performance of SOFCs using Methane Containing Fuel, Fuel Cells. 10 (2010) 1135–1142. https://doi.org/10.1002/fuce.201000012.

[269] A. Hagen, J.F.B. Rasmussen, K. Thydén, Durability of solid oxide fuel cells using sulfur containing fuels, J Power Sources. 196 (2011) 7271–7276. https://doi.org/10.1016/j.jpowsour.2011.02.053.

[270] A. Weber, S. Dierickx, A. Kromp, E. Ivers-Tiffée, Sulfur poisoning of anode-supported SOFCs under reformate operation, Fuel Cells. 13 (2013) 487–493. https://doi.org/10.1002/fuce.201200180.

[271] T. Papadam, G. Goula, I. V. Yentekakis, Long-term operation stability tests of intermediate and high temperature Ni-based anodes' SOFCs directly fueled with simulated biogas mixtures, Int J Hydrogen Energy. 37 (2012) 16680–16685. https://doi.org/10.1016/j.ijhydene.2012.02.147.

[272] J.P. Ouweltjes, N. Woudstra, P. V. Aravind, Biosyngas Utilization in Solid Oxide Fuel Cells With Ni / GDC Anodes, J Fuel Cell Sci Technol. 3 (2006) 495–498. https://doi.org/10.1115/1.2349535.

[273] J.W. Yun, S.P. Yoon, S. Park, H.S. Kim, S.W. Nam, Analysis of the regenerative H_2S poisoning mechanism in $Ce_{0.8}Sm_{0.2}O_2$-coated Ni/YSZ anodes for intermediate temperature solid oxide fuel cells, Int J Hydrogen Energy. 36 (2011) 787–796. https://doi.org/10.1016/j.ijhydene.2010.10.060.

[274] S. Kavurucu Schubert, M. Kusnezoff, A. Michaelis, S.I. Bredikhin, Comparison of the performances of single cell solid oxide fuel cell stacks with Ni/8YSZ and Ni/10CGO anodes with H_2S containing fuel, J Power Sources. 217 (2012) 364–372. https://doi.org/10.1016/j.jpowsour.2012.06.020.

[275] S. Zha, Z. Cheng, M. Liu, Sulfur Poisoning and Regeneration of Ni-Based Anodes in Solid Oxide Fuel Cells, J Electrochem Soc. 154 (2007) B201. https://doi.org/10.1149/1.2404779.

[276] S. Jayaprakash, N. Dewangan, A. Jangam, S. Kawi, H_2S-resistant CeO_2-NiO-MgO-Al_2O_3 LDH-derived catalysts for steam reforming of toluene, Fuel Processing Technology. 219 (2021) 106871. https://doi.org/10.1016/j.fuproc.2021.106871.

[277] A. Cavalli, R. Bernardini, T. Del Carlo, P.V. Aravind, Effect of H_2S and HCl on solid oxide fuel cells fed with simulated biosyngas containing primary tar, Energy Sci Eng. 7 (2019) 2456–2468. https://doi.org/10.1002/ese3.434.

[278] Y. Shiratori, T. Oshima, K. Sasaki, Feasibility of direct-biogas SOFC, Int J Hydrogen Energy. 33 (2008) 6316–6321. https://doi.org/10.1016/j.ijhydene.2008.07.101.

[279] C. Xu, J.W. Zondlo, M. Gong, F. Elizalde-blancas, X. Liu, I.B. Celik, Tolerance tests of H_2S-laden biogas fuel on solid oxide fuel cells, J Power Sources. 195 (2010) 4583–4592. https://doi.org/10.1016/j.jpowsour.2010.02.078.

[280] G.B. Johnson, P. Hjalmarsson, K. Norrman, U.S. Ozkan, A. Hagen, Biogas Catalytic Reforming Studies on Nickel-Based Solid Oxide Fuel Cell Anodes, Fuel Cells. 16 (2016) 219–234. https://doi.org/10.1002/fuce.201500179.

[281] N. Lakshminarayanan, U.S. Ozkan, Applied Catalysis A : General Effect of H_2O on sulfur poisoning and catalytic activity of Ni – YSZ catalysts, Appl Catal A Gen. 393 (2011) 138–145. https://doi.org/10.1016/j.apcata.2010.11.034.

[282] S. Cui, J. Li, A. Jayakumar, J. Luo, K.T. Chuang, J.M. Hill, L. Qiao, Effects of H_2S and H_2O on carbon deposition over $La_{0.4}Sr_{0.5}Ba_{0.1}TiO_3$ / YSZ perovskite anodes in methane fueled SOFCs, J Power Sources. 250 (2014) 134–142. https://doi.org/10.1016/j.jpowsour.2013.10.124.

[283] S.A. Chattanathan, S. Adhikari, M. McVey, O. Fasina, Hydrogen production from biogas reforming and the effect of H_2S on CH_4 conversion, Int J Hydrogen Energy. 39 (2014) 19905–19911. https://doi.org/10.1016/j.ijhydene.2014.09.162.

[284] Y. Gao, J. Jiang, Y. Meng, F. Yan, A. Aihemaiti, A review of recent developments in hydrogen production via biogas dry reforming, Energy Convers Manag. 171 (2018) 133–155. https://doi.org/10.1016/j.enconman.2018.05.083.

[285] J.F.B. Rasmussen, A. Hagen, The Effect of H_2S on the Performance of SOFCs using Methane Containing Fuel, Fuel Cells. 10 (2010) 1135–1142. https://doi.org/10.1002/fuce.201000012.

[286] J.R. Rostrup-Nielsen, J.B. Hansen, S. Helveg, N. Christiansen, A.-K. Jannasch, Sites for catalysis and electrochemistry in solid oxide fuel cell (SOFC) anode, Appl. Phys. A 85 (2006) 427–430. https://doi.org/10.1007/s00339-006-3702-1.

[287] A. Hagen, Sulfur Poisoning of the Water Gas Shift Reaction on Anode Supported Solid Oxide Fuel Cells, Journal OfThe Electrochemical Society. 160 (2013) 111–118. https://doi.org/10.1149/2.060302jes.

[288] M. Cooper, K. Channa, R. De Silva, D.J. Bayless, Comparison of LSV / YSZ and LSV / GDC SOFC Anode Performance in Coal Syngas Containing H_2S, J Electrochem Soc. 157 (2010) 1713–1718. https://doi.org/10.1149/1.3489380.

[289] J. Li, X. Fu, J. Luo, K.T. Chuang, A.R. Sanger, Application of $BaTiO_3$ as anode materials for H_2S-containing CH_4 fueled solid oxide fuel cells, J Power Sources. 213 (2012) 69–77. https://doi.org/10.1016/j.jpowsour.2012.03.106.

[290] A. Kromp, S. Dierickx, A. Leonidea, A. Webera, E. Ivers-Tiffée, Electrochemical Analysis of Sulphur-Poisoning in Anode-Supported SOFCs under Reformate Operation, ECS Trans. 41 (2012) 161–169. https://doi.org/10.1149/1.3702423.

[291] T. Shuai, M. Xu, C. Gao, B. Wang, X. Liu, B. Li, Investigation into the effects of sulfur on syngas reforming inside a solid oxide fuel cell, J Power Sources. 258 (2014) 1–4. https://doi.org/10.1016/j.jpowsour.2014.02.041.

[292] K. Sasaki, K. Haga, T. Yoshizumi, D. Minematsu, E. Yuki, R. Liu, Chemical durability of Solid Oxide Fuel Cells : Influence of impurities on long-term performance, J Power Sources. 196 (2011) 9130–9140. https://doi.org/10.1016/j.jpowsour.2010.09.122.

[293] S.A. Saadabadi, B. Illathukandy, P.V. Aravind, Direct internal methane reforming in biogas fuelled solid oxide fuel cell; the influence of operating parameters, Energy Sci Eng. (2021) 1–17. https://doi.org/10.1002/ese3.887.

[294] G. Goula, V. Kiousis, L. Nalbandian, I. V Yentekakis, Catalytic and electrocatalytic behavior of Ni-based cermet anodes under internal dry reforming of $CH_4 + CO_2$ mixtures in SOFCs, Solid State Ion. 177 (2006) 2119–2123. https://doi.org/10.1016/j.ssi.2006.03.040.

[295] K. De Oliveira-Vigier, N. Abatzoglou, F. Gitzhofer, Dry-reforming of ethanol in the presence of a 316 stainless steel catalyst, Canadian Journal of Chemical Engineering. 83 (2005) 978–984. https://doi.org/10.1002/cjce.5450830607.

[296] Renewables 2018 global status report, REN21 Secretariat, Paris, 2018.

[297] J. Villarroel-Schneider, B. Mainali, J. Martí-Herrero, A. Malmquist, A. Martin, L. Alejo, Biogas based polygeneration plant options utilizing dairy farms waste: A Bolivian case, Sustainable Energy Technologies and Assessments. 37 (2020) 100571. https://doi.org/10.1016/j.seta.2019.100571.

[298] WATT Fuel Cell Corporation, (n.d.). https://www.wattfuelcell.com/portable-power/watt-imperium/ (accessed June 25, 2020).

[299] H. Wasajja, R.E.F. Lindeboom, J.B. Van Lier, P. V Aravind, Techno-economic review of biogas cleaning technologies for small scale off- grid solid oxide fuel cell applications, Fuel Processing Technology. 197 (2020) 106215. https://doi.org/10.1016/j.fuproc.2019.106215.

[300] A.I. Mccord, S.A. Stefanos, V. Tumwesige, D. Lsoto, A.H.M.A. Adong, J.J.S.R.A. Larson, The impact of biogas and fuelwood use on institutional kitchen air quality in Kampala , Uganda, (2017) 1067–1081. https://doi.org/10.1111/ina.12390.

[301] Y. Qian, S. Sun, D. Ju, X. Shan, X. Lu, Review of the state-of-the-art of biogas combustion mechanisms and applications in internal combustion engines, Renewable and Sustainable Energy Reviews. 69 (2017) 50–58. https://doi.org/10.1016/j.rser.2016.11.059.

[302] A. Gonzalez, A.T.W.M. Hendriks, J.B. van Lier, M. de Kreuk, Pre-treatments to enhance the biodegradability of waste activated sludge: Elucidating the rate limiting step, Biotechnol Adv. 36 (2018) 1434–1469. https://doi.org/10.1016/j.biotechadv.2018.06.001.

[303] NASA Prediction of Worl Wide Energy Resources, (n.d.). https://power.larc.nasa.gov/ (accessed December 20, 2020).

[304] J. Mata-alvarez, J. Dosta, M.S. Romero-güiza, X. Fonoll, M. Peces, S. Astals, A critical review on anaerobic co-digestion achievements between 2010 and 2013, Renewable and Sustainable Energy Reviews. 36 (2014) 412–427. https://doi.org/10.1016/j.rser.2014.04.039.

[305] A. Karlsson, A. Björn, S.S. Yekta, B.H. Svensson, IMPROVEMENT OF THE BIOGAS PRODUCTION PROCESS; Explorative project (EP1), Linköping, 2014.

[306] M.J. Taherzadeh, K. Karimi, Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production : A Review, 2008. https://doi.org/10.3390/ijms9091621.

[307] A. Gonzalez, A.T.W.M. Hendriks, J.B. van Lier, M. de Kreuk, Pre-treatments to enhance the biodegradability of waste activated sludge: Elucidating the rate limiting step, Biotechnol Adv. 36 (2018) 1434–1469. https://doi.org/10.1016/j.biotechadv.2018.06.001.

[308] D. Kim, Physico-chemical conversion of lignocellulose: Inhibitor effects and detoxification strategies: A mini review, Molecules. 23 (2018). https://doi.org/10.3390/molecules23020309.

[309] I. Ferrer, S. Ponsá, F. Vázquez, X. Font, Increasing biogas production by thermal (70 ◦ C) sludge pre-treatment prior to thermophilic anaerobic digestion, 42 (2008) 186–192. https://doi.org/10.1016/j.bej.2008.06.020.

[310] A. Rodríguez-abalde, B. Fernández, G. Silvestre, X. Flotats, Effects of thermal pre-treatments on solid slaughterhouse waste methane potential, Waste Management. 31 (2011) 1488–1493. https://doi.org/10.1016/j.wasman.2011.02.014.

[311] H. Carrere, Y. Rafrafi, A. Battimelli, M. Torrijos, J.P. Delgenes, C. Motte, Improving methane production during the codigestion of waste-activated sludge and fatty wastewater : Impact of thermo-alkaline pretreatment on batch and semi-continuous processes, Chemical Engineering Journal. 210 (2012) 404–409. https://doi.org/10.1016/j.cej.2012.09.005.

[312] R. Affes, J. Palatsi, X. Flotats, H. Carrère, J.P. Steyer, A. Battimelli, Bioresource Technology Saponification pretreatment and solids recirculation as a new anaerobic process for the treatment of slaughterhouse waste, Bioresour Technol. 131 (2013) 460–467. https://doi.org/10.1016/j.biortech.2012.12.187.

[313] D. Hidalgo, E. Sastre, M. Gómez, P. Nieto, Evaluation of pre-treatment processes for increasing biodegradability of agro-food wastes, 3330 (2012). https://doi.org/10.1080/09593330.2012.665488.

[314] Y. Chen, J.J. Cheng, K.S. Creamer, Inhibition of anaerobic digestion process : A review, 99 (2008) 4044–4064. https://doi.org/10.1016/j.biortech.2007.01.057.

[315] W. Fang, P. Zhang, X. Zhang, X. Zhu, J.B. van Lier, H. Spanjers, White rot fungi pretreatment to advance volatile fatty acid production from solid-state fermentation of solid digestate: Efficiency and mechanisms, Energy. 162 (2018) 534–541. https://doi.org/10.1016/j.energy.2018.08.082.

[316] W. Fang, X. Zhang, P. Zhang, X. Carol Morera, J.B. van Lier, H. Spanjers, Evaluation of white rot fungi pretreatment of mushroom residues for volatile fatty acid production by anaerobic fermentation: Feedstock applicability and fungal function, Bioresour Technol. 297 (2020) 122447. https://doi.org/10.1016/j.biortech.2019.122447.

[317] Z. Anwar, M. Gulfraz, M. Irshad, ScienceDirect Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy : A brief review, J Radiat Res Appl Sci. 7 (2014) 163–173. https://doi.org/10.1016/j.jrras.2014.02.003.

[318] A. Cesaro, V. Naddeo, V. Amodio, V. Belgiorno, Ultrasonics Sonochemistry Enhanced biogas production from anaerobic codigestion of solid waste by sonolysis, Ultrason Sonochem. 19 (2012) 596–600. https://doi.org/10.1016/j.ultsonch.2011.09.002.

[319] F. Cecchi, P. Pavanb, Anaerobic co-digestion of sewage sludge : application to the macroalgae from the Venice lagoon, 3449 (n.d.).

[320] N.Y. Godi, L.B. Zhengwuvi, S. Adulkadir, P. Kamtu, Effect of cow dung variety on biogas production, 5 (2013) 1–4. https://doi.org/10.5897/JMER12.014.

[321] N. Hamzawi, K.J. Kennedy, D.D. McLean, ANAEROBIC DIGESTION OF CO-MINGLED MUNICIPAL SOLID WASTE AND SEWAGE SLUDGE, Water Science and Technology. 38 (1998) 127–132.

[322] H.N. Chang, Biochemical methane potential a n d solid state anaerobic digestion of korean food wastes, 8524 (1995) 245–253.

[323] P. Kaparaju, J. Rintala, Anaerobic co-digestion of potato tuber and its industrial by-products with pig manure, 43 (2005) 175–188. https://doi.org/10.1016/j.resconrec.2004.06.001.

[324] F.J. Callaghan, D.A.J. Wase, K. Thayanithy, C.F. Forster, Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure, 27 (2002) 71–77.

[325] K.L. Bothi, CHARACTERIZATION OF BIOGAS FROM ANAEROBICALLY DIGESTED DAIRY WASTE FOR ENERGY USE, 2007.

[326] G. Corro, U. Pal, F. Bañuelos, M. Rosas, Generation of biogas from coffee-pulp and cow-dung co-digestion: Infrared studies of postcombustion emissions, Energy Convers Manag. 74 (2013) 471–481. https://doi.org/10.1016/j.enconman.2013.07.017.

[327] L.L. Kasisira, N.D. Muyiiya, Assessment of the Effect of Mixing Pig and Cow Dung on Biogas Yield, The CIGR Ejournal. XI (2009) 1–7.

[328] R.B. Saludes, K. Iwabuchi, F. Miyatake, Y. Abe, Y. Honda, Characterization of dairy cattle manure/wallboard paper compost mixture, Bioresour Technol. 99 (2008) 7285–7290. https://doi.org/10.1016/j.biortech.2007.12.080.

[329] J. Martí-Herrero, R. Alvarez, R. Cespedes, M.R. Rojas, V. Conde, L. Aliaga, M. Balboa, S. Danov, Cow, sheep and llama manure at psychrophilic anaerobic co-digestion with low cost tubular digesters in cold climate and high altitude, Bioresour Technol. 181 (2015) 238–246. https://doi.org/10.1016/j.biortech.2015.01.063.

[330] H. Hartmann, B.K.A. Ã, Anaerobic digestion of the organic fraction of municipal solid waste : Influence of co-digestion with manure, 39 (2005) 1543–1552. https://doi.org/10.1016/j.watres.2005.02.001.

[331] M. Macias-corral, Z. Samani, A. Hanson, G. Smith, P. Funk, H. Yu, J. Longworth, Bioresource Technology Anaerobic digestion of municipal solid waste and agricultural waste and the effect of co-digestion with dairy cow manure, 99 (2008) 8288–8293. https://doi.org/10.1016/j.biortech.2008.03.057.

[332] K. Liu, Y. Tang, T. Matsui, S. Morimura, X. Wu, K. Kida, Thermophilic anaerobic co-digestion of garbage , screened swine and dairy cattle manure, JBIOSC. 107 (2009) 54–60. https://doi.org/10.1016/j.jbiosc.2008.09.007.

[333] L. Zhang, Y. Lee, D. Jahng, Bioresource Technology Anaerobic co-digestion of food waste and piggery wastewater : Focusing on the role of trace elements, Bioresour Technol. 102 (2011) 5048–5059. https://doi.org/10.1016/j.biortech.2011.01.082.

[334] A.T.W.M. Hendriks, J.B. van Lier, M.K. de Kreuk, Growth media in anaerobic fermentative processes: The underestimated potential of thermophilic fermentation and anaerobic digestion, Biotechnol Adv. 36 (2018) 1–13. https://doi.org/10.1016/j.biotechadv.2017.08.004.

[335] L.M. Paulo, J. Ramiro-Garcia, S. van Mourik, A.J.M. Stams, D.Z. Sousa, Effect of nickel and cobalt on methanogenic enrichment cultures and role of biogenic sulfide in metal toxicity attenuation, Front Microbiol. 8 (2017) 1–12. https://doi.org/10.3389/fmicb.2017.01341.

[336] T. Schmidt, M. Nelles, F. Scholwin, J. Pröter, Bioresource Technology Trace element supplementation in the biogas production from wheat stillage – Optimization of metal dosing, Bioresour Technol. 168 (2014) 80–85. https://doi.org/10.1016/j.biortech.2014.02.124.

[337] Y. Yaw, I. Norli, A. Zuhairi, M. Firdaus, Bioresource Technology Impacts of trace element supplementation on the performance of anaerobic digestion process : A critical review, Bioresour Technol. 209 (2016) 369–379. https://doi.org/10.1016/j.biortech.2016.03.028.

[338] I.C. Agani, F. Suanon, B. Dimon, E.B. Ifon, F. Yovo, V.D. Wotto, O.K. Abass, M.N. Kumwimba, Enhancement of Fecal Sludge Conversion Into Biogas Using Iron Powder During Anaerobic Digestion Process To cite this article :, 5 (2016) 179–186. https://doi.org/10.11648/j.ajep.20160506.15.

[339] Yadvika, Santosh, T.R. Sreekrishnan, S. Kohli, V. Rana, Enhancement of biogas production from solid substrates using different techniques - A review, Bioresour Technol. 95 (2004) 1–10. https://doi.org/10.1016/j.biortech.2004.02.010.

[340] E. Kabir, K.H. Kim, H.O. Yoon, Trace metal contents in barbeque (BBQ) charcoal products, J Hazard Mater. 185 (2011) 1418–1424. https://doi.org/10.1016/j.jhazmat.2010.10.064.

[341] J. Nawrocki, D.L. Moir, W. Szczepaniak, Trace metal impurities in silica as a cause of strongly interacting silanols, Chromatographia. 28 (1989) 143–147. https://doi.org/10.1007/BF02319636.

[342] C. Mao, Y. Feng, X. Wang, G. Ren, Review on research achievements of biogas from anaerobic digestion, Renewable and Sustainable Energy Reviews. 45 (2015) 540–555. https://doi.org/10.1016/j.rser.2015.02.032.

[343] I. Angelidaki, B.K. Ahring, Effect of the clay mineral bentonite on ammonia inhibition of anaerobic thermophilic reactors degrading animal waste, (1993) 409–414.

[344] R.E.F. Lindeboom, I. Ferrer, J. Weijma, J.B. van Lier, Silicate minerals for CO2 scavenging from biogas in Autogenerative High Pressure Digestion, Water Res. 47 (2013) 3742–3751. https://doi.org/10.1016/j.watres.2013.04.028.

[345] D. Thiruselvi, M. Yuvarani, T. Amudha, Environmental Effects Synthesis of iron nano-catalyst using Acalypha indica leaf extracts for biogas production from mixed liquor volatile suspended solids, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 40 (2018) 772–779. https://doi.org/10.1080/15567036.2018.1463308.

[346] M.M. Guha, R.L. Mitchell, THE TRACE AND MAJOR ELEMENT COMPOSITION OF THE LEAVES OF SOME DECIDUOUS TREES : II . SEASONAL CHANGES. Plant and Soil, February 1966, 24, 90–112. Available online: https://www.jstor.org/stable/42932622 (accessed on 27 September 2018)., (n.d.).

[347] P.M. Christy, L.R. Gopinath, D. Divya, A review on anaerobic decomposition and enhancement of biogas production through enzymes and microorganisms, Renewable and Sustainable Energy Reviews. 34 (2014) 167–173. https://doi.org/10.1016/j.rser.2014.03.010.

[348] H.J.M.O. Den Camp, F.J.M. Verhagen, A.K. Kivaisi, F.E. De Windt, H.J. Lubberding, H.J. Gijzen, G.D. Vogels, Applied Microbiology Biotechnology Effects of lignin on the anaerobic degradation of (ligno) cellulosic wastes by rumen microorganisms, 1988 (1988).

[349] J.W. Lim, J.Y. Wang, Enhanced hydrolysis and methane yield by applying microaeration pretreatment to the anaerobic co-digestion of brown water and food waste, Waste Management. 33 (2013) 813–819. https://doi.org/10.1016/j.wasman.2012.11.013.

[350] J.E. Johansen, R. Bakke, Enhancing hydrolysis with microaeration, Water Science and Technology. 53 (2006) 43–50. https://doi.org/10.2166/wst.2006.234.

[351] D. Botheju, B. Lie, R. Bakke, Oxygen effects in anaerobic digestion - II, Modeling, Identification and Control. 31 (2010) 55–65. https://doi.org/10.4173/mic.2010.2.2.

[352] I. Díaz, S.I. Pérez, E.M. Ferrero, M. Fdz-Polanco, Effect of oxygen dosing point and mixing on the microaerobic removal of hydrogen sulphide in sludge digesters, Bioresour Technol. 102 (2011) 3768–3775. https://doi.org/10.1016/j.biortech.2010.12.016.

[353] M.T. Kato, J.A. Field, G. Lettinga, Anaerobe tolerance to oxygen and the potentials of anaerobic and aerobic cocultures for wastewater treatment, Brazilian Journal of Chemical Engineering. 14 (1997) 395–407. https://doi.org/10.1590/S0104-66321997000400015.

[354] M.T. Kato, J.A. Field, G. Lettinga, High tolerance of methanogens in granular sludge to oxygen, Biotechnol Bioeng. 42 (1993) 1360–1366. https://doi.org/10.1002/bit.260421113.

[355] A.L. Brioukhanov, R.K. Thauer, A.I. Netrusov, 532_Brioukhanov. 2002. Catalase and superoxide dismutase in the cells of stricktly anaerobic microorganisms. Microbiology., Microbiology (N Y). 71 (2002) 281–285.

[356] P. Jenicek, J. Koubova, J. Bindzar, J. Zabranska, Advantages of anaerobic digestion of sludge in microaerobic conditions, Water Science and Technology. 62 (2010) 427–434. https://doi.org/10.2166/wst.2010.305.

[357] P. Jenicek, F. Keclik, J. Maca, J. Bindzar, Use of microaerobic conditions for the improvement of anaerobic digestion of solid wastes, Water Science and Technology. 58 (2008) 1491–1496. https://doi.org/10.2166/wst.2008.493.

[358] P. Jenicek, C.A. Celis, J. Koubova, I. Ruzickova, Change of the digested sludge quality at microaerobic digestion, Journal of Residuals Science and Technology. 8 (2011) 39–44.

[359] P. Jenicek, C.A. Celis, L. Krayzelova, N. Anferova, D. Pokorna, Improving products of anaerobic sludge digestion by microaeration, Water Science and Technology. 69 (2014) 803–809. https://doi.org/10.2166/wst.2013.779.

[360] L. Krayzelova, J. Bartacek, I. Díaz, D. Jeison, E.I.P. Volcke, P. Jenicek, Microaeration for hydrogen sulfide removal during anaerobic treatment: a review, Rev Environ Sci Biotechnol. 14 (2015) 703–725. https://doi.org/10.1007/s11157-015-9386-2.

[361] W. Mulbry, K. Selmer, S. Lansing, Effect of liquid surface area on hydrogen sulfide oxidation during micro-aeration in dairy manure digesters, PLoS One. 12 (2017) 1–12. https://doi.org/10.1371/journal.pone.0185738.

[362] J.B. Van Lier, High-rate anaerobic wastewater treatment: Diversifying from end-of-the-pipe treatment to resource-oriented conversion techniques, Water Science and Technology. 57 (2008) 1137–1148. https://doi.org/10.2166/wst.2008.040.

[363] Y. Li, Y. Wang, X. Zhang, Z. Mi, Thermodynamic analysis of autothermal steam and CO 2 reforming of methane, Int J Hydrogen Energy. 33 (2008) 2507–2514. https://doi.org/10.1016/j.ijhydene.2008.02.051.

[364] K. Girona, J. Laurencin, J. Fouletier, F. Lefebvre-Joud, Carbon deposition in CH4/CO2operated SOFC: Simulation and experimentation studies, J Power Sources. 210 (2012) 381–391. https://doi.org/10.1016/j.jpowsour.2011.12.005.

[365] J.M. Ginsburg, J. Piña, T. El Solh, H.I. De Lasa, Coke formation over a nickel catalyst under methane dry reforming conditions: Thermodynamic and kinetic models, Ind Eng Chem Res. 44 (2005) 4846–4854. https://doi.org/10.1021/ie0496333.

[366] M. Garfí, J. Martí-Herrero, A. Garwood, I. Ferrer, Household anaerobic digesters for biogas production in Latin America: A review, Renewable and Sustainable Energy Reviews. 60 (2016) 599–614. https://doi.org/10.1016/j.rser.2016.01.071.

[367] C. Sheridan, J. Petersen, J. Rohwer, On modifying the arrhenius equation to compensate for temperature changes for reactions within biological systems, Water SA. 38 (2012) 149–151. https://doi.org/10.4314/wsa.v38i1.18.

[368] K.J. Chae, A. Jang, S.K. Yim, I.S. Kim, The effects of digestion temperature and temperature shock on the biogas yields from the mesophilic anaerobic digestion of swine manure, 99 (2008) 1–6. https://doi.org/10.1016/j.biortech.2006.11.063.

[369] C.A. de Lemos Chernicharo, Principles of Anaerobic Digestion, Anaerobic Reactors. (2007) 7–8.

[370] B. Kanko-Buhwezi, A. Mwesigye, J. Arineitwe, G.P. Colonna, Challenges to the Sustainability of Small Scale Biogas Technologies in Uganda, Second international Conference on Advances in Engineering and Technology, Entebbe, n.d.

[371] A.O. Jegede, G. Zeeman, H. Bruning, A review of mixing, design and loading conditions in household anaerobic digesters, Crit Rev Environ Sci Technol. 49 (2019) 2117–2153. https://doi.org/10.1080/10643389.2019.1607441.

[372] A.A. Adeyanju, Effect of seeding of wood-ash on biogas production using pig waste and cassava peels, Journal of Engineering and Applied Sciences. (2008).

[373] M.K. Misra, K.W. Ragland, A.J. Baker, Wood ash composition as a function of furnace temperature, Biomass Bioenergy. 4 (1993) 103–116. https://doi.org/10.1016/0961-9534(93)90032-Y.

[374] J. Martí-Herrero, M. Ceron, R. Garcia, L. Pracejus, R. Alvarez, X. Cipriano, The influence of users' behavior on biogas production from low cost tubular digesters: A technical and socio-cultural field analysis, Energy for Sustainable Development. 27 (2015) 73–83. https://doi.org/10.1016/j.esd.2015.05.003.

[375] J. Martí-Herrero, Reduced hydraulic retention times in low-cost tubular digesters: Two issues, Biomass Bioenergy. 35 (2011) 4481–4484. https://doi.org/10.1016/j.biombioe.2011.07.020.

[376] J. Martí-Herrero, J. Cipriano, Design methodology for low cost tubular digesters, Bioresour Technol. 108 (2012) 21–27. https://doi.org/10.1016/j.biortech.2011.12.117.

[377] H.M. El-mashad, Solar Thermophilic Anaerobic Reactor (STAR) for Renewable Energy Production, Wageningen University, 2003.

[378] M. Chenglin, L. Rongping, Integrated systems of green house and solar heater for anearobic digestion of excess activated sludge, Transactions of the Chinese Society of Agricultural Engineering. 25 (2009) 210-214(5).

[379] Z. Ren, H. Chen, H. Liu, X.X. Hu, X.L. Luo, Design investigation of a solar energy heating system for anaerobic sewage treatment, Energy Procedia. 14 (2012) 1355–1361. https://doi.org/10.1016/j.egypro.2011.12.926.

[380] J. Martí-Herrero, R. Alvarez, M.R. Rojas, L. Aliaga, R. Céspedes, J. Carbonell, Improvement through low cost biofilm carrier in anaerobic tubular digestion in cold climate regions, Bioresour Technol. 167 (2014) 87–93. https://doi.org/10.1016/j.biortech.2014.05.115.

[381] T. Perrigault, V. Weatherford, J. Martí-Herrero, D. Poggio, Towards thermal design optimization of tubular digesters in cold climates: A heat transfer model, Bioresour Technol. 124 (2012) 259–268. https://doi.org/10.1016/j.biortech.2012.08.019.

[382] J. Martí-Herrero, R. Alvarez, T. Flores, Evaluation of the low technology tubular digesters in the production of biogas from slaughterhouse wastewater treatment, J Clean Prod. 199 (2018) 633–642. https://doi.org/10.1016/j.jclepro.2018.07.148.

[383] G. Kocar, A. Eryasar, An application of solar energy storage in the gas: Solar heated biogas plants, Energy Sources, Part A: Recovery, Utilization and Environmental Effects. 29 (2007) 1513–1520. https://doi.org/10.1080/00908310600626598.

[384] S. Vilms Pedersen, J. Martí-Herrero, A.K. Singh, S.G. Sommer, S.D. Hafner, Management and design of biogas digesters: A non-calibrated heat transfer model, Bioresour Technol. 296 (2020) 122264. https://doi.org/10.1016/j.biortech.2019.122264.

[385] Z. Chen, C. Qin, Experiments and simulation of a solar-assisted household biogas system, Energy Procedia. 61 (2014) 1760–1763. https://doi.org/10.1016/j.egypro.2014.12.206.

[386] Y. Zhong, B.M. Roman, Y. Zhong, S. Archer, R. Chen, L. Deitz, D. Hochhalter, K. Balaze, M. Sperry, E. Werner, D. Kirk, W. Liao, Using anaerobic digestion of organic wastes to biochemically store solar thermal energy, Energy. 83 (2015) 638–646. https://doi.org/10.1016/j.energy.2015.02.070.

[387] P. Axaopoulos, P. Panagakis, A. Tsavdaris, D. Georgakakis, Simulation and experimental performance of a solar-heated anaerobic digester, Fuel and Energy Abstracts. 43 (2002) 123. https://doi.org/10.1016/s0140-6701(02)85284-5.

[388] Y. Hao, W. Li, Z. Tian, P.E. Campana, H. Li, H. Jin, J. Yan, Integration of concentrating PVs in anaerobic digestion for biomethane production, Appl Energy. 231 (2018) 80–88. https://doi.org/10.1016/j.apenergy.2018.09.119.

[389] A. Colmenar-Santos, J.L. Bonilla-Gómez, D. Borge-Diez, M. Castro-Gil, Hybridization of concentrated solar power plants with biogas production systems as an alternative to premiums: The case of Spain, Renewable and Sustainable Energy Reviews. 47 (2015) 186–197. https://doi.org/10.1016/j.rser.2015.03.061.

[390] J. Vidal, A. Carvajal, C. Huiliñir, R. Salazar, Slaughterhouse wastewater treatment by a combined anaerobic digestion/solar photoelectro-Fenton process performed in semicontinuous operation, Chemical Engineering Journal. 378 (2019) 122097. https://doi.org/10.1016/j.cej.2019.122097.

[391] C. Xiao, Q. Liao, Q. Fu, Y. Huang, H. Chen, H. Zhang, A. Xia, X. Zhu, A. Reungsang, Z. Liu, A solar-driven continuous hydrothermal pretreatment system for biomethane production from microalgae biomass, Appl Energy. 236 (2019) 1011–1018. https://doi.org/10.1016/j.apenergy.2018.12.014.

[392] Y. Hao, W. Li, Z. Tian, P.E. Campana, H. Li, H. Jin, J. Yan, Integration of concentrating PVs in anaerobic digestion for biomethane production, Appl Energy. 231 (2018) 80–88. https://doi.org/10.1016/j.apenergy.2018.09.119.

[393] R. Ali, R. Al-Sa'ed, Pilot-scale anaerobic digester for enhanced biogas production from poultry manure using a solar water heating system, International Journal of Environmental Studies. 75 (2018) 201–213. https://doi.org/10.1080/00207233.2017.1392766.

[394] T. Pussayanavin, T. Koottatep, C. Polprasert, Improvement of solar septic tank performance by recovering waste heat from an air conditioner (AC) unit, Desalination Water Treat. 173 (2020) 142–147. https://doi.org/10.5004/dwt.2020.24720.

[395] J. Gong, A. Imbault, R. Farnood, The promoting role of bismuth for the enhanced photocatalytic oxidation of lignin on Pt-TiO2 under solar light illumination, Appl Catal B. 204 (2017) 296–303. https://doi.org/10.1016/j.apcatb.2016.11.045.

[396] Q. Yan, X. Liu, Y. Wang, H. Li, Z. Li, L. Zhou, Y. Qu, Z. Li, X. Bao, Cow manure as a lignocellulosic substrate for fungal cellulase expression and bioethanol production, AMB Express. 8 (2018). https://doi.org/10.1186/s13568-018-0720-2.

[397] G. Krishna, S. Hun, K. Ill, Bioresource Technology Ensiling of fish industry waste for biogas production : A lab scale evaluation of biochemical methane potential (BMP) and kinetics, Bioresour Technol. 127 (2013) 326–336. https://doi.org/10.1016/j.biortech.2012.09.032.

[398] V.C. Kalia, A. Kumar, S.R. Jain, A.E. Joshi, Biomethanation of Plant Materials, 41 (1992) 209–212.

[399] W. Qiao, X. Yan, J. Ye, Y. Sun, W. Wang, Z. Zhang, Evaluation of biogas production from different biomass wastes with / without hydrothermal pretreatment, Renew Energy. 36 (2011) 3313–3318. https://doi.org/10.1016/j.renene.2011.05.002.

[400] L. Pastor, L. Ruiz, A. Pascual, B. Ruiz, Co-digestion of used oils and urban landfill leachates with sewage sludge and the effect on the biogas production, Appl Energy. 107 (2013) 438–445. https://doi.org/10.1016/j.apenergy.2013.02.055.

[401] M. Otero, A. Mor, Anaerobic digestion of solid slaughterhouse waste (SHW) at laboratory scale : Influence of co-digestion with the organic fraction of municipal solid waste (OFMSW), 40 (2008) 99–106. https://doi.org/10.1016/j.bej.2007.11.019.

[402] P. Peu, J. Sassi, R. Girault, S. Picard, P. Saint-cast, F. Béline, P. Dabert, Bioresource Technology Sulphur fate and anaerobic biodegradation potential during co-digestion of seaweed biomass (Ulva sp .) with pig slurry, Bioresour Technol. 102 (2011) 10794–10802. https://doi.org/10.1016/j.biortech.2011.08.096.

[403] F. Lutaaya, QUALITY AND USAGE OF BIOGAS DIGESTERS IN UGANDA Submitted in partial fulfillment of the requirements for the of the degree Of Master of Science in Mechanical Engineering with a specialization in Sustainable Energy Engineering Msc . Thesis Report Departmen, 2013.

[404] A. Case, Biogas Quality across Small-Scale Biogas Plants :, (2018) 1–12. https://doi.org/10.3390/en11071794.

[405] S. Lansing, J.F. Martin, Waste treatment and biogas quality in small-scale agricultural digesters, 2008. https://doi.org/10.1016/j.biortech.2007.09.090.

[406] M. Farooq, I.A. Chaudhry, S. Hussain, N. Ramzan, M. Ahmed, BIOGAS UP GRADATION FOR POWER GENERATION APPLICATIONS IN PAKISTAN 1) INTRODUCTION, VIII (2012) 107–118.

[407] O. Sevimoĝlu, B. Tansel, Effect of persistent trace compounds in landfill gas on engine performance during energy recovery: A case study, Waste Management. 33 (2013) 74–80. https://doi.org/10.1016/j.wasman.2012.08.016.

[408] D. Schieder, P. Quicker, R. Schneider, H. Winter, S. Prechtl, M. Faulstich, Microbiological removal of hydrogen sulfide from biogas by means of a separate biofilter system : experience with technical operation, (2018) 209–212.

[409] S. Kumar, Biogas, InTech, Janeza Trdine 9, 51000 Rijeka, Croatia, 2012.

[410] P.N. Hobson, A.D. Wheatley, Anaerobic digestion: modern theory and practice, N.P., United Kingdom, 1993.

[411] M. Alvarado-Morales, P. Tsapekos, M. Awais, M. Gulfraz, I. Angelidaki, TiO2/UV based photocatalytic pretreatment of wheat straw for biogas production, Anaerobe. 46 (2017) 155–161. https://doi.org/10.1016/j.anaerobe.2016.11.002.

[412] C. Liu, Y. Yang, Q. Wang, M. Kim, Q. Zhu, D. Li, Z. Zhang, Photocatalytic degradation of waste activated sludge using a circulating bed photocatalytic reactor for improving biohydrogen production, Bioresour Technol. 125 (2012) 30–36. https://doi.org/10.1016/j.biortech.2012.08.139.

[413] K.M. Udert, T.A. Larsen, M. Biebow, W. Gujer, Urea hydrolysis and precipitation dynamics in a urine-collecting system, Water Res. 37 (2003) 2571–2582. https://doi.org/10.1016/S0043-1354(03)00065-4.

[414] N. Azbar, F. Tutuk, T. Keskin, Effect of organic loading rate on the performance of an up-flow anaerobic sludge blanket reactor treating olive mill effluent, Biotechnology and Bioprocess Engineering. 14 (2009) 99–104. https://doi.org/10.1007/s12257-008-0065-9.

[415] Zennaki-Bensouda, Z.Zaid, A. Lamini, H. Aubineau, M.Bouif, Methane Fermentation of Cattle Manure : Effects of Hydraulic Retention Time. Temperature and Substrate Concentration, TROPICULTURA. 14 (1996) 134–140.

[416] Weather Atlas, (n.d.). https://www.weather-atlas.com/en/uganda/kampala-climate#climate_text_7 (accessed February 25, 2021).

[417] L. Ioannou-Ttofa, S. Foteinis, A. Seifelnasr Moustafa, E. Abdelsalam, M. Samer, D. Fatta-Kassinos, Life cycle assessment of household biogas production in Egypt: Influence of digester volume,

biogas leakages, and digestate valorization as biofertilizer, J Clean Prod. 286 (2021) 125468. https://doi.org/10.1016/j.jclepro.2020.125468.

[418] S. Cheng, Z. Li, H.P. Mang, E.M. Huba, R. Gao, X. Wang, Development and application of prefabricated biogas digesters in developing countries, Renewable and Sustainable Energy Reviews. 34 (2014) 387–400. https://doi.org/10.1016/j.rser.2014.03.035.

[419] S. Chinwendu, U. Chibueze, E.T. E, Anaerobic Digester Considerations of Animal Waste, 3 (2013) 93–96. https://doi.org/10.5923/j.ajb.20130304.02.

[420] V. Kumar, R.L. Shrivastava, S.P. Untawale, Fresnel lens: A promising alternative of reflectors in concentrated solar power, Renewable and Sustainable Energy Reviews. 44 (2015) 376–390. https://doi.org/10.1016/j.rser.2014.12.006.

[421] W.T. Xie, Y.J. Dai, R.Z. Wang, K. Sumathy, Concentrated solar energy applications using Fresnel lenses: A review, Renewable and Sustainable Energy Reviews. 15 (2011) 2588–2606. https://doi.org/10.1016/j.rser.2011.03.031.

[422] G. Hirn, Energy from a thousand suns: Multi-junction solar cells with concentrator systems utilise a wide solar spectrum, Bonn, 2014.

[423] W. Wang, L. Aichmayer, J. Garrido, B. Laumert, Development of a Fresnel lens based high-flux solar simulator, Solar Energy. 144 (2017) 436–444. https://doi.org/10.1016/j.solener.2017.01.050.

[424] X. Ma, R. Jin, S. Liang, S. Liu, H. Zheng, Analysis on an optimal transmittance of Fresnel lens as solar concentrator, Solar Energy. 207 (2020) 22–31. https://doi.org/10.1016/j.solener.2020.06.071.

[425] H. Wang, J. Huang, M. Song, J. Yan, Effects of receiver parameters on the optical performance of a fixed-focus Fresnel lens solar concentrator/cavity receiver system in solar cooker, Appl Energy. 237 (2019) 70–82. https://doi.org/10.1016/j.apenergy.2018.12.092.

[426] M. Muraleedharan, H. Singh, M. Udayakumar, S. Suresh, Modified active solar distillation system employing directly absorbing Therminol 55–Al2O3 nano heat transfer fluid and Fresnel lens concentrator, Desalination. 457 (2019) 32–38. https://doi.org/10.1016/j.desal.2019.01.024.

[427] L.M. Gutiérrez-Castro, P. Quinto-Diez, J.G. Barbosa-Saldaña, L.R. Tovar-Galvez, A. Reyes-Leon, Comparison between a fixed and a tracking solar heating system for a thermophilic anaerobic digester, Energy Procedia. 57 (2014) 2937–2945. https://doi.org/10.1016/j.egypro.2014.10.329.

[428] Y. Su, R. Tian, X.H. Yang, Research and analysis of solar heating biogas fermentation system, Procedia Environ Sci. 11 (2011) 1386–1391. https://doi.org/10.1016/j.proenv.2011.12.208.

[429] G.W.A. Nyakairu, H. Kurzweil, C. Koeberl, Mineralogical, geochemical, and sedimentological characteristics of clay deposits from central Uganda and their applications, Journal of African Earth Sciences. 35 (2002) 123–134. https://doi.org/10.1016/S0899-5362(01)00077-X.

[430] Cow Urine – It can be used as both pesticide and bio fertilizer | Udayasimha Hindupur, (n.d.). https://udayasimhahindupur.wordpress.com/2013/03/22/cow-urine-it-can-be-used-as-both-pesticide-and-bio-fertilizer/ (accessed October 23, 2018).

[431] M.N.A. Miah, M.R.U. Miah, M.Z. Alam, Determining Chemical Composition of Cattle Urine and Indigenous Plant Extracts, 3 (2017) 23–26.

[432] R. Rajagopal, D.I. Massé, G. Singh, A critical review on inhibition of anaerobic digestion process by excess ammonia, Bioresour Technol. 143 (2013) 632–641. https://doi.org/10.1016/j.biortech.2013.06.030.

[433] J.B. Van Lier, N. Mahmoud, G. Zeeman, Anaerobic Wastewater Treatment, in: G.-H. Chen, M.C.M. van Loosdrecht, G.A. Ekama, D. BrdjanovicEkama (Eds.), Biological Wastewater Treatment: Principles, Modelling and Design, 2nd ed., IWA Publishing, London, London, UK, 2020: pp. 701–756.

[434] A.S. Sambo, B. Garba, B.G. Danshehu, Effect of some operating parameters on biogas production rate, Renew Energy. 6 (1995) 343–344. https://doi.org/10.1016/0960-1481(95)00027-H.

[435] P. Mukumba, G. Makaka, S. Mamphweli, BIOGAS TECHNOLOGY IN SOUTH AFRICA , PROBLEMS , CHALLENGES AND SOLUTIONS Contribution / Originality 2 . BIOMASS POTENTIAL IN SOUTH AFRICA, 5 (2016) 58–69. https://doi.org/10.18488/journal.13/2016.5.4/13.4.58.69.

[436] Antonie van Leeuwenhoek, Interrelations between sulfate-reducing and methane- producing bacteria in bottom deposits of a fresh-water lake . I . Field observations, 40 (1974) 285–295.

[437] L.W. Hulshoff Pol, P.N.L. Lens, A.J.M. Stams, G. Lettinga, Anaerobic treatment of sulphate-rich wastewaters, Biodegradation. 9 (1998) 213–224. https://doi.org/10.1023/a:1008307929134.

[438] I. Staffell, R. Green, The cost of domestic fuel cell micro-CHP systems, (2013). https://doi.org/10.1016/j.ijhydene.2012.10.090.

[439] M.H. Zandvoort, E.D. van Hullebusch, F.G. Fermoso, P.N.L. Lens, Trace metals in anaerobic granular sludge reactors: Bioavailability and dosing strategies, Eng Life Sci. 6 (2006) 293–301. https://doi.org/10.1002/elsc.200620129.

[440] R.E.F. Lindeboom, C. Ilgrande, J.M. Carvajal-Arroyo, I. Coninx, O. Van Hoey, H. Roume, J. Morozova, K.M. Udert, B. Sas, C. Paille, C. Lasseur, V. Ilyin, P. Clauwaert, N. Leys, S.E. Vlaeminck, Nitrogen cycle microorganisms can be reactivated after Space exposure, Sci Rep. 8 (2018) 8–14. https://doi.org/10.1038/s41598-018-32055-4.

[441] S. Assabumrungrat, N. Laosiripojana, P. Piroonlerkgul, Determination of the boundary of carbon formation for dry reforming of methane in a solid oxide fuel cell, J Power Sources. 159 (2006) 1274–1282. https://doi.org/10.1016/j.jpowsour.2005.12.010.

[442] X. Flores-Alsina, K. Solon, C. Kazadi Mbamba, S. Tait, K. V. Gernaey, U. Jeppsson, D.J. Batstone, Modelling phosphorus (P), sulfur (S) and iron (Fe) interactions for dynamic simulations of anaerobic digestion processes, Water Res. 95 (2016) 370–382. https://doi.org/10.1016/j.watres.2016.03.012.

[443] C. Holliger, M. Alves, D. Andrade, I. Angelidaki, S. Astals, U. Baier, C. Bougrier, P. Buffière, M. Carballa, V. De Wilde, F. Ebertseder, B. Fernández, E. Ficara, I. Fotidis, J.C. Frigon, H.F. De Laclos, D.S.M. Ghasimi, G. Hack, M. Hartel, J. Heerenklage, I.S. Horvath, P. Jenicek, K. Koch, J. Krautwald, J. Lizasoain, J. Liu, L. Mosberger, M. Nistor, H. Oechsner, J.V. Oliveira, M. Paterson, A. Pauss, S. Pommier, I. Porqueddu, F. Raposo, T. Ribeiro, F.R. Pfund, S. Strömberg, M. Torrijos, M. Van Eekert, J. Van Lier, H. Wedwitschka, I. Wierinck, Towards a standardization of biomethane potential tests, Water Science and Technology. 74 (2016) 2515–2522. https://doi.org/10.2166/wst.2016.336.

[444] H. Wasajja, S.A.A. Al-Muraisy, A.L. Piaggio, P. Ceron-Chafla, P.V. Aravind, H. Spanjers, J.B. van Lier, R.E.F. Lindeboom, Improvement of biogas quality and quantity for small-scale biogas-electricity generation application in off-grid settings: A field-based study, Energies (Basel). 14 (2021). https://doi.org/10.3390/en14113088.

[445] W.R. Engineering, A. Water, M. Centre, 1,2, *, (2018) 5–8. https://doi.org/10.3390/en11092325.

[446] D.D. Perrin, Ionisation Constants of Inorganic Acids and Bases in Aqueous Solution, 2nd ed., Pergamon Press, Oxford, 1982.

[447] H. Wasajja, S.A.A. Al-muraisy, A.L. Piaggio, P. Ceron-chafla, P.V. Aravind, H. Spanjers, J.B. Van Lier, R.E.F. Lindeboom, Improvement of Biogas Quality and Quantity for Small-Scale Biogas-Electricity Generation Application in off-Grid Settings : A Field-Based Study, Energies (Basel). 14 (2021) 3088. https://doi.org/10.3390/en14113088.

[448] Phreeqc, (n.d.). https://www.usgs.gov/software/phreeqc-version-3.

[449] M. Wichern, M. Lübken, M. Schlattmann, A. Gronauer, H. Horn, Investigations and mathematical simulation on decentralized anaerobic treatment of agricultural substrate from livestock farming, Water Science and Technology. 58 (2008) 67–72. https://doi.org/10.2166/wst.2008.332.

[450] R.E.F. Lindeboom, Autogenerative High Pressure Digestion Biogas production and upgrading in a single step, 2014.

[451] M. Devasena, V. Sangeetha, Cow urine: Potential resource for sustainable agriculture, Elsevier Inc., 2022. https://doi.org/10.1016/b978-0-12-822265-2.00007-7.

[452] H. Wasajja, S.A.A. Al-Muraisy, A.L. Piaggio, P. Ceron-Chafla, P.V. Aravind, H. Spanjers, J.B. van Lier, R.E.F. Lindeboom, Improvement of biogas quality and quantity for small-scale biogas-electricity generation application in off-grid settings: A field-based study, Energies (Basel). 14 (2021). https://doi.org/10.3390/en14113088.

[453] J.S. Cha, S.H. Park, S.C. Jung, C. Ryu, J.K. Jeon, M.C. Shin, Y.K. Park, Production and utilization of biochar: A review, Journal of Industrial and Engineering Chemistry. 40 (2016) 1–15. https://doi.org/10.1016/j.jiec.2016.06.002.

[454] Y. Sun, J.P. Zhang, C. Wen, L. Zhang, An enhanced approach for biochar preparation using fluidized bed and its application for H2S removal, Chemical Engineering and Processing: Process Intensification. 104 (2016) 1–12. https://doi.org/10.1016/j.cep.2016.02.006.

[455] J. Kanjanarong, B.S. Giri, D.P. Jaisi, F.R. Oliveira, P. Boonsawang, S. Chaiprapat, R.S. Singh, A. Balakrishna, S.K. Khanal, Removal of hydrogen sulfide generated during anaerobic treatment of sulfate-laden wastewater using biochar: Evaluation of efficiency and mechanisms, Bioresour Technol. 234 (2017) 115–121. https://doi.org/10.1016/j.biortech.2017.03.009.

[456] A. Converti, R.P.S. Oliveira, B.R. Torres, A. Lodi, M. Zilli, Biogas production and valorization by means of a two-step biological process, Bioresour Technol. 100 (2009) 5771–5776. https://doi.org/10.1016/j.biortech.2009.05.072.

[457] G. Shang, G. Shen, L. Liu, Q. Chen, Z. Xu, Kinetics and mechanisms of hydrogen sulfide adsorption by biochars, Bioresour Technol. 133 (2013) 495–499. https://doi.org/10.1016/j.biortech.2013.01.114.

[458] Shivali Sahota, CAPTURE OF HYDROGEN SULPHIDE FROM RAW BIOGAS AND PRODUCTION OF HIGH S-NUTRIENT NATURAL CHAR AND SLURRY FOR UTILIZATION IN SOIL HEALTH ENHANCEMENT, 2021.

[459] S. Sahota, V.K. Vijay, P.M.V. Subbarao, R. Chandra, P. Ghosh, G. Shah, R. Kapoor, V. Vijay, V. Koutu, I.S. Thakur, Characterization of leaf waste based biochar for cost effective hydrogen sulphide removal from biogas, Bioresour Technol. 250 (2018) 635–641. https://doi.org/10.1016/j.biortech.2017.11.093.

[460] S. Chaiprapat, R. Mardthing, D. Kantachote, S. Karnchanawong, Removal of hydrogen sulfide by complete aerobic oxidation in acidic biofiltration, Process Biochemistry. 46 (2011) 344–352. https://doi.org/10.1016/j.procbio.2010.09.007.

[461] J.F.V. Talavera, Small Biogas Electrical Systems in rural Uganda barriers in an fragmented regime, n.d.

[462] S. Bos, F. Acosta, SNV and FACT Foundation, Productive Biogas : Current and Future Development. Battery charging and agro-processing services on biogas in the Ssese Islands, Uganda, n.d.

[463] E. Dimpl, Small-scale Electricity Generation from Biomass: Part II: Biogas, 2010.

[464] R. Laks, ECN; The potential for electricity generation from Biogas in, 2017.

[465] H. Thijssen, The Impact of Scale-Up and Production Volume on SOFC Manufacturing Cost, 2007.

[466] R. Scataglini, A. Mayyas, M. Wei, S.H. Chan, T. Lipman, D. Gosselin, A.D. Alessio, H. Breunig, W.G. Colella, D. Brian, ERNEST ORLANDO LAWRENCE BERKELEYNATIONAL LABORATORY; A Total Cost of Ownership Model for Solid Oxide Fuel Cells in Combined Heat and Power and Power- Only Applications, California, 2015.

[467] V.M. Maestre, A. Ortiz, I. Ortiz, The role of hydrogen-based power systems in the energy transition of the residential sector, Journal of Chemical Technology and Biotechnology. 97 (2022) 561–574. https://doi.org/10.1002/jctb.6938.

[468] Walekhwa, P.N., J. Lars, D.Mugisha, Economic viability of biogas energy production from family-sized digesters in Uganda,econd RUFORUM Biennial Meeting 20 - 24 September 2010, Entebbe, Uganda Research., in: n.d.

[469] G. Otim, D. Okaka, J. Kayima, Design of Biogas Plant for Rural Households in Uganda (Case Study: Apac District), Second International Conference on Advances in Engineering and Technology, (2011).

[470] Uganda Inflation Rate | 2018 | Data | Chart | Calendar | Forecast | News, (n.d.). https://tradingeconomics.com/uganda/inflation-cpi (accessed December 6, 2018).

[471] What #EnergyMeans to Ugandan biogas users | SNV World, (n.d.). http://www.snv.org/update/what-energymeans-ugandan-biogas-users-1 (accessed December 6, 2018).

[472] K.K. Gupta, K.R. Aneja, D. Rana, Current status of cow dung as a bioresource for sustainable development, Bioresour Bioprocess. 3 (2016). https://doi.org/10.1186/s40643-016-0105-9.

[473] S. Hidayati, T.P. Utomo, E. Suroso, Z.A. Maktub, Technical and technology aspect assessment of biogas agroindustry from cow manure: Case study on cattle livestock industry in South Lampung District, IOP Conf Ser Earth Environ Sci. 230 (2019). https://doi.org/10.1088/1755-1315/230/1/012072.

[474] M. Oketch L., Interest rates drop to 17.4%, Daily Monitor. (2021).

[475] T. Al Seadi, Quality Management of Digestate from Biogas Plants Used as Fertiliser, 2012. https://www.researchgate.net/publication/265227188.

[476] National Fuel Cell Research Center; Stationary Fuel Cell Cost Trends, An assessment produced by the National Fuel Cell Research Center Introduction., (2018) 2017–2019.

[477] K.A. Columbus, Manufacturing Cost Analysis of 100 and 250 kW Fuel Cell Systems for Primary Power and Combined Heat and Power Applications, (2016).

[478] S. Giarola, O. Forte, A. Lanzini, M. Gandiglio, M. Santarelli, A. Hawkes, Techno-economic assessment of biogas-fed solid oxide fuel cell combined heat and power system at industrial scale, Appl Energy. 211 (2018) 689–704. https://doi.org/10.1016/j.apenergy.2017.11.029.

[479] Trading Economics: United States Fed Funds Rate, (n.d.). https://tradingeconomics.com/united-states/interest-rate (accessed June 23, 2021).

[480] Uganda Revenue Athourity, Taxation handbook; Aguide to taxation in Uganda, Second Edi, Uganda Revenuw Authority, Kampala, 2015.

[481] ACTS Suppliment No.8; The Uganda Gazette No. 61 Volume CVII dated 24th October, 2014.

[482] ASYCUDA ++ IMPLEMENTATION PROJECT TEAM, ed., CUSTOMS & EXCISE DEPARTMENT: Under the East African Customs Union Asycuda ++ Trade Manual, ASY 12.05/, Uganda Revenuw Authority, Kampala, n.d.

[483] F. Francesco, Biogas dry reforming for solid oxide fuel cell applications : system modeling and analysis for different reforming approaches, (2020).

[484] M. Casisi, P. Pinamonti, M. Reini, Optimal lay-out and operation of combined heat & power (CHP) distributed generation systems, Energy. 34 (2009) 2175–2183. https://doi.org/10.1016/j.energy.2008.10.019.

[485] W. Parawira, Biogas technology in sub-Saharan Africa : status , prospects and constraints, (2009) 187–200. https://doi.org/10.1007/s11157-009-9148-0.

[486] M.S. Haque, N.N. Haque, Studies on the Effect of Urine on Biogas Production, 41 (2006) 23–32.

[487] T. V. Fernandes, K.J. Keesman, G. Zeeman, J.B. van Lier, Effect of ammonia on the anaerobic hydrolysis of cellulose and tributyrin, Biomass Bioenergy. 47 (2014) 316–323. https://doi.org/10.1016/j.biombioe.2012.09.029.

[488] A.J. Ward, E. Bruni, M.K. Lykkegaard, A. Feilberg, A.P.S. Adamsen, A.P. Jensen, A.K. Poulsen, Real time monitoring of a biogas digester with gas chromatography, near-infrared spectroscopy, and membrane-inlet mass spectrometry, Bioresour Technol. 102 (2011) 4098–4103. https://doi.org/10.1016/j.biortech.2010.12.052.

[489] C. Post, N. Heyden, A. Reinartz, A. Foerderer, S. Bruelisauer, V. Linnemann, W. Hug, F. Amann, Possibilities of Real Time Monitoring of Micropollutants in Wastewater using Laser-Induced

Raman & Fluorescence Spectroscopy (LIRFS) and Artificial Intelligence (AI), Sensors. 22 (2022). https://doi.org/10.3390/s22134668.

[490] J. Das, E.R. Rene, C. Dupont, A. Dufourny, J. Blin, E.D. van Hullebusch, Performance of a compost and biochar packed biofilter for gas-phase hydrogen sulfide removal, Bioresour Technol. 273 (2019) 581–591. https://doi.org/10.1016/j.biortech.2018.11.052.

[491] T. Kwaku Oppong-Addo, Performance of biochar-based packed column for gas-phase hydrogen sulphide removal, 2023.

[492] J.I. Salazar Gómez, H. Lohmann, J. Krassowski, Determination of volatile organic compounds from biowaste and co-fermentation biogas plants by single-sorbent adsorption, Chemosphere. 153 (2016) 48–57. https://doi.org/10.1016/j.chemosphere.2016.02.128.

[493] P. Nowicki, P. Skibiszewska, R. Pietrzak, Hydrogen sulphide removal on carbonaceous adsorbents prepared from coffee industry waste materials, Chemical Engineering Journal. 248 (2014) 208–215. https://doi.org/10.1016/j.cej.2014.03.052.

[494] K.I. Kim, H.S. Kim, H.S. Kim, J.W. Yun, H_2S tolerance effects of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ modification on $Sr_{0.92}Y_{0.08}Ti_{1-x}Ni_xO_{3-\delta}$ anode in solid oxide fuel cells, Journal of Industrial and Engineering Chemistry. 68 (2018) 187–195. https://doi.org/10.1016/j.jiec.2018.07.045.

[495] H. Chen, F. Wang, W. Wang, D. Chen, S.D. Li, Z. Shao, H_2S poisoning effect and ways to improve sulfur tolerance of nickel cermet anodes operating on carbonaceous fuels, Appl Energy. 179 (2016) 765–777. https://doi.org/10.1016/j.apenergy.2016.07.028.

[496] R. Muthudineshkumar, R. Anand, Anaerobic digestion of various feedstocks for second-generation biofuel production, Elsevier Ltd., 2019. https://doi.org/10.1016/b978-0-08-102728-8.00006-1.

[497] A. Safitri, A. Roosdiana, A. Srihardyastutie, Masruri, Fermentation of Cow Urine Collected from Ngabab Village, Malang: Its Potential as Liquid Fertilizer, IOP Conf Ser Earth Environ Sci. 239 (2019) 4–9. https://doi.org/10.1088/1755-1315/239/1/012029.

[498] J. Bertram, Effects of cow urine and its constituents on soil microbial populations and nitrous oxide emissions, 2009.

Annexes

Appendix 1

Appendix 2. Phreeqc code

```
GAS_PHASE 1
Fixed_Pressure
   -fixed_pressure          # 1.2 L (default: 1.0 L)
   -pressure 1.1
   CO2(g) -1.8    # 40% (4Kpa)
   H2S(g) -5.0      # 200 ppm (4kPa)
   Amm(g) -4.7    # 500 ppm (4kPa)
   CH4(g) -1.0
SOLUTION 1
pH 4
Temp 25
units mg/L
C(4) 4117
C(-4)  400
Ca 89
Co 0.0
S(-2) 50
Fe(+2) 6
Mn(+2) 2
```

```
Amm 583   # NH4+
Pb 0.001
Cu 0.2
Cr 0.0
Cd 0.0
Zn 0.6
Cl 48.32
Mg 35.0
Si 87.50
B 0.1
Ba 0.0
Al 2.93
Na 4.0
Ni 0.0
Sr 0.22
Ti 0.09
K 65
P 50 as PO4
N 28600

SELECTED_OUTPUT
            -file selectedoutput.sel
            -temperature
INCREMENTAL_REACTIONS True  # you can also choose False, if you do not want cumulative
            additions)

REACTION

NaOH 1.0; 1.0 moles in 500 steps

USER_GRAPH 1
 -headings head CO2 HCO3- CO3-2 CaHCO3+ CO2(g)
 -chart_title "pH effect carbon speciation"
 -axis_titles "pH" "CO2 speciation (mol)" "Partial pressure (atm)"
   -axis_scale x_axis      5 14 auto auto
   -axis_scale y_axis      0.0 0.07 auto auto
   -axis_scale sy_axis     0.00 0.7 auto auto
   -initial_solutions      true
   -connect_simulations    true
   -plot_concentration_vs  x
  -start
10 graph_x -LA("H+")
20 graph_y  MOL("CO2") MOL("HCO3-") MOL("CO3-2") MOL("CaHCO3+")
30 graph_sy  PR_P("CO2(g)")

USER_GRAPH 2
 -headings head H2S HS- S-2 Fe(HS)2 H2S(g)
 -chart_title "pH effect sulphur speciation"
 -axis_titles "pH" "S-speciation (mol)"  "Partial Pressure (atm)"
   -axis_scale x_axis      5 14 auto auto
```

```
   -axis_scale y_axis      0 0.0016 auto auto
   -axis_scale sy_axis     0 0.011 auto auto
   -initial_solutions      true
   -connect_simulations    true
   -plot_concentration_vs  x
  -start
10 graph_x -LA("H+")
20 graph_y  MOL("H2S") MOL("HS-") MOL("S-2") MOL("Fe(HS)2")
30 graph_sy PR_P("H2S(g)")

USER_GRAPH 3
 -headings head Amm AmmH+ Amm(g)
 -chart_title "pH effect ammonia speciation "
 -axis_titles "pH" "NH4-speciation (mol)"  "Partial pressure (atm)"
   -axis_scale x_axis      4 14 auto auto
   -axis_scale y_axis      0 0.05 auto auto
   -axis_scale sy_axis     0 0.001 auto auto
   -initial_solutions      true
   -connect_simulations    true
   -plot_concentration_vs  x
  -start
10 graph_x -LA("H+")
20 graph_y  MOL("Amm") MOL("AmmH+")
30 graph_sy PR_P("Amm(g)")

USER_GRAPH 4
 -headings head SI("Calcite") SI("Aragonite") SI("FeS(ppt)")
 -chart_title "pH precipitation"
 -axis_titles "pH" "Saturation index"
   -axis_scale x_axis      3 14 auto auto
   -axis_scale y_axis      -10 10 auto auto
   -initial_solutions      true
   -connect_simulations    true
   -plot_concentration_vs  x
  -start
10 graph_x -LA("H+")
20 graph_y  SI("Calcite") SI("Aragonite") SI("FeS(ppt)")

END
```

Appendix 3: Influent parameters of ADM 1

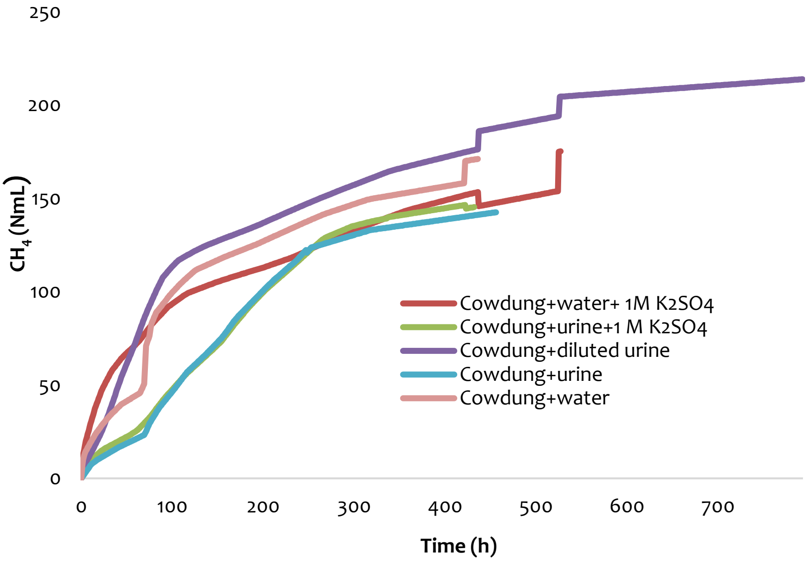
Prameter name	Unit	Concetration in Sewage Sludge (ADM 1 defalut values)	Concentration in Cow dung (Water Dilution)	Concentration in Urine	Concentration in Cowdung+ Urine (Urine dilution)
S_Su (Sugars)	kg COD/m3	0,038659	11,47066667		
S_aa(Amino Acids)	kg COD/m3	0,2468	11,47066667		
S-fa (Faty Acids)	kg COD/m3	0	11,47066667	34,412	
S_va(Total valeric acid)	kg COD/m3	0	0,456		
S_bu(Total butyric acid)	kg COD/m3	0	1,52		
S_pro(Propionate)	kg COD/m3	0	2,66		
S_ac (Total acetic acid)	kg COD/m3	0,03157	3,952	6	
S_h2(Hydrogen)	kg COD/m3	0	0		
S_ch4(Methane)	kg COD/m3	0	0	0,13	
S_IC(Inorganic carbon)	kmol C/m3	0,023601	0,1353985	0,1353985	
S_IN(Inorganic nitrogen)	kmol N/m3	0,04532	0,1	0,2	
S_I(Solube inert Organics)	kg COD/m3	0,026599	0,026599		
X_ch (Carbohydrates)	kg COD/m3	10,4968	32	0	
X_pr (Proteins)	kg COD/m3	11,1151	8.2		
X_li(Lipids)	kg COD/m3	14,9825	2.4		
X_su (microbes)	kg COD/m3	0	0		
X_aa	kg COD/m3	0	0		
X_fa	kg COD/m3	0	0		
X_c4(Butyrate and valerate degraders	kg COD/m3	0	0		

X_pro(Propionate degraders	kg COD/m3	0	0		
X_ac(Acetate degraders)	kg COD/m3	0	0		
X_h2(hydrogenotrophic methanogens)	kg COD/m3	0	0		
X_I(Inert particulate organics)	kg COD/m3	13,9393	86		
S_IP()	kmol P/m3	0,014667	0,083333333	0,01	
X_PHA(Polyhydroxyalkanoates)	kg COD/m3	0,0011947			
X_PP(Polyphosphates)	kmol P/m3	0,021673			
X_PAO(Phosphorus accumulating organisms	kg COD/m3	2,2761			
S_so4(Sulfate)	kmol S/m3	0,0031032	0,0045		0,009
S_IS(Inorganic sulphide)	kg COD/m3	5,99E-05	0,00007599		0,00015198
X_hSRB()	kg COD/m3	0			
X_aSRB()	kg COD/m3	0			
X_pSRB()	kg COD/m3	0			
X_c4SRB()	kg COD/m3	0			
X_So()	kg COD/m3	9,22E-03			
S_Na()	kmol Na/m3	0,063353	0,065217391	0,002435	0,067652
S_K()	kmol K/m3	0,00055676	0,066	0,014346	0,080346
S_Cl()	kmol Cl/m3	0,0090927	0,0090927	0,009027	0,009027
S_Ca()	kmol Ca/m3	0,0014898	0,022	0.001625	0,023625
S_Mg()	kmol Mg/m3	0,0012116	0,034965035	0,001234	0,03619
S_Fe+2()	kg COD/m3	2,08E-01	0,0000537201	0,000152	0,000206
S_Fe+3()	kmol Fe/m3	0	0	0	0
S_Al()	kmol Al/m3	0	0,001890289	0,000964	0,00284

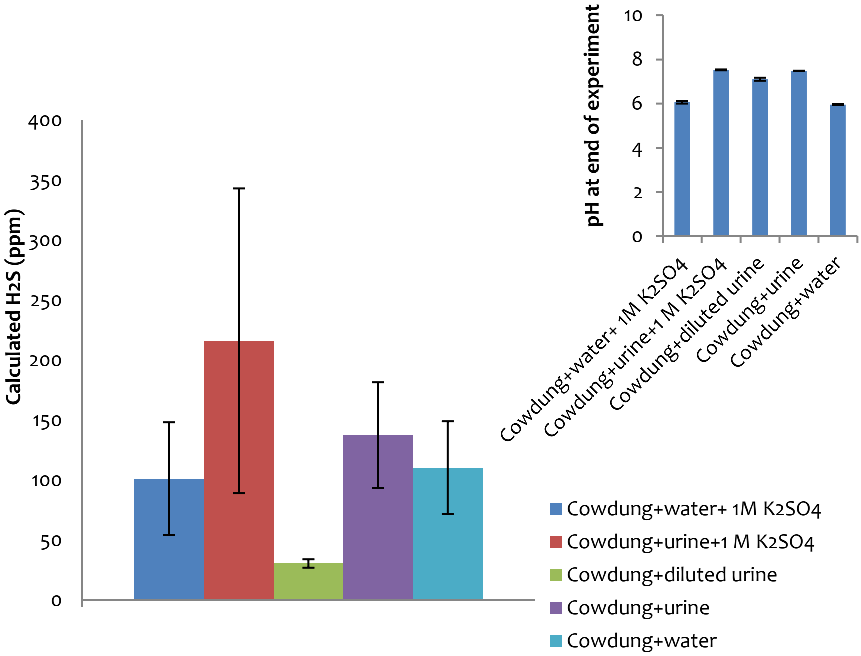
Appendix 4: Calibrated ADM 1 parameters for cow manure

Parameter	Description	Unit	ADM1 Value	Calibrated
k_{Dis}	Disintegration Constant	d^{-1}	0.5	0.05
$k_{m,ac}$	Acetate Uptake rate	$g\ g^{-1}\ d^{-1}$	8.0	4.2
$pH_{UL,acid}$	Upper pH limit for acidogens	-	5.5	8.0
$pH_{LL,acid}$	Lower pH limit for acidogens	-	4.0	6.0
$k_{m,pro}$	Propionate uptake rate	$g\ g^{-1}\ d^{-1}$	13.0	4.5
$K_{S.pro}$	Half saturation coefficient for propionate uptake	Kgm^{-3}	0.1	0.34
$K_{S.H2}$	Half saturation coefficient for hydrogen uptake	Kgm^{-3}	$7x10^{-6}$	$1.65x10^{-5}$
$N_{xc,I}$	Nitrogen content of composite and inert material	$mol_N m^{-3}$	0.002	0.0014

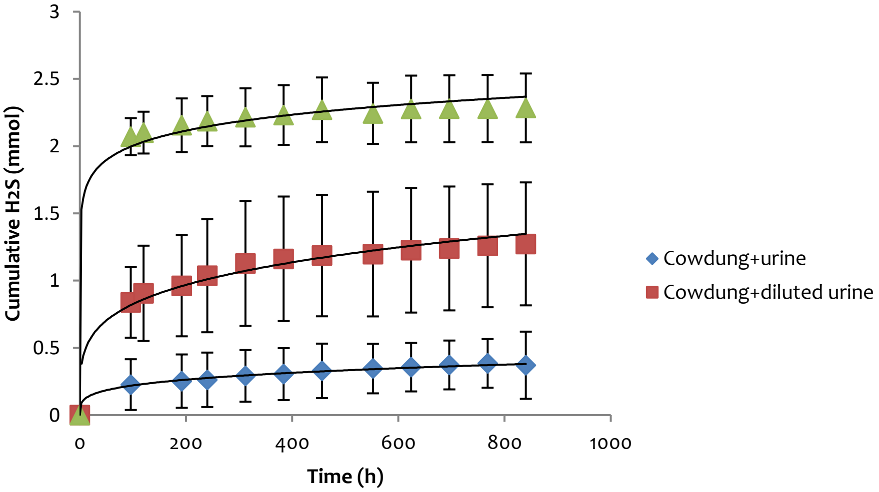
Appendix 5: Cumulative CH_4 production from AMPTS when water, urine and diluted urine is used as solvent (average of triplicates)



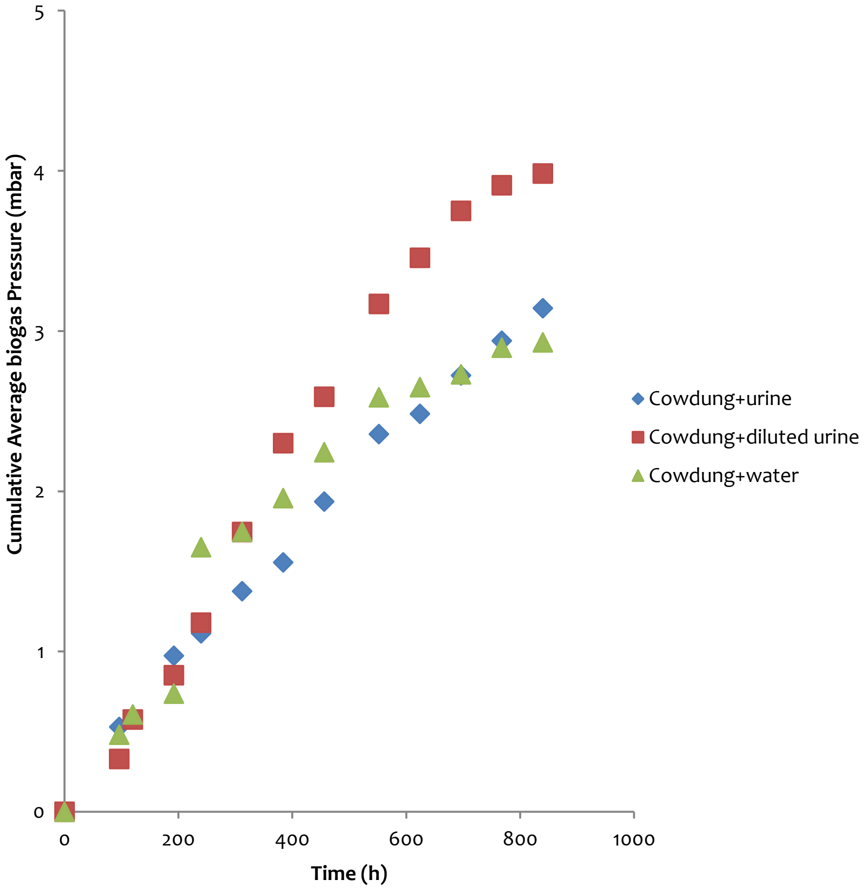
Appendix 6: Calculated content of H_2S (ppm) in biogas based on BSP experiments. Produced H_2S was captured as HS^- in 3M NaOH solution, measured using ICP-OES and subsequently converted into Biological H_2S potential in ppm using the produced biogas volume.



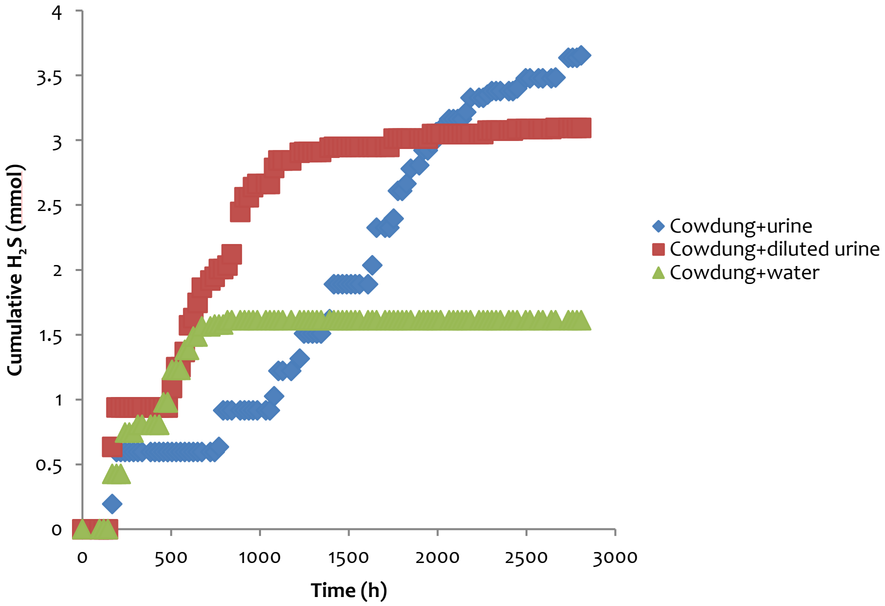
Appendix 7: Cumulative H_2S content in biogas from experiment 1 measured using Dräger tubes



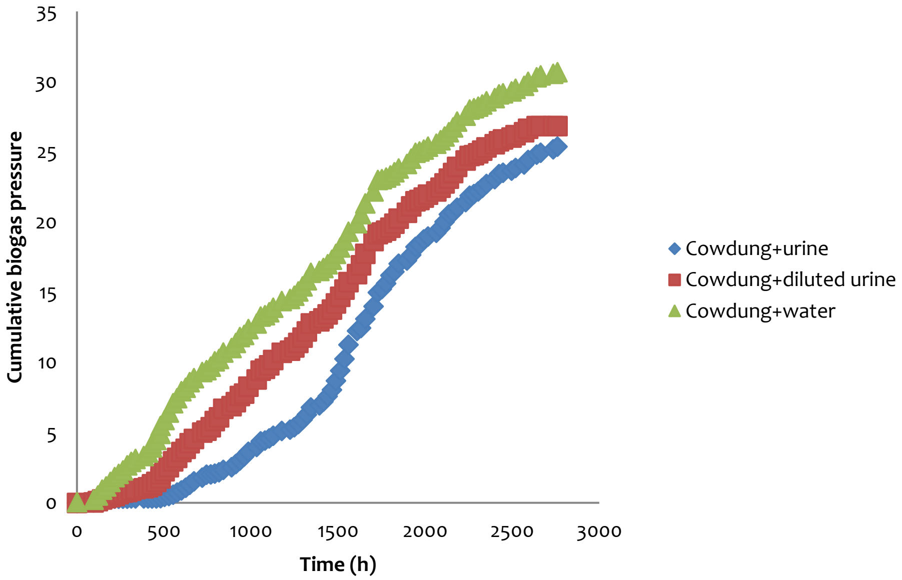
Appendix 8: Cumulative pressure of the biogas in experiment 1



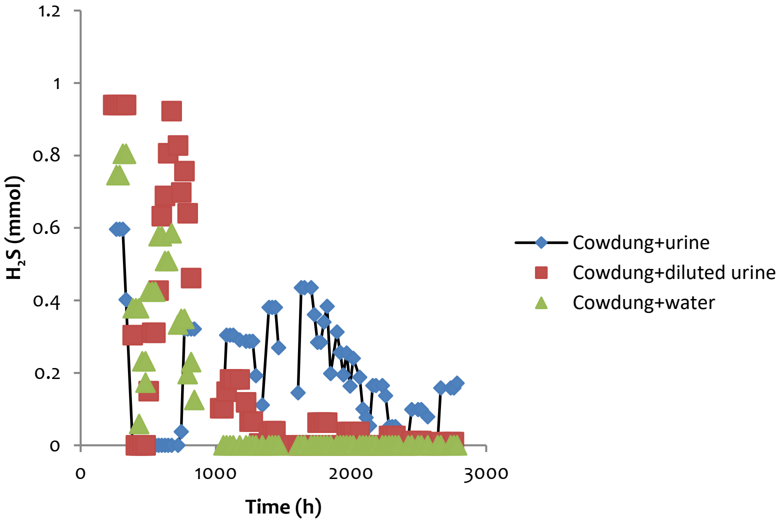
Appendix 9: Cumulative H_2S content in biogas from experiment 2



Appendix 10: Cumulative pressure of the biogas phase before H_2S measurements in experiment 2.

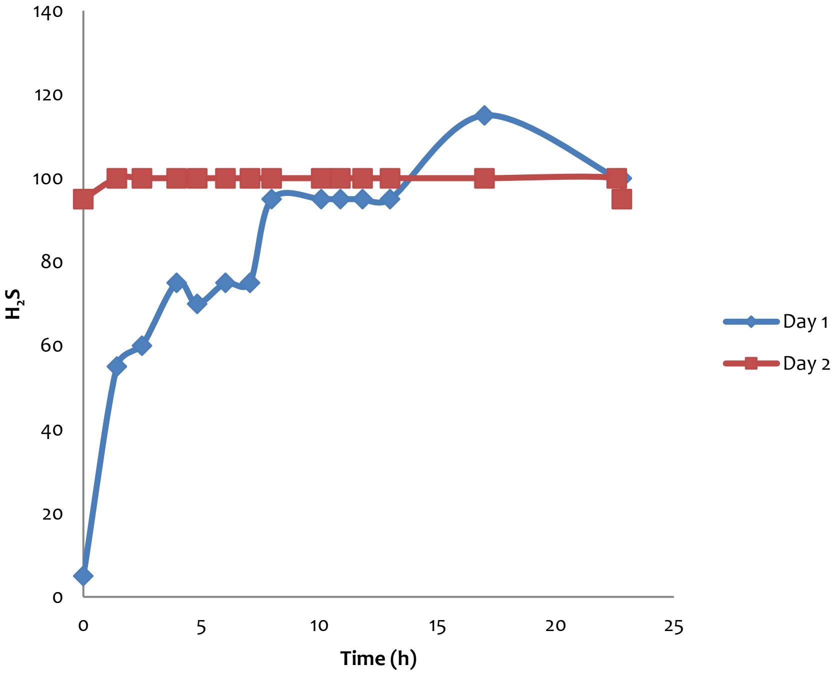


Appendix 11: Variation of H_2S content in the biogas with time in Experiment 2



.

Appendix 10: Typical Daily H_2S content profile of Biogas at the monastery



Appendix 11: Element concentration in biochar from leaves, tree branches, cow-dung and activated carbon (1.5 mg of sample diluted up to 50 ml)

Sample	[Fe] mg/l	[Mn] mg/l	[Pb] mg/l	[Zn] mg/l	[Na] mg/l	[K] mg/l	[P] mg/l	[Ca] mg/l	[Mg] mg/l	[S] mg/l
Leaves	4.5	0.4	0.1	0.1	1.5	20	1.2	16	3.7	1.2
Leaves	2.8	0.4	0.1	0.1	1.6	21	1.3	16	3.9	1.2
Leaves	6.6	0.4	0.1	0.1	1.5	20	1.2	16	3.8	1.2
Tree Branches	0.1	0.1	0.1	0.1	1.3	13	0.5	2.3	0.6	0.2
Tree Branches	0.1	0.1	0.1	0.1	1.4	13	0.5	2.3	0.7	0.2
Tree Branches	0.2	0.1	0.1	0.1	1.2	12	0.5	2.3	0.6	0.2
Cow dung	4.9	0.4	0.1	0.10	1.9	16	2.2	12	4.6	0.9
Cow dung	5.4	0.4	0,1	0.10	2.2	18	2.4	13	5.0	0.9
Cow dung	7.2	0.4	0.1	0.10	2.0	16	2.2	13	4.7	0.9
Activated Carbon	1.5	0.1	0.1	0.1	1.6	0.2	0.1	0.6	0.1	1.5
Activated Carbon	1.4	0.1	0.1	0.1	1.3	0.2	0.1	0.5	0.1	1.0
Activated Carbon	1.6	0.1	0.1	0.1	0.4	0.3	0.1	0.6	0.1	1.2

Appendix 12: shows cost of different biogas plants. However, this cost may vary depending on the region where the biogas is installed. (Exchange rate 4,240.1)

Plant Capacity/Size	Type	Gas Production Capacity	Cost (UGX) for Company 1	Cost (UGX) for Company 2	Cost (UGX) for Company 3	Cost (UGX) for Company 4*	Company 3 HS Green Energy	Average Cost (UGX)	Cost (EUR)	Cost Per Cubic meter
6 m^3	Fixed Dom	2	3,490,500	2,851,000						
6 m^3	Tubular				2,516,000 (680$)					
9 m^3	Fixed Dom, Pig Dung	3.5-4	4,512,500	3,427,000		6,004,100**				
9 m^3	Tubular				3,034,000 (820$)					
13 m^3	Fixed Dom		5,309,500	5,309,500						
20 m^3	Fixed Dom		7,507,500							
26 m^3	Fixed Dom, Cow and Human waste		11,808,000						2784.84	107.11
30 m^3	Fixed Dom		8,623,500							

30 m^3	Bio- Toilet		15,177,150	
30 m^3	Tubular		9,840,000	
45 m^3	Fixed Dom	9,960,000		
65 m^3	Fixed Dom	15,121,000		
75 m^3	Fixed Dom			37,000,000

*Quotation from the receipt of plant owner

** Year of quotation is 2016

List of Figures

List of Tables

Acknowledgements

I thank TU Deft Global initiative colleagues for granting me the opportunity to carry out my research at TU Delft under their financial support. Thank you very much team for the job well done. I thank my supervisors Prof. dr. ir. J.B. van Lier, Prof. dr. P.V. Aravind and Dr. ir. R.E.F. Lindeboom for the mentorship into the world of research, I appreciate your efforts to nature me in the world of research. I thank Dr. ir. Henri Spanjers for his support during the initial proposal writing and his academic advise during the PhD course. Even after failing to secure NFP scholarship, he made sure that I join TU Delft team by looking for alternative source of funding. Thank you, Henri for the job well done, I appreciate your tireless support. I thank Prof. dr.ir. Merle de Kreuk, for her support during grant proposal writing for my PhD funding. Thank you Merle for taking the first step in this long journey! I also thank Baukje Terpstra, Michel van den Brink and Armand Middeldorp for their technical laboratory support throughout the thesis period. I thank Alessandro Cavalli for detailed reading and correcting of manuscripts and also thanks to Ana Teodoru, Pradeep Chundru, Yashar Hajimolana, S. Ali Saadabadi, Vipin Champatan and Biju Illathukandy for being my junior supervisors, thank you so much guys, I am really grateful for your tireless efforts. Thanks to all my colleagues at CiTG and 3mE, TU Delft. I thank my Ndejje University Colleagues and management for the support during my PhD course. Also, my sincere gratitude goes to all my University of Oldenburg teachers for their tireless effort to shape my carrier in renewable energy not forgetting all fellow students at TU Delft with whom I found a home away from home. I thank Fr. Isaac Majoor, Abbot of Konigshoeven Abbey in Tilburg and the entire monastery team both in the Netherlands and in Kijonjo, Uganda for their support throughout this research. Last but not least, I am very grateful to the Rt. Rev. Prof. Micheal Ssenyimba, former vice chancellor, Ndejje University, he ushered me in the world of research at my tender age with his slogan "*it will not always be business as usual*!"

To my family, I am grateful to my dear wife, for the moral support and to stand by my side whenever I was overwhelmed. To My little children, Nathan, Abigail and Naome Wasajja, I thank you for your patience towards me for frequently being away from home. To my extended family, I am very grateful for all your support, thus far, you have been by my side.

Curriculum Vitae

Henry Wasajja is an energy engineer and a researcher from Uganda with over 10 years' experience. He has attended a number of specialised international trainings focusing on sustainable energy and energy efficiency. He started his Bachelors of Science degree at Makerere University, Uganda in 2005. After graduating in 2009 he started teaching at Ndejje University (Uganda), Faculty of Engineering as an assistant lecturer in Renewable Energy. In 2010 he started his MSc in Renewable Energy at University of Oldenburg (Germany). Within his MSc he completed his 6 months internship at TU Delft, Department of Process Energy, Faculty of 3me, The Netherlands where he wrote his master thesis titled "Back casting study to evaluate advanced biomass technologies for rural energy supply". He was working as a lecturer and a researcher at Energy Research Centre, Ndejje University before joining TU Delft for his PhD research. He is also a co-founder of HS Green Energy Engineering Solutions Ltd, a company incorporated in Uganda focusing on design, supply and installation of sustainable energy solutions to off-grid population in Uganda and within the East African region.

List of Publications

Peer reviewed publications

- B. Illathukandy, S.A. Saadabadi, P.C. Kuo, **H. Wasajja**, R.E.F. Lindeboom, V.K. Vijay, P. V. Aravind, Solid oxide fuel cells (SOFCs) fed with biogas containing hydrogen chloride traces: Impact on direct internal reforming and electrochemical performance, Electrochimica Acta. 433 (2022). https://doi.org/10.1016/j.electacta.2022.141198.
- **H. Wasajja**, S.A. Saadabadi, B. Illathukandy, R.E.F. Lindeboom, J.B. van Lier, P. Vellayani Aravind, The effect of H2S on internal dry reforming in biogas fuelled solid oxide fuel cells, Energy Science and Engineering. 10 (2022) 374–383. https://doi.org/10.1002/ese3.1021.
- **H. Wasajja**, S.A.A. Al-Muraisy, A.L. Piaggio, P. Ceron-Chafla, P.V. Aravind, H. Spanjers, J.B. van Lier, R.E.F. Lindeboom, Improvement of biogas quality and quantity for small-scale biogas-electricity generation application in off-grid settings: A field-based study, Energies. 14 (2021). https://doi.org/10.3390/en14113088
- **H. Wasajja**, R.E.F. Lindeboom, J.B. Van Lier, P. V Aravind, Techno-economic review of biogas cleaning technologies for small scale off- grid solid oxide fuel cell applications, Fuel Processing Technology. 197 (2020) 106215. https://doi.org/10.1016/j.fuproc.2019.10621
- G. kasimba, F.W. Mukalazi and **H. Wasajja,** Real-time Loading of Units on Prepaid Energy Meters Using GSM Technology, The 5th National Conference on Communications (NCC 2019), 17th – 18th October 2019, Makerere University.
- **H. Wasajja,** Evaluation of Advance Biomass Technologies for Rural Energy Supply: IEEE IES AFRICON17. (Conference paper)
- **H. Wasajja,** Backcasting study to Evaluate Advanced Biomass Technologies for Rural Energy Supply: 1st International conference on Bio-Waste Recycling, Ndejje University, Kampala September 2016. (Conference paper)
- **H. Wasajja**, Biomass briquette Market Analysis in Uganda: The International Renewable Energy Symposium (IRES 2015), Windhoek, Namibia (conference paper)
- **H. Wasajja**, Contributing Author, Rural Electrification, EEM-PPRE Year book, 2013